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A review of non-equilibrium water flow and solute transport in soil macropores: principles, controlling factors and consequences for water quality

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Summary

This review discusses the causes and consequences of 'non-equilibrium' water flow and solute transport in large structural pores or macropores (root and earthworm channels, fissures and interaggregate voids). The experimental evidence suggests that pores larger than *c*. 0.3 mm in equivalent cylindrical diameter allow rapid non-equilibrium flow. Apart from their large size and continuity, this is also due to the presence of impermeable linings and coatings that restrict lateral mass exchange. Macropores also represent microsites in soil that are more biologically active, and often more chemically reactive than the bulk soil. However, sorption retardation during transport through such pores is weaker than in the bulk soil, due to their small surface areas and significant kinetic effects, especially in larger macropores. The potential for non-equilibrium water flow and solute transport at any site depends on the nature of the macropore network, which is determined by the factors of structure formation and degradation, including the abundance and activity of soil biota such as earthworms, soil properties (e.g. clay content), site factors (e.g. slope position, drying intensity, vegetation) and management (e.g. cropping, tillage, traffic). A conceptual model is proposed that summarizes these effects of site factors on the inherent potential for non-equilibrium water flow and solute transport in macropores. Initial and boundary conditions determine the extent to which this potential is realized. High rain intensities clearly increase the strength of non-equilibrium flow in macropores, but the effects of initial water content seem complex, due to the confounding effects of soil shrinkage and water repellency. The impacts of macropore flow on water quality are most significant for relatively immobile solutes that are foreign to the soil and whose effects on ecosystem and human health are pronounced even at small leached fractions (e.g. pesticides). The review concludes with a discussion of topics where process understanding is still lacking, and also suggests some potential applications of the considerable knowledge that has accumulated in recent decades.

Introduction

The importance of macropores was recognized in 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 in natural structured soil was, however, largely ignored, and it was the empirical but quantitative work of the engineer Darcy, working on saturated flow through artificial packed sand beds, that laid the foundation for soil water physics in the 20th century. In 1931, L. A. Richards combined Darcy's law with an equation of continuity to derive a general equation for transient unsaturated water flow in soil. 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).

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Starting in the 1960s and early 1970s, 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. Based on a computer literature search with a large number of combinations of relevant keywords, Figure 1 shows that the number of publications in this research field has increased exponentially in the last 30 years, and that more than 50 papers per year are now published on macropore flow in soils. These numbers are probably gross underestimates, since this kind of search cannot hope to discover all the relevant articles, but it does illustrate the general trend. However, information does not necessarily equate to understanding, and as the pace of publication accelerates, researchers risk drowning in the 'information flood'. Figure 1 suggests that it would be worthwhile and timely to review and synthesize current understanding on how water flow in soil macropores affects solute transport, and to suggest profitable avenues of future research.

This review is not comprehensive, as it would be impossible to cover all aspects of the subject in one paper. Apart from concentrating on macropore flow, and ignoring other related preferential flow processes that occur in the soil matrix, such as fingering, funnel and heterogeneous flow (e.g. Kung, 1990; Roth, 1995; Ritsema & Dekker, 1995), I have chosen to limit the scope of this paper in three further ways: (i) I focus entirely on soils, and only refer occasionally to the large body of research on water flow and solute transport in fractured rocks. Even though the same fundamental principles apply to both rocks and soils, there are important differences of degree, which have significant implications for the choice of experimental and modelling techniques. In comparison to rock fractures, flow rates in soil macropores are larger and the flow pathways are more easily accessible and observable experimentally. Soil macropores are also ubiquitous, relatively densely distributed, and dynamic, since the soil is exposed to temporal variations in climate, crop development, biological activity and management (e.g. tillage) that strongly affect soil structure. (ii) I have not explicitly attempted to review in detail the various experimental methods, techniques and models that have been employed to characterize and quantify macropore flow in soils. These are only mentioned in passing, insofar as they have made significant contributions to improving our understanding of the processes. The reader is referred to the recent review by Gerke (2006) for a detailed discussion of modelling approaches. (iii) I concentrate almost exclusively on agricultural soils and diffuse pollution, leaving aside water quality problems associated with forested areas and point-source contaminants.

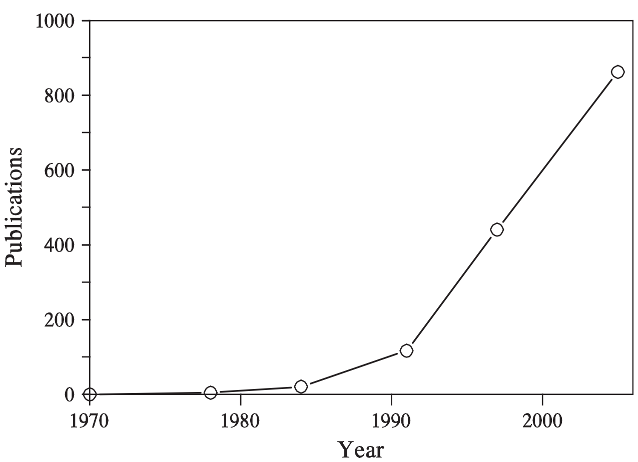

Figure 1 Papers published on macropore flow (source: ISI Web of knowledge).

