Project no. 022704 (SSP)

FOOTPRINT

Functional Tools for Pesticide Risk Assessment and Management

Specific Targeted Research Project

Thematic Priority: Policy-orientated research

Deliverable DL6

State-of-the-art review on preferential flow

Due date of deliverable: July 2006
Actual submission date: July 2006

Start date of project: 1 January 2006 **Duration: 36 months**

Organisation name of lead contractor for this deliverable: SLU

Revision: N/A

Project co-funded by the European Commission within the Sixth Framework Programme (2002-2006)		
Dissemination Level		
PU	Public	**X**
PP	Restricted to other programme participants (including the Commission Services)	
RE	Restricted to a group specified by the consortium (including the Commission Services)	
CO	Confidential, only for members of the consortium (including the Commission Services)	

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Foreword

The present literature review was prepared within the context of the work package WP1 ('Integrated knowledge reviews') of the FOOTPRINT project. Sections 1 to 8 were submitted to the *European Journal of Soil Science* in May 2006 for publication in the journal.

The preferred reference to the present document is as follows:

Jarvis N.J. & Dubus I.G (2006). State-of-the-art review on preferential flow. Report DL#6 of the FP6 EU-funded FOOTPRINT project [www.eu-footprint.org], 60p.

Summary

This review discusses the effects of macropores on water flow and solute transport in soil. Some fundamental concepts and definitions are first presented. Macropores are defined as pores that allow non-equilibrium conditions to develop during rapid water flow, due to their large size and continuity. Non-equilibrium can also be enhanced by the presence of macropore linings and coatings that restrict lateral mass exchange. Experimental work suggests that pores larger than ca. 0.3 mm in diameter allow non-equilibrium flow and transport. Macropores also represent micro-sites in soil that are more biologically active, and often more chemically reactive than the bulk soil. However, sorption retardation during transport is usually weaker than in the bulk soil, due to the small surface areas and significant kinetic effects, especially in larger macropores. The hierarchical structure of soil macropore networks is proposed as the key feature that determines the potential for non-equilibrium water flow and solute transport at the pedon scale, while the initial and boundary conditions determine the extent to which this potential is realized. Degrading the hierarchy, for example, by compaction, increases susceptibility to non-equilibrium macropore flow, until a critical point is reached when macropore continuity becomes limiting.

A range of different models exists that account for macropore flow effects on solute transport, varying in their conceptual basis and degree of detail and complexity. It is concluded that, for practical management applications, simpler dual-permeability models represent a good balance between physical realism and useability. Despite stochastic variation in transport characteristics at the local scale, the soil factors that control macropore flow, including texture and organic matter content, are well known, deterministic, and therefore predictable at the landscape scale. Therefore, it should be feasible to develop soil classification schemes that account for the critical role of macropore flow, to support predictive modelling of the effects of land use and soil management practices on water quality at the catchment and landscape scale.

1 INTRODUCTION

The importance of macropores was recognized as long ago as the late-19th century by Lawes *et al.* (1882) who noted that.....'in a heavy soil, channel drainage will in most cases precede general drainage, a portion of the water escaping by the open channels before the body of the soil has become saturated; this will especially be the case if the rain fell rapidly, and water accumulates on the surface'. This qualitatively accurate description of non-equilibrium flow occurring in natural structured soil was, however, largely ignored, and it was the empirical but quantitative work of the engineer Darcy, working on flow through artificial packed sand beds that laid the foundation for soil water physics in the 20th century. The underlying assumption of homogeneity, that single values of water potential, water content and hydraulic conductivity could adequately characterize a representative elementary volume at a given soil depth remained virtually unchallenged for nearly half a century. Solute transport theory developed along conceptually similar lines, with the advective-dispersive (ADE) theory of transport gaining overwhelming popularity in the last half of the 20th century. This theory assumes that lateral mixing processes are fast in relation to vertical convective transport (Jury & Flühler, 1992).

Starting in the 1960's and early 1970's, new experimental observations of rapid non-equilibrium flow of water in macropores, and the resulting effects on patterns of solute displacement, began to challenge the established paradigm (Thomas & Phillips, 1979). Research into all aspects of macropore flow has subsequently intensified, and this has led to the development of a number of models that can account for the effects of macropores on contaminant leaching. Within the framework of the FOOTPRINT project, this review summarizes the current understanding of the controls on macropore flow and how in turn, it affects pesticide leaching. The review is organized making use of scale as the common thread. We first describe the basic principles governing the generation of macropore flow at the pore scale, the flow mechanisms, and the micro-scale properties of macropores. The important role of initial and boundary conditions in regulating macropore flow is also discussed. This is followed by a review of the literature concerning the relationships between macropore flow and soil morphology, soil properties at the horizon and pedon (soil profile) scale, and the influence of pesticide characteristics and soil and crop management practices on macropore flow. The significance of macropore flow at the landscape scale is then considered. The report concludes with a discussion of the prospects of accounting for macropore flow in predictive large-scale modelling of pesticide impacts on water quality for management purposes.

2 PREFERENTIAL FLOW: CONCEPTS AND DEFINITIONS

Classical theory of water flow (Richards' equation) and solute transport (ADE) is based on the assumption that unique values of soil water pressure and solute concentration can be defined for a representative elementary volume of soil (REV). Physical non-equilibrium occurs in the soil unsaturated zone when heterogeneities result in the generation of lateral differences (non-uniformity) either in water pressures or solute concentrations, or both, during vertical flow and transport. This invalidates the REV concept. More specifically, preferential *flow* and/or *transport* result when rates of lateral equilibration of water pressures and/or solute concentrations are slow in relation to the vertical flow rates (Skopp, 1981; Beven & Germann, 1982; Flühler *et al*., 1996). The occurrence of physical non-equilibrium implies that a more or less spatially uniform precipitation flux becomes highly non-uniform as flow streamlines converge towards conducting flowpaths. Under ponding conditions, this lateral redistribution can occur directly at the surface as overland flow. However, if the soil remains unsaturated, flow converges within a shallow ‘distribution zone’ towards conducting flow channels that comprise only a small fraction of the total pore space (Ritsema & Dekker, 1995; Flühler *et al*., 1996). Three fundamentally different types of preferential flow processes are recognized: rapid flow in large pores termed macropores that are ubiquitous in structured soils, unstable finger flow (Ritsema & Dekker, 1995) and funnel (or simply heterogeneous) flow (e.g. Kung, 1990; Roth, 1995). The latter two processes occur in the soil matrix, predominantly in sandy textured soils. In the case of finger flow, this occurs in uniform (narrow-graded) sands, and can be triggered by a variety of mechanisms, including air entrapment, hydrophobicity, and soil layering (fine layers overlying coarse). Heterogeneous flow, on the other hand, occurs in coarse-textured soils containing lenses or regions of materials with differing characteristic grain sizes. With heterogeneous flow, the pathways taken by the infiltrating water should depend on the relative values of unsaturated hydraulic conductivity of the component materials at the applied water flux. For example, at saturation, a coarse sand fraction might comprise a preferred flow region, while at small fluxes under unsaturated conditions, inter-connected regions of a finer-textured material may conduct all the water since soil water pressures may not increase sufficiently to saturate the coarse sand.

Thus, preferential flow can occur in virtually all types of soils caused by heterogeneities at scales ranging from the single pore to the pedon. However, little is known about the relative significance of finger flow, heterogeneous flow and macropore flow for leaching of pesticides. Intuitively, macropore flow ought to be the most important process, for two main reasons: macropores are ubiquitous, and the transport volume (often fractions of one percent of the soil volume) is appreciably smaller, which will give shorter transit times and minimal adsorption interaction with the matrix. From observed flow velocities (Beven and Germann, 1982), we may expect macropore flow to decrease the transit time through the unsaturated zone by up to two orders of magnitude (i.e. hours instead of years), which clearly invalidates traditional flow and transport theories. In contrast, it may be possible, as a first approximation, to account for finger flow and heterogeneous flow by simply increasing the dispersion coefficient in the advection-dispersion equation. In the remainder of this review, I concentrate on macropore flow processes.

3 GENERATION AND MAINTENANCE OF MACROPORE FLOW

Water will start to flow into a macropore when the water pressure at some point on the interface with the surrounding soil matrix exceeds the 'water-entry' pressure. This is determined by the surface tension of water, the radius of curvature of the air-water interface, and its contact angle with the solid pore walls, as expressed in the Laplace equation (the law of capillarity). As water starts to flow into large structural macropores, the sharp contrast in pore size and tortuosity with the surrounding textural pores leads to an abrupt increase in water flow rate for only a small increase in soil water pressure, resulting in marked non-uniform flow (physical non-equilibrium).

The question now arises: what size of pore is large enough to support non-equilibrium water flow and solute transport? Twenty-five years ago, four of the early pioneers of macropore flow research debated this question. In response to a proposed classification scheme based on pore sizes Luxmoore, (1981), Beven (1981), Skopp (1981) and Bouma (1981) stressed that pore continuity and tortuosity and not size alone, controlled the occurrence of macropore flow and that functional characterization based on transport characteristics and hydraulic conductivity was necessary (see also Beven & Germann, 1982). Scotter (1978) had predicted some years earlier the existence of a dramatic increase in non-equilibrium solute transport when pores with water entry pressures larger than c. -15 cm conducted the flow. These calculations were based on saturated flow in pores of idealized geometry (straight-sided continuous fissures and cylindrical macropores without tortuosity), and the more complex flow geometry in natural macropores would most likely shift the critical pressure potential at which the REV concept (and advective-dispersive theory) fails closer to saturation. Indeed, the weight of experimental evidence that has accumulated in the intervening 25 years suggests that from the point of view of water flow and solute transport, pores of 'equivalent cylindrical diameter' larger than about 0.3 to 0.5 mm (i.e. water-entry pressures of -10 to –6 cm H_2O in the Laplace equation) can be classified as macropores. For example, tracer experiments conducted in structured soils at smaller pressure potentials have shown equilibrium transport, while experiments at larger potentials have demonstrated strong non-equilibrium (e.g. Seyfried & Rao, 1987; Jarvis *et al*., 1987; Jardine *et al*., 1993; Wilson *et al*., 1998; Langner *et al*., 1999). Direct experimental evidence also supports this conclusion. For example, real-time observations of saturated flow using a soft X-ray radiography technique with a resolution of 50 μm revealed that conducting macropores (root channels, inter-aggregate pores) in paddy, upland field and forest soils were larger than ca. 0.4 mm in size (Mori *et al*., 1999a). Indirect supporting evidence is provided by measurements of hydraulic properties made across a range of pressure potentials in structured soils, including the wet range close to saturation. These data consistently show that, starting from a pressure potential of around ca. –10 to –6 cm, unsaturated hydraulic conductivity increases by up to three orders of magnitude as the potential increases towards saturation (e.g. Germann & Beven, 1981; Clothier & Smettem, 1990; Smettem & Kirkby, 1990; Othmer *et al*., 1991; Wilson *et al*., 1992; Messing & Jarvis, 1993; Ross & Smettem, 1993; Durner, 1994; Jarvis & Messing, 1995; Mallants *et al*., 1997; Mohanty *et al*. 1997; Lin *et al*., 1997; Jarvis *et al*., 1999; Coppola, 2000; Poulsen *et al*., 2002). Observations of water flow and solute transport under varying controlled flow rates also provide additional indirect support for this conclusion (e.g. Anderson & Bouma 1977b). Hydraulic conductivity at –10 cm is typically in the range of 0.1 to 1 mm h^{-1} in arable topsoils of loam and clay texture (e.g. Jarvis & Messing, 1995; Jarvis *et al*., 2002) and irrigation intensities larger than about 1 mm h^{-1} have been shown to generate non-equilibrium flow and transport behaviour under field conditions (e.g. Beven & Germann, 1982; Gish *et al*., 2004).