The review is organized by making use of scale as the common thread. I first describe the basic principles governing the generation of macropore flow at the pore scale, the flow mechanisms, and the microscale 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 solute characteristics and soil and crop management practices on macropore flow. The significance of macropore flow at the landscape scale is then considered. The paper concludes with an attempt to synthesize what we have learnt and what is still poorly understood, with suggestions for future research priorities.

What is macropore flow?

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, macropore *flow* and/or *transport* result when rates of lateral equilibration of water pressures and/or solute concentrations with the matrix are slow in relation to the vertical flow rates in macropores (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 very non-uniform as flow streamlines converge towards conducting macropores. 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).

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. The resulting non-uniform flow (physical non-equilibrium) can be illustrated by imagining a soil block that contains macropores wetting up towards saturation during infiltration. In the initial dry state (point A, Figure 2), the macropores are air-filled and their hydraulic conductivity is negligible compared to the matrix, which conducts all the flow. The water entry pressure of smaller macropores is reached at the pressure potential B, and non-equilibrium begins to develop, but the additional contribution of these pores is not dramatic (Figure 2). The pressure potential, C, is only slightly larger than at B or A, but the hydraulic conductivity is orders of magnitude larger, since large, vertically continuous, macropores now start to conduct water. The soil now wets up in a markedly non-uniform manner, with water flowing rapidly in these macropores far ahead of the wetting front in the matrix (Figure 2).

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 0.3–0.5 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, interaggregate pores) in paddy, upland field and forest soils were larger than *c.* 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 *c.* –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 0.1–1 mm $hour^{-1}$ 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 $hour^{-1}$ 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

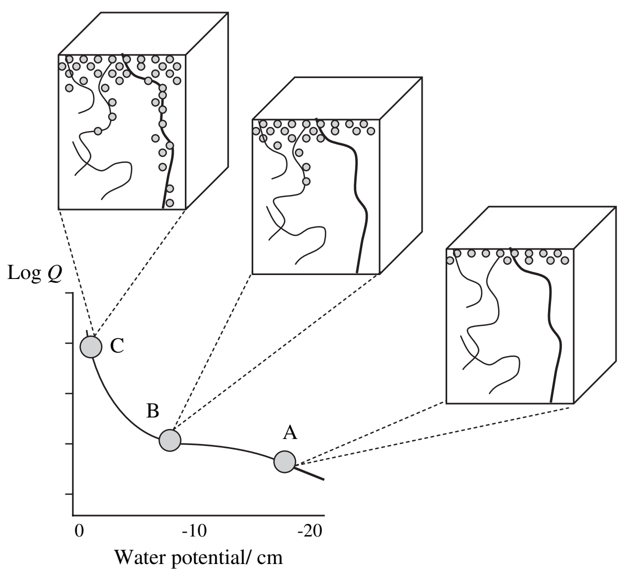

Figure 2 Schematic diagram illustrating the water potential attained at the soil surface under differing infiltration rates, Q, and the generation of non-equilibrium flow in macropores.

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 *c*. –10 cm. Confusion on this point could 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, and is consistent with diffusion into 'stagnant' water zones that comprise 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 with root channels from alfalfa and maize and found non-equilibrium transport behaviour at flux rates that were apparently a factor two to three 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 0.3–0.5 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*., 1999*a*; 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 wetting and drying or freezing and thawing, and irregularly shaped 'packing voids' between denser aggregates in cultivated topsoils (Bouma *et al*., 1977; Ringrose-Voase, 1996).

Types of macropores and their physical characteristics

Biopores

Under favourable conditions, individuals of deep-burrowing anecic earthworm species such as *Lumbricus terrestris* L. can produce several hundred channels per m^2, 2–12 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, 2001*a*). The tortuosity of channels produced by deep-burrowing earthworms has been reported to be in the range of 1.1–1.2 (Shipitalo & Butt, 1999). In contrast, since endogeic earthworm species feed and burrow only within the topsoil, they produce temporary burrows that are more randomly oriented, shorter, more tortuous and branched (Capowiez *et al*., 2001; Jégou *et al*., 2001), and which therefore may have more limited effects on water flow and solute transport (Ela *et al*., 1991). 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 3-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 *c*. 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, which corresponds to a total macroporosity of between 2 and 4%. The networks had a geometric mean volume of *c*. 50 mm^3 and a tortuosity between 1.2 and 1.3, and their modal length was *c*. 40 mm.

Smaller channels created by decaying plant roots also constitute important pathways for non-equilibrium flow and transport. For example, Tippkötter (1983) reported interconnected networks of tubular pores 0.1–0.6 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 of 2–3 (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.

Soil 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 cohesion 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 the volume of 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, width and connectivity decrease (Chertkov & Ravina, 1998, 1999). The tortuosity of crack networks in clay soils has been reported to be in the range 1.2–2.0 (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 subunits separated by planes of weakness that will also potentially serve as preferential flow pathways. These smaller subunits 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 interaggregate 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 hierarchical 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 two-dimensional 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 could 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 of reality, which is likely to be valid only across a limited range of scales (Rieu & Sposito, 1991; Preston *et al*., 1997; Vogel *et al*., 2002).

Chemical and biological 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). Little is known about the extent to which enhanced biological activity in macropores influences the degradation of organic contaminants in soils, and even less is known about how it will affect the potential for leaching. In one study, Mallawatantri *et al*. (1996) measured more than 10 times larger mineralization rates of 2,4-D in macropore wall material from an argillic Bt horizon, compared with the bulk soil material. 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 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 trace metals (Turner & Steele, 1988) and 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, which indicates leaching of soluble, readily decomposable, organic matter. Similarly, Bundt *et al*. (2001a) inferred from ^{13}C and ^{15}N abundances, that organic carbon was younger and N cycling more rapid in the preferential flow paths of a forest soil compared to the matrix. Many inorganic contaminants are strongly adsorbed by Fe, Al and Mn oxides in soil. Pierret *et al*. (1999) found enhanced Fe and Mn contents in macropore 'sheath' soil sampled from the B horizon of a Palexeralf in Australia. Conversely, Hansen *et al*. (1999) found weaker adsorption of phosphate to fracture linings in the subsoil of a poorly drained pseudogley, compared to the bulk soil, due to leaching of iron oxide from fracture surfaces under fluctuating redox conditions.

The physics of water flow and solute transport in macropores

Water flow in soil pores is driven by the momentum balance between the governing forces of gravity, capillarity, viscous forces due to friction with the solid surfaces and within the fluid itself, and inertial forces. 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 in their relative importance can be identified. Based on the considerations noted earlier, capillary pressure potential gradients in conducting macropores are not 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 hour^{-1}, 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. This can be illustrated by calculating the Reynolds number as a function of pore diameter, assuming fully saturated laminar flow in straight-sided cylindrical macropores in accordance with Hagen–Poiseuille's law. The Reynolds number, which is a measure of the ratio of inertial to viscous forces, exceeds unity and therefore invalidates Darcy's law (Childs, 1969) at pore diameters larger than *c*. 0.15 mm. Based on real-time measurements of water-flow rates in soil macropores under ponded conditions by 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. nearly fully turbulent conditions) 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 can 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 thicker and the pressure increases above *c*. –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 & Narasimhan, 1985), which leads to intermittent or 'pulse' flow (Germann, 1987; Gjettermann *et al*., 2004; Ghezzehei & Or, 2005). The soil macroporosity is rarely full of water even under nominally saturated flow 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 10–50% of the total macroporosity conducted water during 'saturated' flow through intact cores. Dragila & Wheatcraft (2001) and Ghezzehei (2004) presented detailed treatments of the physical causes and consequences of these different flow regimes. Dragila & Wheatcraft (2001) 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 millimetres in thickness exhibit laminar flow, but are inherently unstable and sometimes chaotic, and develop travelling waves that greatly increase the effective pore-water velocity. Intermittent 'pulse' flow occurs when a wave contacts the opposite wall of the macropore, thereby establishing a capillary 'bridge' that dramatically reduces the flow velocity. Any small perturbation will allow film flow to re-establish quickly, 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, input flow rate, or the effects of channel geometry such as pore 'necks' and surface irregularities (Ghezzehei & Or, 2005). 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; Dragila & Weisbrod, 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 about one sixth of that 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; Ellerbrock & Gerke, 2004).

Analogous to the case of water flow, non-equilibrium solute 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 solute 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 large 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 could be an important additional factor limiting sorption retardation in such pores. Particulate matter is efficiently filtered out in matrix flow, but significant particle-bound transport in macropores has been demonstrated for strongly sorbing solutes, including some pesticides (e.g. Worrall *et al.*, 1999; Villholth *et al.*, 2000; De Jonge *et al.*, 2000; Zehe & Flühler, 2001a; Petersen *et al.*, 2002) and phosphorus (Ulén & Persson, 1999; Stamm *et al.*, 1998; Laubel *et al.*, 1999; Uusitalo *et al.*, 2001; De Jonge *et al.*, 2004). 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 (and therefore loads) are clearly dependent on sorption, presumably reflecting the concentration in soil solution in the distribution zone (the 'source-strength'). 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.

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 greater 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 triggered only 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 fairly moist soils (Hallett & Young, 1999; Doerr *et al.*, 2006).

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 maize 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 is usually more strongly expressed in undisturbed no-till arable or permanently vegetated soils such as grassland (e.g. Hallett *et al.*, 2001; Doerr *et al.*, 2006), where macropores are also often continuous to the soil surface (see 'Soil tillage and traffic'). In this case, the surface microrelief 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 microdepressions will preferentially conduct most of the water (Dixon & Peterson, 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 chemicals, 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 (Dekker & Bouma, 1984; Gish *et al.*, 1991a), since before flowing into macropores at the surface, incoming water interacts by diffusion and physical mixing (e.g. 'rainsplash') with the resident soil water in the distribution zone at or 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 solute 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 Jonge *et al.*, 2000). Once the bulk of the chemical has penetrated into the soil matrix below the distribution zone, 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 (e.g. 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, 2000).

Macropore flow and the properties and morphology of soil horizons

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, 1977*a*; 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.* (2007) showed that *c*. 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 13 out of 14 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 horizons of differing texture, vertically oriented 'tongues' and water repellent layers, while strongly developed macropore structures promoted weak lateral mixing at large flow rates in fine-textured soils. Long-term outdoor lysimeter tracer breakthrough experiments on contrasting soil types have also demonstrated that soil structure exerts a strong control on solute transport at the soil profile scale under more natural boundary conditions with intermittent fluxes at the soil surface (e.g. Bergström & Jarvis, 1993; Brown *et al.*, 2000).