In summary, although ponding (i.e. water at atmospheric pressure) is not needed, water pressures must reach close to saturation (> -10 cm) to generate non-equilibrium flow and transport in soil macropores. It should be emphasized that this does not imply that the entire soil profile must wet up to near saturation: by definition, macropore flow is a non-equilibrium process whereby water at pressures close to atmospheric rapidly by-passes a drier soil matrix. Furthermore, despite occasional claims to the contrary (e.g. Kung *et al*., 2000a), there is no convincing evidence in the literature that significant non-equilibrium flow and transport in natural soil macropores can be generated at potentials smaller than ca. –10 cm. Confusion on this point may have sometimes arisen because near-saturated conditions need only occur in very localized spots (e.g. millimetre thick layers at the soil surface or above centimetre thick compacted soil zones at plough depth), which are not easy to detect with traditional field measurement techniques. Tracer experiments conducted at pressure potentials somewhat smaller than -10 cm H_2O can sometimes show a degree of physical non-equilibrium behaviour, but this is much weaker than the effects of macropore flow at larger potentials, being consistent with diffusion into 'stagnant' water zones comprising only a limited part of the total pore space (e.g. Kamra *et al*., 2001). Li & Ghodrati (1994) compared nitrate breakthrough curves in packed soil columns containing root channels from alfalfa and maize and found non-equilibrium transport behaviour at flux rates that were apparently a factor 2 to 3 smaller than the saturated matrix conductivity measured on control columns without roots. However, it cannot be excluded that root growth in the columns altered the matrix hydraulic properties, for example, by root growth induced compaction (e.g. Angers & Caron, 1998). Thus, although any cut-off pore size is bound to be an approximation, the overwhelming weight of empirical evidence suggests that for all practical purposes, macropores can be functionally defined (with respect to water flow and solute transport) as pores with equivalent diameters larger than about 0.3 to 0.5 mm. It is not a coincidence that pores of this size are also characterized by relatively large length (high continuity) and low tortuosity (pore length divided by sample length, e.g. Mori *et al*., 1999a; Perret *et al*., 1999). Three types of pore match this 'blueprint': cylindrical biopores made by burrowing soil animals and plant roots, planar fissures formed by wet/dry or freeze/thaw, and irregularly-shaped 'packing voids' between denser aggregates in cultivated topsoils (Bouma *et al*. 1977; Ringrose-Voase, 1996).

3.1 Types of macropores and their physical characteristics

3.1.1 Biopores

Under favourable conditions, individuals of deep-burrowing anecic earthworm species such as *Lumbricus terrestris* L. can produce several hundred channels per m^2, 2 to 12 mm in diameter, which are vertically continuous from the soil surface deep into the subsoil (e.g. Ehlers, 1975; Edwards *et al*. 1988; Pitkänen & Nuutinen, 1997; Shipitalo & Butt, 1999; Zehe & Flühler, 2001a). The tortuosity of channels produced by deep-burrowing earthworms has been reported to be in the range of 1.1 to 1.2 (Shipitalo & Butt, 1999). In contrast, endogeic earthworm species only feed and burrow within the topsoil, producing temporary burrows that are more randomly oriented, shorter, more tortuous and more branched (Capowiez *et al*., 2001; Jégou *et al*., 2001). Earthworm burrow systems can be highly dynamic, with a short turnover time. For example, Daniel *et al*. (1997) calculated that the surface casts produced in a three-month period by *Aporrectodea nocturna* in a grass meadow would be equivalent to a soil macroporosity of 4% in the upper 50 cm of soil, and would cover the surface to a depth of 20 mm. However, many of these pores were apparently short-lived, since the measured burrow volume was only ca. 20% of the pore volume equivalent to the casts. Perret *et al*. (1999) investigated the geometry of macropore networks consisting of cylindrical biopores larger than 1 mm in diameter in an uncultivated sandy loam soil under grass. The origin of the biopores was not specified in this study, but they were presumably mostly faunal. They identified more than 13,000 such branching networks per m^3 soil, corresponding to a total macroporosity varying between 2 and 4%. The networks had a geometric mean volume of ca. 50 mm^3 and a tortuosity between 1.2 and 1.3, and their modal length was ca. 40 mm.

Smaller channels created by decaying plant roots also constitute important pathways for non-equilibrium flow and transport. For example, Tipkötter (1983) reported inter-connected networks of tubular pores 0.1 to 0.6 mm in diameter, with a similar morphology to that of living root systems, at more than 1 m depth in a loess soil. Edwards *et al*. (1988) counted more than 14,000 cylindrical macropores per m^2 larger than 0.4 mm in diameter in an untilled silt loam soil cropped with maize. Of these, 80% were less than 1 mm in diameter and were presumed to be channels created by decayed roots. Species differences can be important. For example, alfalfa produces large vertically oriented taproots. Meek *et al*. (1989) counted more than 100 stained root channels per m^2 under a 3-year old alfalfa stand. Of these, 68% were between 0.5 and 2.5 mm in diameter, while 8% were larger than 4.5 mm in diameter. These biopores increased ponded infiltration rates by a factor 2 to 3 (Meek *et al*., 1989). Mitchell *et al*. (1995) showed that final infiltration rates were larger and dye penetration deeper in a flood-irrigated clay soil containing decaying alfalfa root channels, compared to soil previously cropped with wheat.

3.1.2 Aggregation

Aggregation results when stresses develop in a soil body containing swell/shrink clay minerals due to wetting and drying and/or freezing and thawing that locally overcome the coherence of the soil material. The ‘flaws’ or failure planes that result are the precursors of aggregate or ped surfaces that are subsequently stabilized and enhanced, both by physical processes and biological activity (see ‘*Chemical and biological properties of macropores*’). As a ‘rule of thumb’, soils with clay contents larger than about 15% to 20% usually exhibit moderate to strong aggregate structure (Horn *et al*., 1994). The structure of clay soils is dynamic, especially in soils dominated by 2:1 clay minerals, where water lost by evapotranspiration is partly or completely replaced by shrinkage of the clay matrix. Thus, in dry periods, the crack volume in clay soils can be substantial, especially in dry near-surface layers (Bronswijk, 1991; Chertkov & Ravina, 1998). The spacing and tortuosity of cracks generally increases with depth, while their volume, individual width and connectivity decrease (Chertkov & Ravina, 1998; Chertkov & Ravina, 1999). The tortuosity of crack networks in clay soils has been reported to be in the range 1.2 to 2.0 (Chertkov & Ravina, 1999). It follows that flow and transport characteristics in swelling clay soils are also strongly affected by seasonal changes in soil wetness. Thus, near-saturated and saturated hydraulic conductivity in clay soils are positively correlated to macroporosity and inversely related to the soil moisture content (e.g. Messing & Jarvis, 1990; Lin *et al*., 1998).

Soil aggregation is hierarchical (Hadas, 1987; Dexter, 1988; Oades & Waters, 1991), such that aggregates of a given size consist of smaller sub-units separated by planes of weakness that will also potentially serve as preferential flow pathways. These smaller sub-units are in turn comprised of even smaller aggregates separated by planes of weakness. The lower the order in the hierarchy, the denser and stronger are the aggregates, since they exclude the pore space (and planes of weakness) between the aggregates of all higher orders (Hadas, 1987; Horn *et al*., 1994). Since larger aggregates are associated with larger, more widely spaced, and more continuous inter-aggregate fissures and ‘packing voids’, higher orders in the structure hierarchy should be associated with stronger non-equilibrium flow and transport. Similar relationships between pore size and density (large pores are more infrequent and more widely spaced) also hold for biopores (Brakensiek *et al*., 1992). These kinds of observations have prompted increasing interest in the application of fractal geometry to quantify soil structural porosity. Fractals are ‘self-similar’ objects of hierarchal structure whose properties can be described by a scale-invariant power-law characterized by an exponent termed the ‘fractal dimension’. Several different fractal dimensions can be defined (Perfect & Kay, 1995): mass and pore volume fractal dimensions describe how bulk density and porosity change with the scale of observation. Significantly smaller values than the Euclidian dimension (i.e. 2 for 2D objects) imply a more spatially heterogeneous arrangement of the pore space. Fractal power laws can also be used to describe aggregate and macropore size distributions, where larger values of the exponent imply that the hierarchy of structure is better expressed. Finally, ‘surface’ and ‘spectral’ fractal dimensions can be used to quantify the irregularity and tortuosity of the pore-solid boundaries and the connectivity of the pore system, both of which are important controls on non-equilibrium flow in macropores. The attraction of the fractal approach is that it may provide a unifying theoretical framework to enable prediction of the effects of structure on transport processes as a function of scale (Perfect & Kay, 1995). Several studies have shown that macroporosity does show an apparent fractal geometry (e.g. Peyton *et al*., 1994; Preston *et al*., 1997; Perret *et al*., 2003), which suggests that fractal concepts may prove useful in characterizing macropore flow and transport. However, like any model, true (mono)fractal scaling is only an approximation, which is only likely to be valid across a limited range of scales (Rieu & Sposito, 1991; Preston *et al*., 1997; Vogel *et al*., 2002).

3.2 Biological and chemical properties of macropores

Apart from physical characteristics such as size, continuity and surface area, the biological and chemical properties of macropores are also very different to those of the bulk soil. Macropores are biological ‘hot-spots’ in soils, partly due to a better nutrient supply and oxygen status, but also because living roots tend to grow preferentially in macropores, such as large earthworm channels or along aggregate faces (Bouma & Dekker, 1978; Jarvis *et al*., 1987; Hatano *et al*., 1988; van Noordwijk *et al*., 1993; Pitkänen & Nuutinen, 1997; Stewart *et al*., 1999). As roots are the main agents of soil drying, they also strongly influence the development of aggregate structure, especially in finer-textured soils (Kay, 1990; Materechera *et al*., 1994; Angers & Caron, 1998). Macropore soil is also characterized by larger carbon contents and greater microbial biomass, activity and functional diversity due largely to the carbon inputs from root exudates and root turnover (Stehouwer *et al.*, 1993; Mallawatantri *et al.*, 1996; Vinther *et al.*, 1999; Stewart *et al.*, 1999; Pierret *et al.*, 1999; Bundt *et al.*, 2001a,b; Vinther *et al.*, 2001; Pankhurst *et al.*, 2002). However, little is known concerning the extent to which enhanced biological activity in macropores influences the potential degradation and leaching of pesticides in soils. Vinther *et al.* (2001) found greater microbial activity and numbers in macropore wall materials compared to matrix in the subsoil of a moraine till, but only slightly larger degradation rates for the herbicides mecoprop and isoproturon. However, the overall degradation potential was small, presumably because the samples were taken at more than 1 m depth. Also, prior to sampling, no attempt was made to determine (i.e. by staining) whether the macropores represented active flow pathways. Accelerated degradation of organic contaminants has been found in artificial macropores, which was attributed to microbial growth due to favourable conditions for biofilm development, especially an improved aeration and supply of substrate (Pivetz & Steenhuis, 1995; Pivetz *et al.*, 1996).