Based on the ideas originally introduced by Deurer *et al.* (2003) to model heterogeneous preferential flows 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 has been observed in 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). Furthermore, non-equilibrium flow cannot continue to strengthen *ad infinitum* as structure deteriorates in the subsoil, as the continuity of the macropore network must eventually limit flow rates. 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.

Macropore flow and agrochemical leaching

The impact of macropore flow on leaching depends strongly on the properties of the chemical under consideration, particularly its sorption characteristics, the nature of any biological transformations and whether the solute is surface-applied or whether it is indigenous to the soil (White, 1985*a*; Elliott & Coleman, 1988; Jarvis, 1998). The following sections briefly discuss the influence of macropore flow on the leaching of different agrochemicals.

Pesticides

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 litre^{-1}. For a dose of 0.2 kg ha^{-1} and an annual recharge of 200 mm, this implies a maximum allowed leaching loss of only 0.1% of the applied amount. 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 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 increase 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 (1999a) 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 only a 4-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).

Phosphorus

Until recently, phosphorus losses from agricultural land were thought to be dominated by surface runoff and erosion. This is because P is strongly sorbed and therefore rather immobile, unless saturation of the sorption sites occurs. However, recent research suggests that significant leaching of P can occur in structured soils due to macropore flow (e.g. Stamm *et al*., 1998; Ulén & Persson, 1999; Laubel *et al*., 1999; Akhtar *et al*., 2003; De Jonge *et al*., 2004; Kleinman *et al*., 2005). In field experiments, leaching losses of P in macropore flow to subsurface drainage systems have been reported in the range from 0.2 to 5 kg ha^{-1} year^{-1} in loam and clay soils, with particle-bound transport accounting for *c*. 10–75% of the total (e.g. Heckrath *et al*., 1995; Ulén & Persson, 1999; Hooda *et al*., 1999; Addiscott *et al*., 2000). The largest losses, which were reported from soils with excessive topsoil P contents due to over-fertilization, are sufficient to cause significant eutrophication of surface water.

Nitrate

The effects of macropore flow should in principle be less dramatic for a mobile solute like nitrate. Some short-term studies have shown large N leaching losses due to macropore flow following fertilizer application (e.g. Dekker & Bouma, 1984; Priebe & Blackmer, 1989; Edwards *et al*., 1992). However, short-term monitoring of nitrate leaching following fertilization gives a distorted picture of long-term losses in arable cropping systems. This is because nitrate-N derived from the mineralization of soil organic matter is the main source of N leaching, which usually occurs predominantly after harvest due to the absence of the plant uptake sink (e.g. Bjorneberg *et al*., 1996). Magesan *et al*. (1995) showed that peak nitrate concentrations coincided with peak drainflows soon after fertilizer application (i.e. macropore flow enhanced leaching), but at later times peak water flows caused dilution, since indigenous nitrate produced by mineralization of organic N is located within aggregates and less accessible to water flowing in macropores (Elliott & Coleman, 1988). These contrasting effects of macropore flow on N leaching were analysed by Larsson & Jarvis (1999b), who applied a dual-permeability model to 6 years of measurements made on a structured clay soil. They deduced that leaching losses were enhanced by macropore flow shortly after fertilization in only 1 year, but even then, the fertilizer-derived N only accounted for 7% of the annual leaching. Overall, the occurrence of macropore flow was calculated to reduce N leaching by *c*. 28% (Larsson & Jarvis, 1999b).

Trace metals

Agricultural soils have been widely contaminated by trace metals through a combination of atmospheric emissions and aerial deposition, impurities in fertilizers, and sewage sludge applications. Trace metals are usually considered immobile in soil due to very strong sorption, and this may be one reason why little research on the effects of macropore flow on trace metal leaching has been conducted. Camobreco *et al*. (1996) reported significant leaching of four trace metals through macropores in undisturbed soils, which was also enhanced by the presence of soluble organo-metal complexes in the case of Cu and Pb. However, in this laboratory experiment, trace metals were applied as inorganic salts at large concentrations in the inlet water. This may exaggerate leaching risks under natural field conditions, as metals are normally applied in adsorbed form, for example in sludge. Richards *et al*. (1998) found little evidence of major leaching losses of trace metals at a heavily sludged site, despite the potential for macropore flow demonstrated by a dye tracing experiment. They did find elevated concentrations of trace metals in wick samplers from the subsoil of the sludged plot compared to the control, but calculated annual fluxes represented less than 1% of the total deposited metal amount in the topsoil. Furthermore, only small differences were found in trace metal concentrations between samples of dye-stained preferential flow pathways and non-stained soil. Bergkvist *et al*. (2003) measured the distribution of cadmium in a structured clay soil after 41 years of sludge amendment. Some evidence of deep displacement of cadmium was found, which was attributed to macropore flow. However, mass balance calculations showed that 92% of the applied cadmium remained in the topsoil and that less than 1% had leached below 60-cm depth. Of course, even small losses can be a cause for concern, depending on the toxicity of the chemical in question. In the case of cadmium, the recommended limit for groundwater set by the World Health Organization (WHO) is 3 μg litre^{-1}. Given the current legislative restrictions on metal accumulation in soil in many countries, it seems unlikely that macropore leaching could lead to widespread exceedances of this limit, except at heavily contaminated industrial sites.