The interfaces between natural macropores and bulk soil have especially distinct characteristics. For example, either clay or organic carbon, or both, can be enriched in aggregate coatings and biopore linings (e.g. Buol & Hole, 1959; Turner & Steele, 1988; Stehouwer *et al.*, 1993, 1994; Mallawatantri *et al.*, 1996; Worrall *et al.*, 1997; Mori *et al.*, 1999b), especially in undisturbed soil (i.e. grassland, forest soils or subsoil horizons in arable land). On a mass basis, this makes them more chemically reactive than the bulk soil, as evidenced by significantly larger sorption constants for organic compounds (Stehouwer *et al.*, 1993, 1994; Mallawatantri *et al.*, 1996). The composition of organic matter in macropore linings and aggregate coatings also differs significantly from the bulk soil. Thus, Ellerbrock & Gerke (2004) found that the content of functional groups in soil organic matter largely responsible for adsorption of cations and hydrophobic organic compounds was larger in coatings compared with subsoil aggregate interiors, but was smaller in coatings from the topsoil, indicating leaching of soluble, readily decomposable, organic matter. Similarly, Bundt *et al.* (2001a) inferred from ^{13}C and ^{15}N abundance, that organic carbon was younger and N cycling more rapid in the preferential flow paths of a forest soil compared to the matrix.

3.3 Water flow and solute transport in macropores

Water flow in soil pores is governed by the momentum balance between the driving forces (gravity and the pressure potential gradient), inertial forces, and the viscous resistance to flow arising from friction with the solid surfaces and within the fluid itself. These same forces operate on water in pores of all sizes, so that in this fundamental respect, the flow of water in a macropore does not differ from flow in any other pore. Nevertheless, major differences of degree can be identified. Based on the considerations noted earlier, capillary pressure potential gradients in conducting macropores are never likely to become large, so that gravity dominates the driving force. Furthermore, flow velocities in macropores under some conditions (e.g. near-saturated or ponded infiltration) may become so large (in the order of metres per hour, Beven & Germann, 1982), that the acceleration terms in the momentum balance may not always be negligible, an assumption which is implicit in the derivation of Darcy's law and Richards equation. Based on real-time measurements of water flow rates in soil macropores under ponded conditions using soft X-ray radiography, Mori *et al*. (1999a) reported Reynolds numbers varying between 50 and 80 for flow in natural soil macropores under ponded infiltration, which suggested that the flow regime was even transitional to turbulent. Logsdon (1995) reported Reynolds numbers larger than 1000 (i.e. turbulent flow) for flow through a partially saturated artificial macropore 6 mm in diameter open to a supply of free water at the soil surface.

The balance between the supply of water and losses to the matrix due to lateral infiltration controls the degree of saturation in individual macropores and therefore the prevailing flow mechanism, configuration and geometry. 'Film' or 'rivulet' flow may take place along macropore surfaces at low saturations (Bouma & Dekker, 1978; Tokunaga & Wan, 1997; Dragila & Wheatcraft, 2001). If the macropore surfaces are rough, thin film flow may occur at smaller pressure potentials than would be nominally required to generate flow according to the Laplace equation. However, calculations suggest that significantly faster flow than in the soil matrix only occurs when the films become larger and the pressure increases above ca. –10 cm (Or & Tuller, 2000; Tokunaga *et al*., 2000). If the degree of saturation continues to increase, capillary 'bridging' across the narrowest sections of variable-width fissures may occur (e.g. Bouma & Dekker, 1978; Wang & Naramsimhan, 1985), while 'pulse' flow has been observed in near-saturated artificial cylindrical macropores (Germann, 1987; Gjettermann *et al*., 2004). The soil macroporosity rarely flows full of water even under nominally saturated conditions, as a result of pore 'necks' in individual flow pathways and because not all macropores form continuous pathways open to the water supply, due to the existence of 'dead-end' or otherwise isolated pores (Bouma *et al*., 1977; Perret *et al*., 1999). Mori *et al*. (1999a) found that only 10 to 50% of the total macroporosity conducted water during 'saturated' flow through intact cores. Dragila & Wheatcraft (2001) presented a detailed treatment of the physical causes and consequences of these different flow regimes. They demonstrated that for thick film flow (> 1 mm), the Reynolds number is large and the flow regime is turbulent. Films of the order of a few tenths of millimeter in thickness exhibit laminar flow, but are inherently unstable and sometimes chaotic, developing traveling waves that greatly increase the effective pore water velocity. Intermittent 'pulse' flow occurs when a wave contacts the opposite wall of the macropore, establishing a capillary 'bridge' that dramatically reduces the flow velocity. Any small perturbation will allow film flow to quickly re-establish, de-saturating the 'plug', since from an energy point of view, the fluid prefers to maintain a free surface (Germann, 1987; Dragila & Wheatcraft, 2001). Of course, the same kind of intermittent pulse flow can be generated by changes in air pressure or input flow rate, or channel geometry (e.g. pore 'necks'). Although the effects on solute transport of variations in flow velocity due to film and pulse flow seem intuitively obvious with respect to convective flow, the full consequences of these different flow mechanisms for solute transport are not completely understood. For example, little is known about how different flow mechanisms influence kinetically-controlled sorption interactions with adjacent solid surfaces and the extent of diffusive exchange with surrounding matrix pores (Dragila & Wheatcraft, 2001; Gjettermann *et al*., 2004).

Non-equilibrium flow in macropores can only be sustained if vertical water flow rates are large in relation to the lateral infiltration losses into the matrix due to the prevailing pressure potential gradient. In this respect, lateral infiltration can be severely restricted by relatively impermeable clay coatings on aggregates and organic and clay linings in biopores. Thus, Gerke & Köhne (2002) found that the hydraulic conductivity of aggregate coatings in a loam subsoil was ca. six times smaller than in the bulk soil. The enhanced biological activity in macropores noted earlier can lead to water repellency of aggregate surfaces and macropore linings caused by microbial and root exudates, which also contributes significantly to a reduced water exchange with the matrix (Hallett & Young, 1999; Kätterer *et al*., 2001; Ellerbrock & Gerke, 2004).

Analogous to the case of water flow, non-equilibrium transport can only be sustained if the convective travel time is short compared with the characteristic time scales for the sum of losses due to sorption to macropore walls, diffusion into the matrix, and any transformation processes. Aggregate skins and macropore linings tend to reduce solute exchange by diffusion and enhance non-equilibrium solute transport. For example, Köhne *et al*. (2002) found that the effective diffusion coefficient of anionic tracers through aggregate skins was more than 30 times smaller than in the bulk matrix. However, these skins and linings can also be highly reactive. For example, concentrations of herbicides in water flowing through individual earthworm channels were reduced by between 20 and 90%, even at very high macropore flow velocities (Edwards *et al*., 1992; Stehouwer *et al*. 1994). Nevertheless, irrespective of the relative reactivity of macropore coatings, retardation of solute transport in macropore flow pathways is generally less than in the bulk soil (Andreini & Steenhuis, 1990; Vanderborght *et al*., 1999; Vanderborght *et al*., 2002), presumably due to a much smaller surface area per volume of large pores (Luxmoore *et al*., 1990) and because sorption kinetics play an important role in macropores, with advective transit times often being much shorter than the time required to reach sorption equilibrium (Worrall *et al*., 1997; Jensen *et al*., 1998; Hansen *et al*., 1999). Sorption to mobile colloids and clay-sized particles transported with flowing water in macropores may be an important additional factor limiting sorption retardation in macropores. Particulate matter is efficiently filtered out in matrix flow, but significant particle-bound transport in macropores has been demonstrated for strongly sorbing pesticides (e.g. Worrall *et al*., 1999; Villholth *et al*., 2000, de Jonge *et al*., 2000; Zehe & Flühler, 2001a; Petersen *et al*., 2002). An absence of significant sorption retardation during flow in larger macropores has also been indirectly demonstrated in several field experiments that show an equally fast initial breakthrough of solutes irrespective of their sorption characteristics (e.g. Kladivko *et al*., 1991; Traub-Eberhard *et al*., 1994; Brown *et al*. 1995; Elliott *et al*., 2000; Kung *et al*., 2000a; Jaynes *et al*., 2001), and in laboratory column experiments carried out either at saturation or at pressure heads very close to saturation (Jensen *et al*., 1998; Haws *et al*., 2004). Although these experiments show equally fast initial breakthrough irrespective of sorption, concentrations are clearly dependent on sorption, presumably reflecting the concentration in soil solution in the distribution zone. Significant sorption retardation occurs in smaller macropores, as demonstrated by a comparison of breakthrough curves for reactive and non-reactive solutes observed in the field (Kung *et al*., 2000a) and in the laboratory (Jensen *et al*., 1998; Akhtar *et al*., 2003; Haws *et al*., 2004). Scotter (1978) demonstrated theoretically the simultaneous arrival of tracers and strongly sorbing solutes in larger macropores, and the separation of breakthrough curves due to sorption effects during transport in smaller macropores.

3.4 Initial and boundary conditions

From the foregoing, it should be evident that (all other things being equal) increases in rainfall intensity will enhance macropore flow, since the soil water pressures attained during rainfall will be closer to saturation (and may even reach saturation if the intensity is greater than the saturated conductivity of the soil). This means that larger macropores will conduct water, which in turn will lead to a faster effective pore water velocity and shorter solute travel times (Kung *et al*., 2000a,b; Jaynes *et al*., 2001; Haws *et al*., 2004). Indeed, many experiments have demonstrated that higher rainfall intensities increase the leaching of surface-applied solutes (Bouma & Dekker, 1978; Trojan & Linden, 1992; Gjetterman *et al*., 1997; McLeod *et al*., 1998; Williams *et al*., 2000; Gish *et al*., 2004). Flow in a macropore of any given size is only triggered when the pressure potential exceeds its water-entry pressure. Therefore, in addition to the rain intensity, the initial soil moisture content, the duration of rainfall and the saturated hydraulic conductivity of the matrix determine when macropore flow occurs. It is well known that matrix hydraulic properties are strongly controlled by soil texture, and that clay soils generally have smaller saturated conductivities (Lin *et al*., 1999; Smettem & Bristow, 1999; Jarvis *et al*., 2002), but it is perhaps not as well recognized that water repellency can also reduce matrix infiltration capacity, even in relatively moist soils (Hallett & Young, 1999). Some field experiments suggest that this can greatly enhance non-equilibrium flow in macropores. For example, Edwards *et al*. (1993) found that water flow in earthworm channels under no-till corn was largest for intense storms that fell on initially dry soil, while Shipitalo & Edwards (1996) demonstrated greater leaching of tracers and pesticides from dry soil monoliths than from pre-wetted samples, following a 30 mm simulated rainfall. Water repellency appears stronger in undisturbed no-till arable or grassland soils (e.g. Hallett *et al*., 2001), where macropores are also often continuous to the soil surface (see '*Soil tillage and traffic*'). In this case, the surface micro-relief may enhance the channeling of water deep into the soil (Hallett *et al*., 2004). Under surface ponding, macropores open at the soil surface and located in micro-depressions will preferentially conduct most of the water (Dixon & Petersen, 1971; Trojan & Linden, 1992; Weiler & Naef, 2003).

The timing of rainfall events is an important control on solute leaching in soils prone to macropore flow, especially for surface-applied contaminants that are foreign to the soil, like pesticides, where the resident concentrations are very large in the first few millimetres of soil immediately following application. Thus, heavy rain soon after application often leads to large leaching losses (Gish *et al*., 1991a), since before flowing into macropores at the surface, incoming water interacts by diffusion and physical mixing ('rainsplash') with the resident soil water at and close to the soil surface. Conversely, leaching can be considerably reduced, either if dry weather follows application so that sufficient time is allowed for the solute to diffuse away from the soil surface, or if the pesticide is 'washed' into the soil matrix by one or more light rain showers which do not generate macropore flow (Isensee *et al*., 1990; Shipitalo *et al*., 1990; Edwards *et al*., 1993; de Jong *et al*., 2000). A similar effect has been noted for nitrate leaching following surface fertilization (Dekker & Bouma, 1984). Once the bulk of the chemical has penetrated into the matrix away from the soil surface, it is no longer so readily exposed to macropore flow (Gish *et al*., 1991a), since the micropore volume is much larger than the volume of macropores and very slow diffusion towards macropores becomes the rate-limiting factor. The frequency and duration of alternating wetting and draining periods in soil macropores also exert a significant control on solute leaching. For example, leaching of indigenous solutes contained within soil aggregates (i.e. salt, nitrate) is more efficient when it is driven by intermittent infrequent wetting cycles of short duration, due to the influence of intra-aggregate concentration gradients on diffusive exchange with the macropores (e.g. Cote *et al*., 1999; Cote *et al*. 2000).

4 MACROPORE FLOW AND HORIZON PROPERTIES AND MORPHOLOGY

Tracer breakthrough experiments carried out on clayey soils of contrasting macro-structure provided early qualitative evidence of the importance of soil structure and horizon morphology for solute transport, with more strongly developed structure resulting in more pronounced non-equilibrium transport than weaker structures (Anderson & Bouma 1977a; Bouma & Wösten, 1979). More recently, researchers have attempted to develop quantitative links between basic soil properties, horizon morphology, and model parameters describing non-equilibrium water flow and transport. For example, Vervoort *et al*. (1999) correlated the parameters of the 'mobile-immobile' ADE derived from column tracer breakthrough experiments to textural and structural properties in two soils of contrasting structure. They demonstrated that a strongly-developed structure was associated with subsoil horizons of larger clay content, which produced larger effective dispersivities, smaller mobile water contents and weaker lateral mass exchange. Shaw *et al*. (2000) also found the strongest non-equilibrium and smallest fraction of 'mobile' water in soil horizons with larger clay contents. Ersahin *et al*. (2002) related mobile-immobile ADE parameters to the characteristics of horizons in one soil profile. They found non-equilibrium solute transport in A and Bw horizons with a well-developed macroporosity and equilibrium transport in an albic E horizon that lacked larger macropores. Akhtar *et al*. (2003) noted that the degree of non-equilibrium transport of phosphorus in four contrasting soil types was closely related to the observed soil macro-structure, and concluded that '*survey description of soil structure seemed to be a good indicator of the rate at which preferential flow may occur and when preferential P leaching could occur*'.

Applying a dual-permeability model to the results of tracer experiments carried out on 30 columns sampled from cultivated topsoils, Jarvis *et al*. (2006) showed that ca. 60% of the variation in the coefficient controlling lateral mass exchange could be explained by variations in texture and organic carbon content. Lateral mass exchange was stronger in soils of coarser texture and larger organic matter content. The underlying reason for the effect of texture on mass exchange is reasonably clear, since swell/shrink in response to wetting and drying cycles is an important structure-forming process. Two reasons were put forward to explain why larger organic matter contents were associated with increased mass exchange and reduced non-equilibrium macropore flow, i.) organic matter stabilizes the soil against structural 'coarsening' caused by traffic compaction (see '*Soil tillage and traffic*'), and ii.) organic-rich soils were located in topographic depressions and footslopes, where the soil was generally wetter and thus less affected by structure-forming wetting and drying cycles.

Profile-scale dye tracing studies in field soils have provided further convincing visual evidence of the important control of horizon morphology and structure on non-equilibrium solute transport. For example, Flury *et al*. (1994) found marked preferential flow in thirteen out of fourteen Swiss agricultural soils and the observed dye patterns could be related qualitatively to the texture and visible structural development in individual horizons and profiles. Kim *et al*. (2004) showed a similar close qualitative correspondence between staining patterns under ponded infiltration and the texture and structure of soil horizons in three forest soil pedons. Kulli *et al*. (2003a) applied cluster analysis to the results of dye tracing experiments to demonstrate in a more quantitative manner the clear links between the texture and morphology of soil horizons and the extent of lateral mixing and non-equilibrium transport in six contrasting soil profiles. For seven contrasting Belgian soils, Vanderborght *et al*. (2001) demonstrated that the degree of lateral solute mixing could be linked to morphological features of soil horizons. In sandy soils, lateral mixing was controlled by vertical layering of horizons of differing texture, vertically-oriented 'tongues' and water repellent layers, while strongly developed macropore structures promoted weak lateral mixing at high flow rates in fine-textured soils. Long-term outdoor lysimeter tracer breakthrough experiments have confirmed that soil structure also exerts a strong control on solute transport at the soil profile scale under more natural boundary conditions with intermittent fluxes (e.g. Bergström & Jarvis, 1993; Brown *et al*., 2000).

Based on the ideas originally introduced by Deurer *et al*. (2003) to model heterogeneous preferential heterogeneous flow in a sandy soil matrix, Haws & Rao (2004) postulated that the strength of non-equilibrium macropore flow should generally increase with depth in the soil profile, as soil structure deteriorates and macroporosity becomes smaller. They quantified this effect by assuming exponential decreases in the macroporosity and mass transfer coefficient in a dual-porosity model. Although a strengthening of preferential flow with depth is probably common to many soils (e.g. Chen *et al*., 1999; Heuvelman & McInnes, 1999; Vervoort *et al*., 1999; Vanderborght *et al*., 2002), this will not always be the case, depending on the characteristics of soil horizons in the profile. For example, macropore flow dissipates when coarse-textured sand or gravel horizons are encountered in the subsoil (e.g. Flury *et al*., 1994; Kulli *et al*., 2003a). Therefore, rather than making 'a priori' assumptions about vertical variation in non-equilibrium flow, it seems more fruitful to relate transport parameters in models to the texture and observed morphological features of soil horizons. Predictions of how macropore flow changes with depth will then follow naturally from soil profile characteristics.

5 MACROPORE FLOW AND PESTICIDE LEACHING

The effects of macropore flow on pesticide leaching have been widely documented in many experiments on field soils and undisturbed lysimeters (see papers cited elsewhere in this review, and also in Flury, 1996). Losses due to macropore flow are typically less than 1% of the applied dose, but losses of between 1 and 5% may also occur (FOCUS, 2001). This is clearly a cause for concern, both for the environment and for human health (e.g. drinking water). For example, the EU drinking water standard states that concentrations of a single pesticide may not exceed 0.1 μg L-1. Assuming 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. In some hydrogeological formations, such as clayey glacial tills, or fractured chalk and limestone, non-equilibrium transport in fissures can be continuous to great depth, and can be a dominant mechanism for pesticide transport towards important underlying drinking water aquifers (Jørgensen *et al*., 1998; Haria *et al*., 2003; Stenemo *et al*., 2005; Roulier *et al*., 2006). However, in many loamy and clay soils prone to macropore flow, the deeper subsoil below rooting depth is much less permeable due to the absence of structure-forming processes, so that most excess water is routed to surface water via field drainage systems rather than to groundwater. In such situations, peak concentrations in drainage water in the hundreds of micrograms per litre range have been reported for many pesticides (FOCUS, 2001, and many papers cited elsewhere in this review), values that may harm aquatic ecosystems, depending on the toxicity of the compound in question.

Many hundreds of different pesticide compounds are used in agriculture, with widely contrasting physico-chemical properties. This makes it difficult to generalize about the effects of macropore flow on pesticide leaching. However, broadly speaking, the occurrence of macropore flow should dramatically increases the leaching of otherwise 'non-leachable' (i.e. strongly sorbed or fast degrading) compounds, although it will have less effect on highly mobile or persistent compounds (Larsson & Jarvis, 2000). Indeed, in a few cases, macropore flow may actually decrease pesticide leaching. For example, by calibrating a dual-permeability model against field data, Larsson & Jarvis (1999) showed that the leaching of the highly mobile herbicide bentazone to tile drains in a structured clay soil was reduced by c. 50% due to macropore flow. After application, most of the compound had moved into the soil matrix, where it was protected from water flowing in macropores, moving with a reduced convective velocity due to continued infiltration through macropores (see also Heathman *et al*., 1995). One consequence of the differential effects of macropore flow on inherently 'leachable' and 'non-leachable' pesticides is that the differences in leaching losses between agrochemicals of widely differing properties are significantly reduced in the presence of macropore flow. Thus, in one simulation study, two compounds were predicted to show a 100-fold difference in leaching in the absence of macropore flow, but showed only a four-fold difference in the presence of macropore flow (Larsson & Jarvis, 2000). However, model sensitivity analyses suggest that even in the presence of macropore flow, compound properties such as degradation half-life and sorption parameters still exert an important control on leaching (Dubus & Brown, 2002).

6 SOIL AND CROP MANAGEMENT PRACTICES

Soil and crop management practices strongly modify soil structure and, therefore, the extent of non-equilibrium flow and transport in macropores. In principle, this affords us the possibility of 'managing' macropore flow to limit undesirable impacts on the environment, although in practice, some conflicts may arise in trying to meet a range of different objectives concerning agricultural production and water quality. These aspects are discussed in the following sections.

6.1 Cropping and land use

There are some indications that the rooting characteristics of different crop species may induce differences in macropore flow and transport. One example has already been mentioned: the forage crop alfalfa develops a large strong taproot that has been shown to increase infiltration and non-equilibrium solute transport under conditions at and close to saturation (e.g. Meek *et al*., 1989; Mitchell *et al*., 1995; Caron *et al*. 1996). However, it seems better to approach this topic from a holistic point of view, by focusing on land management systems, since apart from the crop itself, many other factors related to land use can have profound impacts on the potential for non-equilibrium solute transport, not least tillage and traffic (see next section). This can be illustrated by comparing conventionally cultivated arable land with farming systems that include long-term leys or permanent grassland, which generally seem to show less susceptibility to non-equilibrium water flow and solute transport. For example, Edwards *et al*. (1992) compared water flows measured from large diameter earthworm burrows (*Lumbricus terrestris L.*) in paired fields under no-till maize and grassland, and found 60% less macropore flow at the grassland site during one growing season. Leaching of non-reactive tracers in structured clay soils has also been shown to be significantly slower from lysimeters sampled from grass leys compared to columns taken from plots under long-term continuous cereal cultivation (Jarvis *et al*., 1991b; Jarvis *et al*., 1996). It may seem strange that macropore transport is usually weaker in grassland soils, since they are generally considered 'well' structured. This paradox can be explained by the fact that the 'hierarchy' of soil structure (Hadas, 1987; Dexter, 1988) is better developed in grassland soils (Watts & Dexter, 1998) due to larger organic carbon contents, enhanced root turnover and intensive earthworm casting (Six *et al*., 2004) and less traffic compaction (see

'*Soil tillage and traffic*'). Thus networks of small, densely spaced and tortuous macropores apparently conduct more of the infiltrating water in grassland soils, even in climates characterised by frequent intense storms (Edwards *et al*., 1992).