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.

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. Thus, Edwards *et al.* (1992) compared water flows measured from large diameter earthworm burrows (of *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 conventionally tilled plots under long-term continuous cereal cultivation (Jarvis *et al.*, 1991; Jarvis *et al.*, 2007). These results can probably 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 may conduct more of the infiltrating water in grassland soils, even in climates characterized by frequent intense storms (Edwards *et al.*, 1992). However, comparatively few studies have been published on the effects of contrasting cropping systems on solute leaching in macroporous soils, and care should be taken not to generalize too much from the scanty data. For example, the development of water repellency under dry conditions can be much more pronounced in grassland soils that are left undisturbed by tillage (Tillman *et al.*, 1989; Doerr *et al.*, 2006), which may favour the generation of macropore flow.

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.*, 2007). 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 4.5–12.5 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 17–1100 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 a soil cultivated with shallow tines. 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.*, 2007). Finally, it can be noted that differences in water flow and solute transport patterns induced by various primary tillage implements (e.g. mouldboard ploughs versus spring tines or chisel ploughs) seem small (e.g. Petersen *et al.*, 2001; Fortin *et al.*, 2002), especially compared with 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), due mainly 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 and phosphorus). Indeed, one important reason for the introduction of no-till was the desire to reduce P losses by surface runoff and erosion. For reasons discussed earlier, no-till systems generally reduce nitrate leaching in soils prone to macropore flow (e.g. Kanwar *et al*., 1985; Elliott & Coleman, 1988; Bjorneberg *et al*., 1996).

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 raindrop impact and 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 fairly 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 after 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 sugarbeet 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.

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 on to the surface or 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 phosphorus 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).

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 more deeply 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 only one third as much isoproturon as did 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). Bacteria added to soil in manure can also be a cause for concern. Despite rapid die-off and substantial straining and filtering during leaching, bacteria are especially prone to macropore transport in structured soils, since they are prevented from moving into smaller matrix pores by size exclusion (e.g. White, 1985b; Smith *et al*., 1985; Germann *et al*., 1987; McMurry *et al*., 1998).

Drainage

Artificial drainage systems installed in slowly permeable fine-textured soils can also influence the extent of macropore flow. A greater abundance of earthworms has been found in the vicinity of drains in clay soils due to a better aeration status (Nuutinen *et al*., 2001), and direct connections have been demonstrated between earthworm burrows open to the soil surface and subsurface drain pipes (Shipitalo & Gibbs, 2000). Some drainage implements (e.g. mole ploughs) are designed to create extensive fissure systems that enhance macropore flow in order to improve soil drainage (Leeds-Harrison *et al*., 1982), but which also provide a mechanism for surface water pollution by agrochemicals (Harris *et al*., 1994).

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 influence 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 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 micro-lysimeters 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 emphasized by Vervoort *et al*. (1999), and has also 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 on hydrology and 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 shallow water tables, due to the effects of the capillary fringe on saturation of 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 very transient (<2 hours) and contributed only *c*. 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 loss 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. In the case of phosphorous, Kronvang *et al*. (1997) found that macropore flow to field drainage systems contributed up to 18% of the total particulate P load to a stream draining a 10-km^2 catchment in Denmark, while surface runoff and erosion only contributed P during 1 year of the study, when it accounted for 7% of the catchment export. It was inferred that stream bank erosion was the major source of particulate P to the stream.

Discussion and conclusions

Can we rely on the experimental evidence?

Before drawing some general conclusions and identifying and discussing some future research priorities, it seems prudent to first consider the extent to which we can rely on the available experimental evidence. One danger is the risk of gaining biased impressions when research in a particular subject area is dominated by a small number of research groups working in similar soil, climate and agronomic conditions. One good example is the effects of no-till management on agrochemical leaching. Most studies have been carried out for fairly mobile pesticides applied to weakly structured silt and loam soils in the continental climate of the US maize belt. As discussed above, this research has demonstrated increased leaching of pesticides under no-till due to well-developed biopore networks. However, this conclusion should not be uncritically extrapolated to contrasting situations. For example, the leaching of strongly sorbing pesticides may be greater in conventional-tilled heavy clay soils where particle-bound transport in interaggregate voids may be the dominant mechanism.

Care should also be taken in interpreting the results of experiments where relatively large flux rates have been imposed, since macropore flow is known to be strongly dependent on the surface boundary condition. Table 1 classifies the papers cited in this review dealing with solute transport, sorting them into four basic types, depending on the kind of boundary condition employed (natural, controlled flux, ponded or saturated flow, controlled potential near saturation). Table 1 shows that *c*. 20% of experiments were carried out under ponded infiltration or saturated flow. These experiments are clearly relevant to irrigated agriculture, but the results may be difficult to extrapolate to solute transport in the unsaturated zone under rain-fed agriculture. Roughly 33% of studies were carried out using controlled input fluxes. Figure 3 shows that *c*. 60% of these studies were carried out with irrigation intensities larger than 10 mm $hour^{-1}$. In most studies, the equivalent rainfall return period of the applied irrigation is not stated. However, considering the amounts of water supplied as well as the intensity, it is probably fair to say that the return periods should in most cases be counted in years rather than months. The probability that such an extreme storm event will fall in the critical period