6.2 Soil tillage and traffic

Tillage affects the total macroporosity, size distribution of large pores, and also their continuity. Different tillage implements and systems affect soil structure differently. For example, macropore flow is often generated at or very close to the surface in undisturbed soils under grass or no-till arable management (Bouma & Dekker, 1978; Gjetterman *et al*., 1997; Stamm *et al*., 1998; Petersen *et al*., 2001; Kulli *et al*., 2003a). In contrast, secondary tillage (e.g. harrowing or rotovating) for seedbed preparation usually results in uniform flow and transport in the uppermost shallow disturbed layer (Petersen *et al*., 2001; Jarvis *et al*., 2006). The more intensive the cultivation, the more the existing structure is pulverized and the more effective this barrier to macropore flow becomes (Petersen *et al*., 1997; Brown *et al*., 1999a,b). This effect of intense cultivation is also indicated by comparisons of solute breakthrough curves measured on repacked and undisturbed soil columns (e.g. Elrick & French, 1966). However, it is not clear exactly how small these seedbed aggregates must be to prevent non-equilibrium flow and transport. For example, Heathman *et al*. (1995) demonstrated that the addition of a 1 cm thick surface layer of air-dry aggregates 4.5 to 12.5 mm in diameter on the surface of packed, homogenized, soil consisting of aggregates less than 3.5 mm in size, produced non-equilibrium effects on solute transport, albeit under very intense rain. Tillage also disrupts the continuity of biopores in the disturbed layer (e.g. Heard *et al*., 1988). For example, Ehlers (1975) found that even though worm channels were present in the ploughed horizon of a loess soil, they did not conduct any dye tracer. Logsdon (1995) showed that water flow in artificial 6 mm diameter macropores with the upper 12 cm disrupted by tillage was 17 to 1100 times smaller than in macropores of the same diameter continuous to the surface. Pitkänen & Nuutinen (1997) found that only 1% of *Lumbricus* burrows counted at 10 cm depth were open at the soil surface in an unploughed treatment with shallow tine cultivation. Nevertheless, despite the fine tilth in the seedbed and the lack of functioning biopores in the ploughed layer, macropore flow can still be generated in conventionally tilled soils under persistent or intense rain, either along ped faces or loose soil volumes between denser structural elements within the ploughed horizon in strongly aggregated soils, or at the compacted interface (plough pan) with the undisturbed subsoil if the topsoil is only weakly structured (Petersen *et al*., 1997; Gjetterman *et al*., 1997; Schwartz *et al*., 1999; Petersen *et al*., 2001; Kulli *et al*., 2003a; Jarvis *et al*., 2006). Finally, it can be noted that differences in water flow and solute transport patterns induced by various primary tillage implements (e.g. mouldboard ploughs vs. spring tines or chisel ploughs) seem small (e.g.

Petersen *et al.*, 2001; Fortin *et al.* 2002), especially compared to the dramatic effects of intensive secondary tillage operations carried out to produce a seedbed.

Tracer studies have shown that macropore flow is more pronounced under no-till arable compared to conventional tillage management (e.g. Bicki & Guo, 1991; Vervoort *et al.*, 2001), particularly in weakly aggregated soils. Apart from the reasons discussed above, earthworm numbers are also usually significantly larger in no-till systems, especially deep-burrowing anecic species such as *Lumbricus terrestris* (Ehlers, 1975; Edwards & Lofty, 1982), mainly due to the presence of crop residues that encourage these surface feeders. Trojan & Linden (1994) showed that the presence of surface crop residues increased earthworm activity and also the depth of penetration of adsorbing red dye following short-term high intensity rainfall. In contrast, Farenhorst *et al.* (2000) showed that feeding activity of earthworms at the soil surface reduced the availability of atrazine residues for leaching. They suggested that short-term studies carried out under artificial 'worst-case' conditions (e.g. by irrigating immediately after pesticide application) ignore such effects and therefore can over-estimate the potential for pesticide transport in worm burrows to shallow groundwater in no-till systems in the field. Nevertheless, most studies (though not all, e.g. Gish *et al.*, 1995) have demonstrated an increased leaching of relatively mobile pesticides under no-till (e.g. Isensee *et al.*, 1990; Gish *et al.*, 1991a; Granovsky *et al.*, 1993; Heatwole *et al.*, 1997; Kumar *et al.*, 1998; Elliott *et al.*, 2000). However, caution should be exercised when generalizing the effects of tillage on leaching by macropore flow. For example, intensive tillage tends to reduce aggregate stability and stimulate particle leaching in macropores (e.g. Petersen *et al.*, 2004), which may in turn increase the leaching of strongly sorbed solutes prone to particle-facilitated transport (e.g. glyphosate).

The structure of the tilled soil layer is not static. For example, the fine seedbed created by secondary tillage is gradually modified under the influence of soil wetting and drying cycles, which alters the hydraulic properties of structural pores (Mapa *et al.*, 1986). In fine-textured soils, wetting and drying after tillage leads to consolidation, sealing and crack formation, which creates a surface structure more susceptible to macropore flow (Messing & Jarvis, 1993). There are some indications, although little hard evidence, that continuous macropores can also relatively quickly re-establish from the soil surface after disruption by tillage. Andreini & Steenhuis (1990) reported that spring harrowing eliminated macropore flow, but when the tracer and dye breakthrough experiments were repeated on samples taken post-harvest, they found strong macropore flow and no difference between tilled and no-tilled plots. They attributed this to the re-establishment of continuous earthworm channels through the tilled layer.

Field operations carried out by tractors, harvesters and other heavy vehicles induce long-term changes to the soil structure due to traffic compaction. Compaction degrades the aggregate hierarchy discussed earlier, resulting in a coarser structure (Hadas, 1987; Dexter, 1988; Lipiec *et al*., 1998; Watts & Dexter 1998) that enhances non-equilibrium water flow and solute transport. For example, Kulli *et al*. (2003b) showed that sprinkler irrigation on soil compacted by multiple passes of a sugar beet harvester resulted in surface ponding and strong non-equilibrium solute transport into the subsoil, primarily through earthworm burrows. Similar worm channels were also observed in the control plot, but the more densely distributed finer macropore system, which had been degraded in the trafficked plot, infiltrated most of the applied water without ponding, and preferential flow was much less pronounced.

6.3 Chemical application method and product formulations

In structured soils, the method of chemical application will significantly affect the degree of exposure to macropore flow and therefore solute transport. This is clearly indicated by tracer studies, where less pronounced leaching due to macropore flow was demonstrated when solute was either slowly dripped onto the surface or injected/incorporated at a shallow depth, compared to surface applications under ponded conditions (Kluitenberg & Horton, 1990; Ressler *et al*., 1998; Kätterer *et al*., 2001). The importance of the method of application is apparently less well documented for agrochemicals under realistic field conditions. However, Geohring *et al*. (2001) found that phosphorous leaching losses were an order of magnitude smaller when liquid dairy manure was ploughed into the soil compared with the less efficient incorporation achieved by shallow disking. Gish *et al*. (1991a) reported that soil-incorporated carbofuran leached less than atrazine and cyanazine, which were applied as surface broadcast sprays, despite a much larger inherent mobility. Alternative product formulations may also influence susceptibility to macropore flow. Slow-release herbicide formulations have been shown to leach less than technical grade material in laboratory columns, and were less mobile and more persistent than commercial broadcast sprays in field experiments (Gish *et al*., 1991a,b; Gish *et al*., 1994).

6.4 Organic waste management

Application of manure and organic wastes can also influence agrochemical leaching by macropore flow. Many complex interacting processes and factors are involved, so again, it is difficult to draw general conclusions. Firstly, the soil structure itself may be altered by organic amendments. For example, a soil that had received liquid dairy manure for 8 years had deeper penetrating earthworm burrows that were continuous to the surface, due to the presence of *Lumbricus terrestris*, and showed a more rapid tracer breakthrough (Munyankusi *et al*., 1994). The leaching of some strongly adsorbing solutes may also be promoted by colloidal particles and dissolved organic matter released by decomposition of organic waste amendments (Graber *et al*. 2001). On the other hand, incorporation of manure and straw in a heavy clay soil has been shown to almost double both the biodegradation rate and the sorption constant of the relatively mobile herbicide isoproturon (Johnson *et al*., 1997). In short-term 'forced' laboratory column leaching experiments, a clay soil amended with manure leached three times less isoproturon than control columns (Johnson *et al*., 1997). However, simulations based on a calibrated field experiment on the same soil type suggested that manure incorporation would only reduce long-term total leaching to field drains by c. 10% (Besien *et al*., 1997).

7 MACROPORE FLOW IN THE LANDSCAPE

Additional factors influence the occurrence and significance of macropore flow when scaling up from the soil profile to the landscape scale. Topography exerts a strong control on hydrological processes on hillslopes, which in turn strongly influences soil genesis and properties. Indeed, spatial patterns of soil type and landform are usually strongly correlated (Lin *et al*., 2005). Nonetheless, despite the huge amount of research that has been conducted on hillslope hydrology, apparently only a few studies have specifically focused on topographic controls of macropore flow, at least in agricultural landscapes. Zehe & Flühler (2001b) investigated the spatial patterns of macropore transport revealed by plot-scale dye and bromide tracer experiments carried out at different slope locations in a small hilly catchment with weakly structured loamy soils. They found stronger macropore transport at wetter footslope locations due to somewhat finer-textured soils and larger, more active, earthworm populations. However, it can be noted that their footslope site number 10 was also under no-till management, which as we have seen earlier, also strongly promotes the development of earthworm burrow systems.

Roulier & Jarvis (2003) compared the extent of macropore flow in microlysimeters sampled from a slope catena in the 'hummocky' landscape typical of clayey moraine till. Using a dual-permeability model to interpret the data, they found equilibrium transport in lysimeters taken from topographic depressions, whereas strong macropore flow was found in samples from hilltop locations, where the soil was characterized by a larger clay content and much smaller organic matter content. This was attributed to the effects of drying intensity on the decomposition of organic matter and aggregate formation: in the topographic depressions at this site, lateral downslope flow maintains a shallow water table throughout the year (Lindahl *et al*., 2005), which prevents soil drying and reduces organic matter decomposition. The importance of 'drying intensity' for structure development and solute leaching in finer-textured soils was also emphasized by Vervoort *et al*. (1999), and has been indirectly demonstrated in lysimeter experiments where the amount of precipitation was adjusted by artificial irrigation (Bergström & Jarvis, 1993; Beulke *et al.* 1999).

Aside from the effects of topography and local hydrology on soil properties, the fact that the depth to the water table varies systematically with slope position may also directly influence the generation of macropore flow. For shallow soils overlying fissured chalk, Haria *et al.* (2003) demonstrated that fissure flows at the interface between soil and rock were generated more frequently at downslope locations with shallower water tables, due to the effects of the capillary fringe on water saturation in the chalk matrix. A similar effect was predicted for moraine clay soils in the catchment modelling study reported by Christiansen *et al.* (2004).