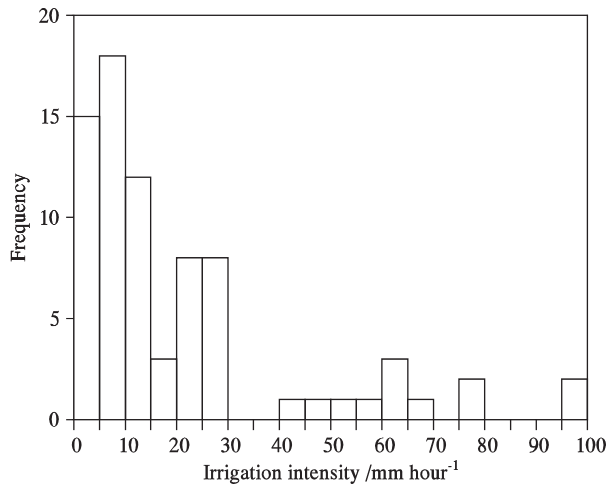

Figure 3 Irrigation intensities employed in solute leaching experiments cited in this review.

shortly after a surface application of an agrochemical is even smaller. For example, a 1-year return period storm will occur in a given 2-week period following an annual pesticide application on average only once every 26 years. There may be several reasons why many experiments are carried out using extreme fluxes. One may be the belief that only ponded conditions allow non-equilibrium flow and transport in macropores. The pressure to publish may be another more practical issue. This is illustrated by studies where the original ambition was to measure fluxes under natural boundary conditions, but where frustration with the weather eventually led to supplemental irrigation (e.g. Roulier & Jarvis, 2003; Köhne & Gerke, 2005). Although well-designed controlled irrigation experiments have greatly improved our knowledge and understanding of macropore flow processes, for example by identifying causal links with the morphological characteristics of soil horizons and pedons and by elucidating the effects of different management practices, there is clearly a risk of gaining biased impressions, for example concerning the frequency of occurrence of macropore flow and its significance for long-term leaching. In this respect, it is encouraging that roughly 41% of the studies cited in this review reported the results of long-term experiments carried out under natural boundary conditions (Table 1) and often also under normal agricultural practice, as these serve as healthy ‘reality checks’ and counter-balances to short-term ‘forced’ experiments.

Extreme input fluxes also give a false impression of the kinds of macropores that normally function as preferential flow pathways under natural conditions. For example, many ‘forced’ experiments point to the decisive role of large earthworm channels. However, in many climates, such large macropores will remain air-filled during most rain events, and infiltration will be dominated by smaller macropores such as root channels

Table 1 Summary of the different types of boundary condition employed in the solute transport experiments cited in this review ($n = 115$)

Type of boundary condition	% of cited studies
Natural (long-term)	41
Controlled irrigation flux (short-term)	33
Saturated flow or ponded infiltration	20
Controlled potential (near-saturation)	6

and interaggregate fissures. Shipitalo *et al.* (1993) compared water and solute outflows sampled by large pan lysimeters with those monitored from individual *Lumbricus terrestris* burrows under no-till maize during a 2-year period. Despite intense summer rainstorms, they found that the earthworm channels conducted only 1.4% of the percolation and 0.7 and 1% of the leached amounts of nitrate and bromide, respectively. On the other hand, macropores do not need to transmit a large proportion of the recharge water to have significant effects on the transport of strongly sorbing contaminants characterized by only very small leaching fractions. In the same study, Shipitalo *et al.* (1993) reported that the earthworm channels conducted 29% of the leached ammonium. Thus, one worthwhile task for the future would be to quantify the significance of macropores of different sizes for long-term solute leaching under field conditions. This work would help to place into context the results of short-term high-flux experiments. Indeed, it is surprising that so few experiments are carried out under controlled supply potentials in the near-saturated range (see Table 1). This kind of experiment should provide interesting insights, since it enables us to define the pore classes involved in flow and transport under different rain intensities.

What have we learnt?

Despite the reservations expressed in the previous section, it seems clear from the review of the literature presented in this paper that much is known about the effects of macropore flow on solute transport. Indeed, in some respects, a remarkable consensus has emerged from the 'information flood' despite the complexity of the processes. At the risk of irritating the reader, I deliberately tried to emphasize this consensus on several key points by citing many articles that essentially arrived at the same conclusion. In passing, this should also serve as a warning that more research on these topics may not be needed. The main conclusions identified from this review are outlined in the following section, grouped under four main headings.

1. The pore scale: macropores and flow and transport processes. Macropores are structural pores (root channels, earthworm channels, fissures and interaggregate packing voids) of large diameter, great continuity and little 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 *c.* 0.3 mm in equivalent cylindrical diameter can be considered as macropores. 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 open to a ponded surface. The physical, chemical and biological microenvironment of macropores contrasts strongly with the bulk soil. Organic and inorganic linings in biotic macropores and aggregate coatings 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 small ratio of surface area to pore volume, but also due to kinetic (chemical non-equilibrium) effects during transport.

2. The pedon scale: factors that control the potential for non-equilibrium flow and transport. The degree of non-equilibrium water flow and solute transport in macropores is closely related to the morphology of soil horizons (e.g. size distribution of macropores, grade of aggregate development, aggregate skins). Basic soil properties (e.g. texture, organic matter content) also exert a strong indirect control on macropore flow and transport, both through their effect on matrix hydraulic properties (and therefore the likelihood of generating pressure potentials close to saturation for a given surface flux) and also due to their strong influence on soil aggregation. Soil macropore networks are hierarchical in nature. Larger macropores are generally more continuous, less tortuous and more widely spaced, which results in potentially faster water flow, weaker lateral mass exchange, less sorption interaction and therefore stronger physical and chemical non-equilibrium. The aggregate hierarchy seems 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.

Soil tillage and traffic also strongly affect the potential for macropore flow and transport. Physical non-equilibrium is practically eliminated in the upper few centimetres 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 with 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 might 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. Land use and cropping systems may also influence soil structure and therefore macropore flow. In the few studies to date, non-equilibrium flow and transport have been found to be 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. However, undisturbed grassland soils are more susceptible to the development of water repellency on drying, which will tend to enhance non-equilibrium flow in macropores.

Figure 4 summarizes these conclusions in a simple conceptual model of the factors of structure formation and degradation, the soil structure that results, and how this should affect the potential for non-equilibrium water flow and solute transport in macropores. This qualitative model is based on the concept of the hierarchy of soil structure, with the central hypothesis that the potential for 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. This conceptual model is by no means complete as it ignores the role of biotic macropores and does not explicitly consider the links between landscape attributes (e.g. slope position) and the factors of structure formation. However, the same principles should apply to networks of biotic macropores, so that Figure 4 may serve as a useful starting point for the development of a more complete explanatory model of the potential for macropore flow and transport.

3. Initial and boundary conditions. These determine the extent to which the potential for non-equilibrium flow and transport in macropores is realized. High intensity and/or long duration rain generates water pressures close to saturation that allow larger macropores to fill with water, and lead to rapid flow and marked non-equilibrium. 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 generate more macropore flow.

4. Consequences of macropore flow and transport for water quality. The impact of macropore flow on solute transport depends strongly on the nature and extent of any 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 relatively non-leachable substances that are foreign to the soil (e.g. strongly sorbing pesticides), it may actually decrease the leaching of indigenous and mobile solutes like nitrate. The impact of macropore flow on water quality depends on whether the concentrations and loads transported to surface water and groundwater represent significant threats to ecosystem or human health. In many agro-environmental situations, this is certainly the case for pesticides and probably also for phosphorus.

Implications for modelling

The advances in our understanding of macropore flow outlined in the previous section are also reflected in the development of many models. It is beyond the scope of this review to discuss in depth the advantages and disadvantages of different modelling approaches, not least because it is difficult to be too prescriptive about the suitability of a model, as it depends strongly on the purpose for which it is used (Rykiel, 1996). However, some general comments may be relevant and worthwhile. Macropore flow in near-surface soil is very intermittent and depends sensitively on initial and boundary conditions. In principle, this implies that models for field use should be strongly based in the physics of transient water flow, since only then can they properly reflect the response of solute fluxes to varying initial and boundary conditions. On the other hand, it might not be necessary or even wise to use exact physics-based models of water flow at the pore scale,

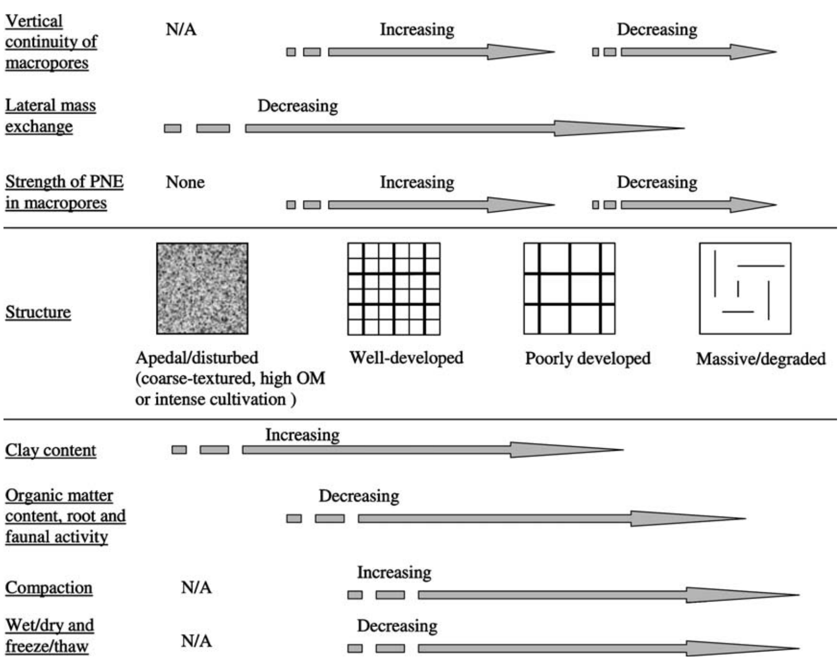

Figure 4 Conceptual model of the potential for non-equilibrium flow and transport in macropores. The centre of the diagram shows for illustrative purposes four classes of structural development. The bottom third shows how the various factors of structure formation and degradation influence structural development, while the top third illustrates the probable consequences for non-equilibrium water flow and solute transport in macropores (PNE = physical non-equilibrium, OM = organic matter).