Little is known about the quantitative significance of macropore flow for contamination of water resources at the larger catchment scale. As the scale increases, other processes, loss pathways and sources (e.g. surface runoff, point sources) also contribute to the total contaminant loading. Based on high time-resolution monitoring of pesticide losses following simultaneous controlled applications across a 2 km^2 catchment in Switzerland, Leu *et al.* (2004a,b) showed that point sources from farmyards produced the largest concentrations in the stream, but these were also highly transient (< 2h) and contributed only ca. 20% of the total load. They also showed that the diffuse loss, which was dominated by preferential flow to subsurface drainage systems and surface runoff, showed a very large spatial variation, despite the small size of the catchment. Most of the losses originated from a few fields, or parts of fields ('hot spots') that for reasons of topography and soil permeability were susceptible to these fast runoff mechanisms. Lindahl *et al.* (2005) also showed that point sources due to spills when cleaning and washing spraying equipment contributed significantly to the pesticide loadings to a small stream draining a 9 km^2 agricultural catchment in Sweden, and that macropore flow to field drainage systems dominated the diffuse losses.

8 SUMMARY OF CURRENT UNDERSTANDING

It seems clear from the review of the literature presented in this paper that a great deal is known and understood about the effects of macropore flow on solute transport. Indeed, despite the complexity of the processes, a broad consensus seems to have emerged. The following ten major conclusions can be identified:

1.) macropores are structural pores (root channels, earthworm channels, fissures and inter-aggregate packing voids) of large diameter, high continuity and low tortuosity that allow the maintenance of marked lateral physical non-equilibrium conditions during vertical flow and transport. From a pragmatic 'functional' point of view, pores larger than ca. 0.3 mm in diameter can be considered as macropores.

2.) Although the physical mechanisms of water flow in macropores are complex, it is clear that the assumptions underlying Darcy's law are not always met: macropore flow occurs predominantly under the influence of gravity (capillarity is negligible), inertial forces are certainly not negligible, and turbulent flow may even occur in large macropores at high input rates (e.g. under ponding).

3.) The physical, chemical and biological micro-environment in macropores contrasts strongly with the bulk soil. Organic and inorganic linings and coatings in biotic macropores and on aggregate surfaces restrict lateral mass transfer, enhancing non-equilibrium water flow and solute transport. Macropores are biological 'hot-spots' in soil, and may also have more chemically reactive surfaces. However, sorption retardation in macropores seems always less than in the bulk soil, partly due to the low ratio of surface area to pore volume, but also due to kinetic (chemical non-equilibrium) effects during transport.

4.) Soil macropore networks are hierarchical in nature. Larger macropores are generally more continuous, less tortuous and more widely spaced, which generates faster water flow, weaker lateral mass exchange, less sorption interaction and therefore stronger physical and chemical non-equilibrium.

5.) Surface boundary conditions exert a strong control on non-equilibrium water flow and solute transport. High intensity and long duration rain generates pressures closer to saturation that allow larger macropores to take part in the transport process, leading to the consequences listed under point 4.) above.

6.) The effects of initial conditions are complex, especially for soils that become water repellent when dry, or where the structure is a dynamic function of water content (i.e. swell/shrink clay soils). However, in the absence of such complications (which are not especially unusual), wetter soils will clearly generate more macropore flow.

7.) The strength of non-equilibrium water flow and solute transport is closely related to the observed morphology of soil horizons and pedons (e.g. size distribution of biotic macropores, grade of aggregate development and presence of aggregate skins). Basic soil properties (e.g. texture, organic matter content) also exert a strong control on macropore flow and transport, both through their effect on matrix hydraulic properties and also due to their strong influence on soil aggregation. The aggregate hierarchy is better developed in soils of smaller clay content and larger organic matter content, which are therefore less susceptible to non-equilibrium water flow and solute transport (see point 4. above).

8.) The impact of macropore flow on agrochemical leaching depends strongly on the solute properties controlling sorption and transformation processes, and on whether the chemical is indigenous to the soil or not. Although macropore flow will dramatically increase leaching losses of otherwise non-leachable substances that are foreign to the soil (e.g. strongly sorbing organic contaminants that are quickly degraded), it may actually decrease the leaching of indigenous mobile solutes like nitrate.

9.) Soil tillage and traffic strongly affect macropore flow and transport. Physical non-equilibrium is practically eliminated in the upper few centimeters of soil by intensive secondary cultivation performed to create a seedbed. Primary cultivation implements that invert and break up the soil disrupt the continuity of biopores (at least for some months), but non-equilibrium flow and transport can still take place along inter-aggregate packing voids. Macropore flow can also be generated by the abrupt change in matrix conductivity in compacted zones or 'pans' at the base of the plough layer. Compared to conventional tillage, many soils under no-till arable management (especially weakly aggregated ones) show a greater propensity for non-equilibrium solute transport, due to well-developed networks of earthworm channels. However, this may not always lead to increases in agrochemical leaching. For example, conventional tillage may result in greater losses if particle-bound transport in macropores is a dominant leaching mechanism.

10.) Land use and cropping influence soil structure and macropore flow. Non-equilibrium flow and transport seems generally weaker under long-term grassland than on arable land, presumably due to increased organic matter contents under grass, increased earthworm casting activity and root development, and less traffic compaction, all of which results in the preservation of a 'finer' soil structure and therefore slower flow and stronger lateral mass exchange.

9 MACROPORE FLOW MODELS

Given the broad consensus outlined in the previous section, the question now naturally arises as to whether we can make use of this knowledge to make quantitative predictions of macropore flow impacts on water quality. The huge experimental research effort described in previous sections has certainly stimulated the development of many models that are intended to be used for this purpose. Before discussing the advantages and disadvantages of some specific examples of the more widely used models, some general comments may be relevant and worthwhile. Macropore flow in near-surface soil is highly intermittent and depends sensitively on initial and boundary conditions. In principle, this implies that models should be strongly based in the physics of the processes, since only then can they properly reflect the response of pesticide fluxes to varying initial and boundary conditions. On the other hand, it may not be necessary (or even wise) to use exact physics-based models of water flow at the pore scale, since their assumptions are too restrictive. The mechanisms of water flow in macropores are complex and the geometry or configuration of the flow is highly variable and will always be 'a priori' unknown. Thus, simpler quasi-physical approaches may be preferable. For example, generalizing Newton's law of shear stress for gravity-driven 'film flow' along macropore walls leads to a 'kinematic wave' approximation that has been widely used in various analytical and numerical forms to model macropore flow in soil, and which can broadly match observed flow patterns (e.g. Beven & Germann 1981; Germann, 1985, Germann & Di Pietro, 1999; Alaoui *et al*., 2003; Larsbo *et al*., 2005). Clearly, from a pragmatic point of view, Darcy's law might also be acceptable as a reasonable quasi-empirical model of macropore flow, even though it makes several simplifying assumptions that are not strictly valid (Gerke & van Genuchten, 1993).

For completeness, macropore flow models are usually incorporated into larger models dealing with flow and transport processes in the entire pore system. Different approaches can be adopted and the choice of appropriate model is really a question of striking a reasonable balance between physical realism and usability for a defined purpose. In principle, three-dimensional 'hybrid/discrete-pore' models that apply continuum physics both to individually-defined macropores and to a soil matrix domain (e.g. Vogel *et al*., 2006) should allow for the most explicit and physically-realistic representation of soil structure. However, although computer power is rapidly increasing, numerical limitations mean that such approaches are not yet practical for larger routine applications, given the density and geometric complexity of macropore networks in soils (e.g. Perret *et al*., 1999) and the importance of micro-scale features such as macropore linings and coatings. These problems are especially acute for near-surface soils subject to low-intensity natural rainfall, when networks of densely distributed smaller macropores will constitute the preferential flow pathways. Thus, for operational reasons, models based on the concept of effective parameters for representative elementary volumes characterizing two or more flow domains are more often used. Dual-permeability models (e.g. Gerke & van Genuchten, 1993; Larsbo *et al*., 2005) lump all macropores into one domain, which may introduce errors when the surface boundary fluxes change, as the size of the dominant macropores conducting water changes. They also ignore lateral concentration gradients in the matrix, which introduces a time-dependence to the mass exchange coefficient. However, these models are simple and they can reproduce most (if not all) of the phenomena discussed in this review. When calibrated for a specific situation, they may be accurate enough for many purposes, especially for predicting long-term average leaching losses.

9.1 Examples of pesticide leaching models dealing with macropore flow

In the following section, a number of simulation models that account for macropore flow, as well as other key processes affecting pesticide leaching such as sorption and degradation, are briefly described and compared with respect to their strengths and weaknesses. Emphasis is placed on a suitable balance between model realism and useability with respect to ease of parameterisation for the purposes envisaged in the FOOTPRINT project. Strongly non-mechanistic (empirical) models are not discussed for the reasons outlined above.

9.1.1 The Root Zone Water Quality Model (RZWQM)

RZWQM is a comprehensive agricultural systems model intended as a research tool to investigate the effects of agricultural management on crop production and environmental quality (Malone et al., 2004a). The model was recently adapted to account for pesticide fate (Wauchope et al., 2004) and accounts for preferential flow processes. The 1D model is now an integrated physical, biological and chemical process model that simulates plant growth, and movement and interactions of water, nutrients and pesticide over and through the root zone. The model can simulate the presence of a fluctuating water table and the flow of water and chemical to tile drains. Although development work on the model started in 1985, the first version of the code was released in 1992 (RZWQM team, 1992) and the model has been upgraded on a regular basis since. Comprehensive presentations of the model and its governing equation can be found in Ahuja et al. (2000) and in a special issue of Pest Management Science (volume 60, issue 3, March 2004, ISSN 1526-498X). The model has benefited from ca. 40 evaluation studies against measured data (Malone et al., 2001, 2004a). The model can simulate both the rapid gravitational transport of surface-applied pesticides through macropores and the preferential transport of chemicals within the soil matrix via mobile-immobile zones.

In the model, rainfall is assumed to infiltrate into the soil according a modified version of the Green-Ampt equation (Ahuja et al., 1983) until the maximum soil infiltration capacity of the soil is exceeded. The excess rainfall is then routed into macropores. The maximum macropore flow rate is calculated using Poiseuille's law assuming gravity flow (Ahuja et al., 1993) while the lateral infiltration of macropore water into the unsaturated soil matrix is simulated by a lateral (radial) Green-Ampt type equation (Ahuja et al., 1999). The movement of water from the macropores into the soil matrix may be restrained by the presence of compacted zones or organic coatings surrounding macropore walls and this is accounted for by adjusting the radial infiltration rate in the macropores using an arbitrary lateral sorptivity factor (Malone et al., 2004b). While it is considered in the model that the water entering macropores is evenly distributed among macropores, it is known that only a fraction of the total macroporosity contributes to the transmission of water and most percolate originates from a relatively small percentage of percolate-producing macropores (Quisenberry et al., 1994). This is accounted for by considering a number of macropores per unit area which are most effective in transmitting water, which is calculated from the effective macroporosity and an average macropore radius. In essence, water and associated chemicals moving through the macropores mix with a portion of the soil surrounding the macropore walls (effective soil radius), and react with soil according to chemical partitioning. The use of a soil radius is designed to account for i) the greater partitioning between soil and pesticides in natural macropores compared with the soil matrix, ii) the blockage and tortuosity of natural macropores; and, iii) the lateral water movement through soil into macropores rather than ponded water movement into macropores as simulated by RZWQM (Malone et al., 2004c). Any flow in excess of the maximum flow rate (if macropores are present) or in excess of the infiltration rate (if macropores are not present) contributes to runoff. Soil water is redistributed in the soil using Richards' equation. Chemical transfer to macropore flow is simulated using a non-uniform (exponential) mixing model (Ahuja, 1986; Heathman et al., 1986). Partitioning is assumed to occur in both macropores and the soil matrix.

The soil matrix is divided into mobile (mesopore) and immobile (micropores) regions and is treated separately from macropore flow. During infiltration events, water and chemicals are assumed to only move through mobile regions in the saturated zone by 'partial piston displacement', which introduces a degree of preferential transport of chemicals in the soil matrix. During each infiltration step, partial piston displacement is followed by partial chemical mixing in each 1-cm soil increment, which simulates dispersion. Chemicals are transferred between mobile and immobile regions during each infiltration time step by diffusion. The only two controlling parameters specific to these processes are the fractional microporosity and the chemical diffusion rate in water.

Parameters which are specific to the simulation of macropore flow in the model are:

- *The lateral sorptivity reduction factor*, which accounts for impeded lateral water movement into the soil surrounding macropores due to organic coatings or compaction (Ahuja et al., 1995).
- *The effective soil radius* (Malone et al., 2001), which represents the lateral radius of soil surrounding macropore walls that interacts with water moving through macropores. This parameter indirectly relates to the volume of soil surrounding macropores available for sorption. Soil radius values ranging from 0.5 mm to 0.6 cm have been used in earlier

applications of the model (Ahuja et al., 1995; Malone et al., 2001, 2004b) to bromide and pesticide cases.

- *The fraction of dead-end macropores.*
- *The average radius of cylindrical pores*.
- and *the width, length and depth of cracks*.

The preferential flow component of the model has been tested in a range of applications involving structured soils (Malone et al., 2001; Jaynes and Miller, 1999; Farahani et al., 1999; Kumar et al., 1998). These studies demonstrated that water predictions for drainage, percolation and/or runoff were improved by accounting for macropore flow (Singh et al., 1996; Bakhsh et al., 1999; Kumar et al., 1998). Further modifications of the model to simulate cracking soils, dynamic effective macroporosity and/or the dynamic lateral sorptivity factor have the potential to further improve the capabilities of the model (Malone et al., 2004c; Ghidley et al., 1999). Short summaries of the evaluation studies undertaken with RZWQM are presented in Malone et al. (2004a).

The main weaknesses of the model are that i.) it is overparameterised: for example, parameters are needed for both the Green-Ampt and Richards equations, when Richards equation alone is in principle sufficient, while seven parameters are needed to describe the macropore flow domain and its interaction with the matrix. ii.) despite this overparameterisation, some processes are poorly captured. For example, diffusive exchange between macropores and matrix is not considered. A further simplification is that convective transfer from the matrix to the macropores within the soil apparently cannot be modelled, so that the only source of water and solutes for the macropores is at the soil surface.

9.1.2 PEARL

The PEARL model (Tiktak et al., 2000; Leistra et al., 2001) is a one-dimensional leaching model that has been extensively used for research purposes in the Netherlands and to evaluate the potential for pesticides to contaminate water resources in Europe. The model is an integration of two Dutch codes: PESTLA (PESTicide Leaching and Accumulation) and PESTRAS (PESTicide TRansport ASsessment). Separate versions of PEARL have been developed for spatially distributed applications, including GEOPEARL (Tiktak et al., 2003, 2004) and EUROPEARL (Tiktak et al., 2004) which is designed for pan-European applications. As part of the APECOP project (Vanclooster et al., 2003), the PEARL model was refined to account for losses of pesticides through volatilisation and transport of water and pesticides through preferential flow. The new version of the model which integrates these processes will be released in 2006 under a FOCUS version of the model which will enable its use in the European pesticide registration context. The standard version of the PEARL model is based on the resolution of the Richards' equation for water flow and on the convection-dispersion equation for solute transport. The water component of the model is handled through the SWAP soil water model (Van Dam et al., 1997).

The new preferential flow component of PEARL for water is based on a revised version of the Richards' equation modified to deal with preferential flow, taken from the FLOCR model (Bronswijk, 1988; Oostindie & Bronswijk, 1992; Hendriks et al., 1999). The reader is referred to this publication and the PhD thesis of van Dam (2000) for a list of the equations underpinning the approach. Two classes of macropores are distinguished based on their continuity. Macropores running throughout the profile (i.e. from the surface to the bottom of the soil profile) define the 'main bypass domain' while those ending at different depths in the profile are referred to as the 'internal catchment domain'. The volume of macropores in the main bypass domain consists of a network of interconnected macropores and is constant with depth up to the depth where the internal catchment domain stops. Thereafter, the volume of pores in the main bypass domain is assumed to decrease linearly with depth. The volume of macropores in the internal catchment domain consists of pores which are poorly connected and which end at different depths. The decrease in the number of internal catchment macropores is described using a power law function.

In addition, two types of macropores are distinguished based on the dynamics of the macropore volume which varies according to shrinking and swelling processes: i) permanent macropores whose volumes are independent of the soil moisture status; and, ii) shrinkage cracks whose volume varies according to their shrinkage characteristics and the current soil moisture content. The change of volumes in this latter class of macropores is simulated in a simplified way in SWAP, which assumes that the soil level remains fixed and that shrinking and swelling only influence pore volumes.

Water falling at the soil surface is assumed to reach the macropore network directly or if the rainfall intensity exceeds the infiltration capacity of the soil matrix. Water in the macropores will accumulate at their bottom. Uptake into the matrix is assumed to occur if the macropores become saturated. Solute transfer to macropores at the soil surface is simulated using a mixing cell concept which is similar to that used in the MACRO model. It is assumed that the two classes of macropores (main bypass and internal catchment) each have a uniform pesticide concentration. Exchange of pesticide between macropores and the matrix is computed as the product of the water uptake rate and the pesticide concentration in the corresponding domain. The description of solute transport in macropores is therefore simple and only requires one parameter (the thickness of the mixing layer).

The refined version of PEARL, which includes a description of macropore flow has benefited from very little testing at this stage, an exception being its application to bentazone leaching data at the Andelst experimental site (Vanclooster et al., 2003). Simulations without considering preferential flow resulted in zero concentration of bentazone for the first and most important drain-flow event about 20 days after application. An adequate simulation of the first peak concentration could be obtained using the revised version of the PEARL model using a mixing-cell thickness of 1 mm and a saturated hydraulic conductivity of the soil matrix of ca. 1 cm/d. The weaknesses of the version of PEARL including preferential flow are similar to those of RZWQM: an excessive number of parameters combined with a treatment of mass exchange between the flow domains that ignores some important aspects.

9.1.3 Vertical Infiltration through MACroporous swelling soils (VIMAC)

The physically-based VIMAC model, which is conceptually similar to PEARL, is described in detail in Greco (2002). The model simulates the movement of water in swelling and shrinking clay soils. The model consists of three flow domains: the soil matrix, with flow modelled using a Darcy equation, and macropores. Macropores are divided in two sub-domains: shrinkage cracks, with aperture dynamically depending on matrix water content, and permanent macropores, independent of the saturation of the matrix. In the shrinkage cracks sub-domain, a kinematic wave equation was derived by considering laminar motion of thin water films, along two parallel vertical walls. In the permanent macropores sub-domain, a kinematic wave equation is assumed, with parameters physically related to macropores shape and dimension. Exchange of water between the macropore domains and the matrix is introduced in the form of sink terms in the macropore mass balance equations, and as source terms in the matrix continuity equation. Infiltration through macropore walls is modelled using a diffusivity function derived from aggregates sorptivity measurements. The internal catchment is included by considering at each layer a fraction of dead end permanent macropores. Water ponding at the bottom of dead end macropores is infiltrated into the corresponding matrix layer. The VIMAC model was tested against the results of infiltration experiments through a large undisturbed swelling and shrinking clay soil column. Parameters relating to the soil matrix were obtained through determinations of the hydraulic conductivity curve, the water retention curve, shrinkage characteristics and aggregates diffusivity. All other parameters were inferred from direct observation of the soil structure except for morphologic parameters relating to macropores (the horizontal areas of permanent macropores for each soil layer), which were obtained through model calibration. The model adequately simulated observed breakthrough curves and soil moisture content in the structured lysimeter.

9.1.4 Adaptations of the Gerke and Van Genuchten model

The S_1D_DUAL model (Ray et al., 2004) and the DUAL model described by Gerke and Köhne (2004) are adaptations of a dual-permeability model developed by Gerke and Van Genuchten (1993) and Ray et al. (1997) to simulate the reactive transport of pesticides in macroporous soil. This dual-permeability concept is based on application of Richards equation and the ADE to two overlapping pore continua. S_1D_DUAL allows the consideration of depth-dependent parameters for the preferential flow domain, the uptake of water by roots, sorption distribution coefficients and kinetic sorption coefficients. The model also allows for variable rates of degradation in the matrix and macropores domains to be considered. Ray et al. (2004) report an application of the model for atrazine and trifluralin for four hypothetical scenarios: i) single-permeability simulations as benchmark simulations; ii) dual-permeability simulations with the assumption of equilibrium sorption in the matrix domain and the preferential flow domain; iii) dual-permeability simulations with no sorption in the PFD and equilibrium sorption in the matrix domain; and, iv) dual-permeability simulations with kinetic sorption in the preferential flow domain and equilibrium sorption in the matrix domain. A range of tests was also undertaken using various hypotheses for the variation of degradation rates with depth.

The 1D model of Gerke & Van Genuchten (1993) was further extended by Vogel et al. (2000) to a 2D dual-permeability water flow and solute transport model by modifying a finite element code (Vogel, 1987). The model allows for 2D two-domain simulations involving water and solute transfer between the fracture and matrix domains. The model explicitly considers the spatially distributed nature of soil hydraulic properties and can differentiate between heterogeneities due to macro-scale variability in the soil hydraulic properties and heterogeneities caused by micro-scale soil structural effects. The model accounts for linear sorption and first-order degradation.

Compared with the models described earlier, this ‘family’ of dual-permeability models has the advantage of conceptual simplicity, a minimal content of empiricism, and a limited number of parameters to be identified. One disadvantage is that numerical stability is difficult to maintain for parameter settings in the macropore domain that truly reflect large macropores. These models have not been so often tested, but their validation status can be judged from that of the widely used model MACRO (see below), since they are in many respects similar.

9.1.5 MACRO

The macropore flow model MACRO (Jarvis et al., 1991a; Larsbo and Jarvis, 2003; Larsbo et al., 2005) is a physically based 1D model which considers two flow domains (i.e. 'micropores' and 'macropores') to describe the transport of water and reactive solutes in soils. In the micropores, the water retention curve is described using the Van Genuchten function (Van Genuchten, 1980) while the hydraulic conductivity function is simulated using the Mualem's model (Mualem, 1976). In the macropores, and in contrast to the model of Gerke and Van Genuchten (1993a), flow is simulated using a non-capillary ‘kinematic wave’ driven by gravity (Germann, 1985). The hydraulic conductivity in the macropores is expressed as a power function of the macropore water content. The division between micropores and macropores is made through the definition of a water potential defining a minimum macropore size and the corresponding saturated micropore water content and hydraulic conductivity. Lateral water flow from macropores to micropores is described using a first-order approximation to the water diffusion equation while an instant transfer of excess water from micropores to macropores is assumed should the micropores become saturated. Solute transport in the micropores is described using the convection-dispersion equation with a source-sink term representing diffusive mass exchange between flow domains. Solute transport in the macropore region is assumed to be a purely convective transport. The solute concentration in the water routed into the macropores at the soil surface is calculated assuming instantaneous equilibrium in a thin surface layer.