since their assumptions are too restrictive. The mechanisms of water flow in macropores are complex and the geometry or configuration of the flow is very 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' approach to model macropore flow in soil, which has been widely used in both analytical and numerical forms (e.g. Beven & Germann, 1981; Germann, 1985; Germann & Di Pietro, 1999; Alaoui *et al*., 2003; Larsbo *et al*., 2005). Figure 5 illustrates this approach, and demonstrates that macropore water velocities are predicted to increase as the 'kinematic exponent', n, decreases towards its theoretical minimum value of 2. In natural soils, n should reflect the size distribution and tortuosity of conducting macropores, with larger values representing a better-developed structural hierarchy (i.e. a broader size distribution and/or more tortuous macropores). 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 that deal 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 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 microscale 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 may 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 scenario, they may be accurate enough for many management purposes (Vanclooster *et al*., 2004). Even simpler physics-based models that completely ignore matrix transport and lateral mass exchange (e.g. Kim *et al*., 2005) may simulate the leaching of strongly adsorbing agrochemicals such as phosphorus with sufficient accuracy for many management purposes.

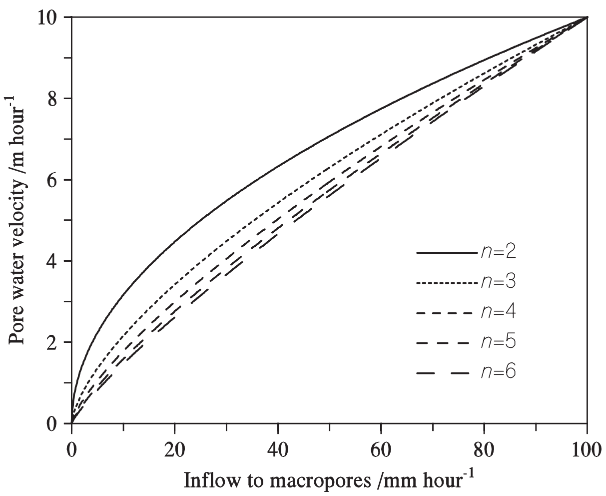

Figure 5 Pore water velocities, v, at steady-state predicted by the kinematic wave model as formulated in the dual-permeability model MACRO (Alaoui *et al*., 2003) for varying values of the kinematic exponent, n, and input rates, I, to a soil with a macroporosity, ε, of 0.01 $m^3\ m^{-3}$ and a saturated macropore conductivity, K, of 100 mm hour^{-1}. The velocity, v, is given by $I/((I/K)^{1/n}\,\varepsilon)$.

Future research

Despite the significant advances made in recent years, several 'knowledge gaps' still undeniably exist, and there is considerable scope for more basic research.

1 Although macropore transport processes are reasonably well-investigated for non-reactive or weakly reactive and conservative solutes, our understanding of the influence of macropore flow on the fate of very strongly adsorbing and biologically reactive chemicals is, in some critical respects, still limited. Thus, more research is clearly needed on the role and significance for long-term leaching of enhanced biodegradation in macropores and (kinetic) non-equilibrium sorption effects, including sorption interactions with mobile colloids and particulate matter.

2 Many advances in understanding during recent years have resulted from the use of novel experimental techniques and technologies. For example, new three-dimensional computer tomography techniques that combine geometric descriptions of soil macropore structure with continuous real-time measurements of solute transport show great promise in furthering our detailed knowledge of the processes (e.g. Mori *et al*., 1999*a*; Perret *et al*., 2000a,b). Further advances can be expected from research that exploits these and other new experimental techniques to relate macropore structure to observations of solute transport and, ultimately, to model parameters.

3 Fractals should be further explored as a potentially powerful model of structural pore systems and their impacts on macropore flow and transport. Strong non-equilibrium transport should result from pore networks in the scale range of macropores (i.e. > 0.3 mm) that display small pore volume fractal dimensions (e.g. Hatano *et al*., 1992). However, consideration of both pore space heterogeneity and continuity is clearly necessary (Crawford *et al*., 1993; Anderson *et al*., 1996). One working hypothesis is that a coarser, more heterogeneous, structure (often also associated with a decrease in macroporosity) promotes strong non-equilibrium macropore flow, but only until some critical limit is reached when the structure deteriorates to the point where macropore connectivity becomes limiting (Figure 4). These competing effects of pore volume and spectral fractal dimensions have been investigated for transport by diffusion (Crawford *et al*., 1993), but not apparently for gravity-driven convective processes such as macropore flow.

4 One important applied research question for the future will be to develop methods to support predictive modelling of the impacts of macropore flow on water quality at the landscape scale. Considering the uncertainties involved, this task may seem overly ambitious. However, one saving grace in this respect is that for many purposes (e.g. product comparisons, assessment of mitigation practices, identifying contamination sources) reasonable 'broad-brush' assessments of relative risk may be sufficient. 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. For example, 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 the susceptibility of soil horizons and profiles to macropore flow (Weiler & Flühler, 2004). These indices could be, for example, fractal dimensions calculated from images of pore structures or dye staining patterns 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 transport characteristics to data and information contained in existing soil survey data bases 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, nor are they sufficiently comprehensive and generally applicable, since they fail to consider the significant effects of management practices such as tillage, traffic and cropping on non-equilibrium flow and transport. It remains a major challenge to account for such factors in improved models and classification schemes.

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