The dual-permeability model MACRO has benefited from a large program of evaluation against laboratory and field data (e.g. Jarvis et al., 1995; Bergström et al., 1994; Larsson and Jarvis, 1999; Jarvis et al., 2000) due to the model being retained for risk assessments for pesticides in a number of EU member states. Generally speaking, the model has been shown to perform adequately in numerous instances with regard to the prediction of the timing and magnitude of percolation/drainflow and pesticide concentrations in percolation/drainflow. Sensitivity and uncertainty analyses of MACRO were undertaken by Dubus & Brown (2002). Predictions of percolation were only marginally affected by changes in input parameters. In contrast, predictions for pesticide losses were found to be influenced by a large number of parameters and to a much greater extent. Results were found to be dependent on the soil/climate scenario considered. In most scenarios, predictions of pesticide losses by the model were found to be most dependent on parameters describing sorption and degradation in the model. Under specific instances, the predictions for pesticide losses were also found to be strongly affected by the soil hydrological properties.

MACRO is the simplest physically-based dual-permeability model available, only requiring four additional parameters compared to Richards/ADE based models. Nevertheless, the treatment of macropore transport is physically-based and comprehensive enough to capture most aspects of the process. Unlike RZWQM, PEARL and VIMAC, MACRO is strictly a dual-domain model, accounting neither for preferential flow in the matrix (like RZWQM), nor for different types of macropores (e.g. bypass and internal catchment, like in PEARL or VIMAC). As a simple model, it may not have the same flexibility in matching observed pesticide fluxes and distributions. On the other hand, it is doubtful whether the information and data is available to parameterise the more complex models. It is also likely that calibrations of such models will suffer strongly from 'equifinality', with many combinations of parameter values fitting the available data equally well (Larsbo and Jarvis, 2005).

9.2 Prospects for predictive modelling

No model is perfect, and even if it were, true prediction of macropore flow and transport would still be highly uncertain because the flow pathways and mechanisms are in principle 'a priori' unknowable (Jury & Flühler, 1992). Although prediction is difficult, models can be calibrated at the column scale making use of experimental data on solute transport. Macropore flow models calibrated in this way for a limited number of well-chosen 'benchmark' or worst-case sites can still be very useful, and are already being used, for some management applications (e.g. leaching risk assessments for pesticide registration, FOCUS, 2001). However, even pre-calibrated predictions are still likely to be highly uncertain, because calibrated parameter sets are unlikely to be unique given the usual paucity of data (Beven, 1991). The predictive uncertainty arising from this 'equifinality' should be quantified (e.g. Larsbo & Jarvis, 2005), but this is rarely done.

We would also like to make predictions at much larger scales (both spatial and often also temporal) than the observation scale at which models can be calibrated (e.g. mapping leaching risks at catchment or even regional scales, Vanclooster *et al*., 2004). Macropore flow models must then be used predictively, with very limited possibilities for calibration. This is only possible if the sources of spatial variation in macropore flow at any given scale are known and understood. In this respect, Addiscott & Mirza (1998) noted that our ability to make predictions of soil processes at any given level in a hierarchy of scales …*'may depend simply on the degree of certainty attached to our knowledge of the dominant forces…at that level*'. They also suggested, that…*'larger areas of land should behave in a more determinate and therefore* *predictable way than small volumes of soil*'. To illustrate this contention, Addiscott & Mirza (1998) take the example of denitrification in soils, which together with macropore flow is surely the most often cited example of a highly variable and essentially unpredictable soil process. At the small-scale, denitrification is difficult to predict because the micro-sites ('hot-spots') responsible for most of the nitrous oxide emission are highly spatially variable, their locations are unknown, and their activity is very sensitive to small variations in soil wetness. However, predictive relationships for denitrification are much easier to establish at the landscape scale, since soil wetness, which is the major control on denitrification, can be assessed from topography and soil type (Groffman & Tiedje, 1989; Addiscott & Mirza, 1998; Lilly *et al*., 2003). The analogy with macropore flow seems obvious, since its occurrence is closely related to soil morphology and other properties of the soil that are observable or measurable at the pedon scale, and to site management factors that are known. In turn, these controlling factors are in principle predictable, since the soil landscape is deterministic with the spatial distribution of soil types depending on the well-known factors of soil formation described more than 100 years ago by Dokuchaev, including parent material, topography and vegetation (Heuvelink & Webster, 2001; Lin *et al*., 2005). Using a range of examples from catchment hydrology, Seyfried & Wilcox (1995) also convincingly made the point that the significance of deterministic variability has been underestimated in the hydrological sciences, even though it dominates hydrologic variability at larger scales. Therefore, a major research question for the future will be to develop methods to map the impacts of macropore flow on water quality at the landscape scale, including algorithms that quantify the effects of alternative management strategies and mitigation practices. Lin *et al*. (2005) suggested that the gap between soil structure quantification and the prediction of impacts on water flow and solute transport can be closed by integrating classical pedological approaches to describing soil-landscape patterns with the process knowledge gained from soil physics and hydrology. Some efforts in this direction have already been made. Thus, Weiler & Flühler (2004) proposed classifying soil types in terms of their susceptibility to preferential flow based on image analysis of the results of plot-scale dye tracing experiments. Simple indices or descriptors of soil macropore structure and/or resulting flow patterns could be used to support the development, refinement and testing of schemes that aim to classify soil susceptibility to macropore flow. These could be, for example, fractal dimensions calculated from images of pore structures or dye staining patterns (see next section) or mathematical indices that characterize the spatio-temporal heterogeneity of fluxes measured in solute breakthrough experiments (Stagnitti *et al*. 1999; de Rooij & Stagnitti, 2002). Classification schemes that link these transport characteristics to data and information contained in existing soil survey databases may gain rather immediate and widespread application (Vervoort *et al*., 1999; Lin *et al*., 2005). Some proposals along these lines have already been put forward (Quisenberry *et al*., 1993; Jarvis *et al*., 1997) but they have neither been extensively and systematically tested and nor are they sufficiently comprehensive and generally applicable. For example, they fail to consider the major effects of management practices such as tillage, traffic and cropping on non-equilibrium flow and transport. It remains a major challenge to adequately account for such aspects in model-based decision-support systems designed to predict the effects of soil management and mitigation practices on contaminant transport to water resources. However, Figure 1 may offer a start in this direction. It summarizes the factors of structure formation and degradation, the soil aggregation that results, and how this should affect the potential for non-equilibrium water flow and solute transport. The concept of the hierarchy of soil structure is the basis for this scheme, with the central hypothesis that the strength of non-equilibrium water flow and solute transport increases in structural pore systems with a poorly developed hierarchy, at least until some critical point is reached when the continuity of macropores becomes limiting, for example in massive or severely compacted soil. Figure 1 is still incomplete in some respects. For example, it focuses on aggregation, and ignores the role of biotic macropores, and nor does it explicitly consider the links between landscape attributes and the factors of structure formation. However, the same principles should apply to networks of biotic macropores, so that Figure 1 may serve as a useful starting point for the development of more comprehensive soil classification schemes.

The intention of such a scheme would be to provide a framework for ‘broad-brush’ large-scale predictive modelling applications. Considering the uncertainties involved, this objective may seem ambitious. However, one saving grace in this respect is that in many such applications, reasonable assessments of relative risk are sufficient and accurate predictions of absolute concentrations are not required (e.g. product comparisons, assessment of mitigation practices, identifying contamination sources). Although the replication is often limited, the results of lysimeter tests on contrasting soils suggest that it should be possible to make such comparative assessments, since the variation between soil types is usually larger than the within-soil variation (Bergström & Jarvis, 1993; Brown *et al.*, 2000). Nevertheless, no simple deterministic scheme can fully capture the complexity of soil variation, and it would be important to assess and quantify the predictive uncertainty associated with both the adequacy of the classification itself (i.e. that within-class variation is smaller than between-class variation) and the inherent stochastic variation remaining within each class (Beven, 1991). Methods for combining deterministic methods for soil mapping with statistical treatments of the residual uncertainty and within-class variation have been discussed by Heuvelman & Webster (2001).

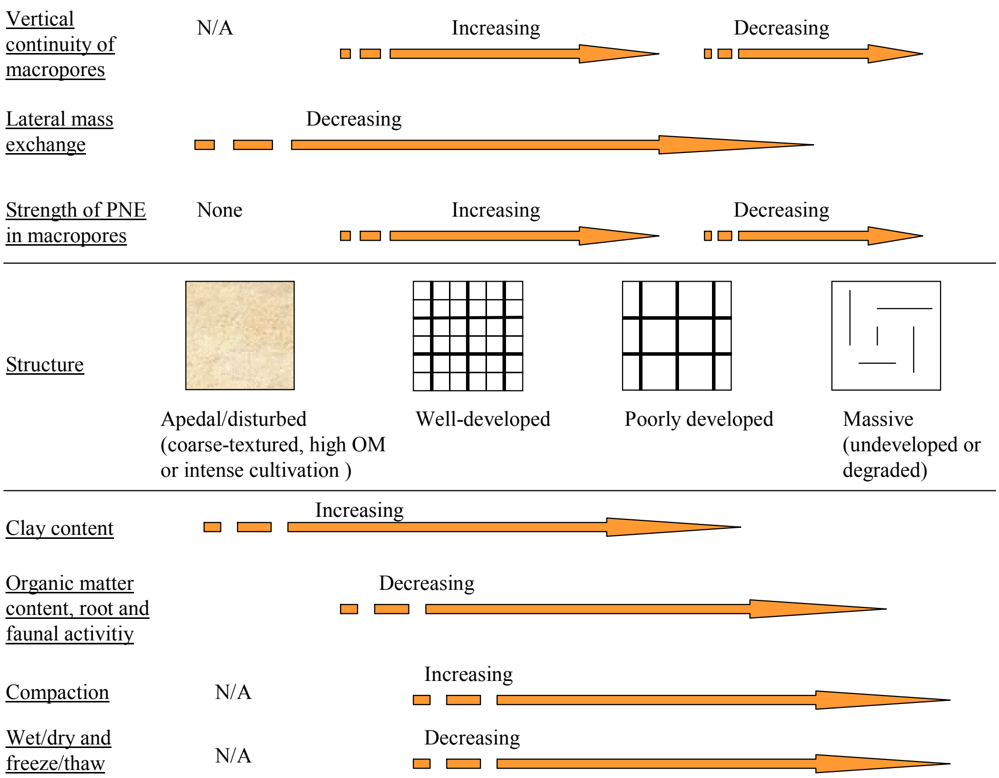

Figure 1. Conceptual model of macropore flow and transport.

The center of the diagram shows for illustrative purposes four classes of structural development. The bottom third of the diagram shows how the various factors of structure formation and degradation influence structural development, while the top third of the diagram illustrates the probable consequences for non-equilibrium water flow and solute transport in macropores (PNE = physical non-equilibrium, OM = organic matter).

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