Pure Appl. Chem., Vol. 80, No. 1, pp. 105–160, 2008.
doi:10.1351/pac200880010105
© 2008 IUPAC

INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

CHEMISTRY AND THE ENVIRONMENT DIVISION*

TRANSPORT OF PESTICIDES VIA MACROPORES

(IUPAC Technical Report)

Prepared for publication by
WERNER KÖRDEL[1,‡], HANS EGLI[2], AND MICHAEL KLEIN[1]

[1]Fraunhofer Institute for Molecular Biology and Applied Ecology, D-57392 Schmallenberg, Germany; [2]Syngenta Crop Protection AG, CH-4002 Basel, Switzerland

*Membership of the Division Committee during the preparation of this report was as follows:

***President*:** W. Klein (Germany); K. D. Racke (USA); ***Secretary*:** P. T. Holland (New Zealand); ***Titular Members*:** E. Anklam (Belgium, 2002–2005); H. Behret (Germany, 1998–2001); P. Dysseler (Belgium, 2000–2005); J. Gilbert (UK, 2000–2001); L. Klasinc (Croatia, 2002–2005); W. Klein (Germany, 1994–2005); L. McConnell (USA, 2004–2007); J. Miyamoto (Japan, 1990–2001); W. J. G. M. Peijnenburg (Netherlands, 2000–2005); N. Senesi (Italy, 2002–2005); D. Turner (Sweden, 2000–2001); R. D. Wauchope (USA, 2002–2007); ***Associate Members*:** R. Battalglia (Switzerland, 2002–2003); W. R. Benson (USA, 2004–2005); R. Cantrill (USA, 2002–2005); A. Felsot (USA, 2002–2003); O. Hertel (Denmark, 2004–2005); P. M. Huang (Canada, 2002–2005); W. Kördel (Germany, 2004–2005); R. P. Martin (France, 1998–2001); S. W. Page (Switzerland, 2000–2001); Y. Shevah (Israel, 2000–2005); K. Tanaka (Japan, 2004–2005); H. P. van Leeuwen (Netherlands, 2002–2003); ***National Representatives*:** P. S. Fedotov (Russia, 2002–2005); M. Fritzgerald (Australia, 2004–2005); R. M. Harrison (UK, 2002–2003); S. H. Herve (Finland, 2004–2005); Y. H. Kim (Korea, 2002–2005); J. J. Pienaar (South Africa, 2002–2003); E. Resto (Puerto Rico, 2002–2005); J. Scott (Australia, 2002–2003); T. Tavares (Brazil, 2000–2005).

‡Corresponding author: E-mail: werner.koerdel@ime.fraunhofer.de

---

Republication or reproduction of this report or its storage and/or dissemination by electronic means is permitted without the need for formal IUPAC permission on condition that an acknowledgment, with full reference to the source, along with use of the copyright symbol ©, the name IUPAC, and the year of publication, are prominently visible. Publication of a translation into another language is subject to the additional condition of prior approval from the relevant IUPAC National Adhering Organization.

Transport of pesticides via macropores

(IUPAC Technical Report)

Abstract: This report provides an overview of the transport of solutes via macropores focusing on the practical relevance of the phenomenon. After a description of matrix flow and preferential flow in soil, information related to macropores, including their formation and measurement techniques, is briefly presented. Then, the influence of experimental conditions and of environmental and agricultural factors and pesticide properties is discussed, based on a statistical evaluation of all published studies offering sufficient quantitative information. Most of the analyzed parameters do not significantly influence the experimental pesticide losses. The groundwater ubiquity score (GUS) index turned out to be the most important compound property to describe substance losses through macropore flow.

In a third section, tools for modeling pesticide transport through macropores are presented and critically evaluated. Results of the computer model MACRO, which is also used in the EU pesticide registration process, are compared with experimental losses. For five out of seven investigated pesticides (A–D, F), the simulated losses are in agreement with the experimental data. However, for two compounds with very low K_{OC} values, MACRO overestimated the losses.

Finally, the significance of pesticide transport via macropores for contamination of ground and surface water is assessed. Losses caused by macropore transport may considerably exceed losses caused by matrix transport at a specific site. Therefore, a site-specific assessment of pesticide leaching is needed.

Keywords: preferential flow; pesticides; groundwater pollution; preferential flow models; IUPAC Chemistry and the Environment Division.

CONTENTS

1. INTRODUCTION

While matrix flux is dominant in sandy soils, in structured (silty and/or clayey) soils, preferential flow is of highest importance. In clayey soils, macropores are predominantly formed by shrinking cracks and fissures, often starting at inhomogeneous microregions such as humus particles, small stones, or taproots. Formation and stability depend on the water regime of the soil, which is strongly influenced by weather conditions, plant cover, and management practices. In silty soils, biopores are the most important factor.

Soil chemical and physical properties, such as soil texture and humus content, determine the matrix or homogeneous water flux through soils. Sandy soils contain the highest amount of large pores leading to a hydraulic conductivity that permits an infiltration capacity which is sufficient for heavy rainfalls. However, in finer soils, hydraulic conductivity may be exceeded during heavy rainfalls. This leads to surface run-off or—if the soil contains a sufficient amount of active macropores—to macropore flux. Management practices (e.g., ploughing or non-ploughing) and weather conditions can significantly influence the soil surface (e.g., clogging after a rainfall) and, accordingly, the infiltration capacity.

There is a large variability in soil physical and chemical properties, in soil biological activity, and weather conditions in space and time. Thus, solute transport in soils is highly variable.

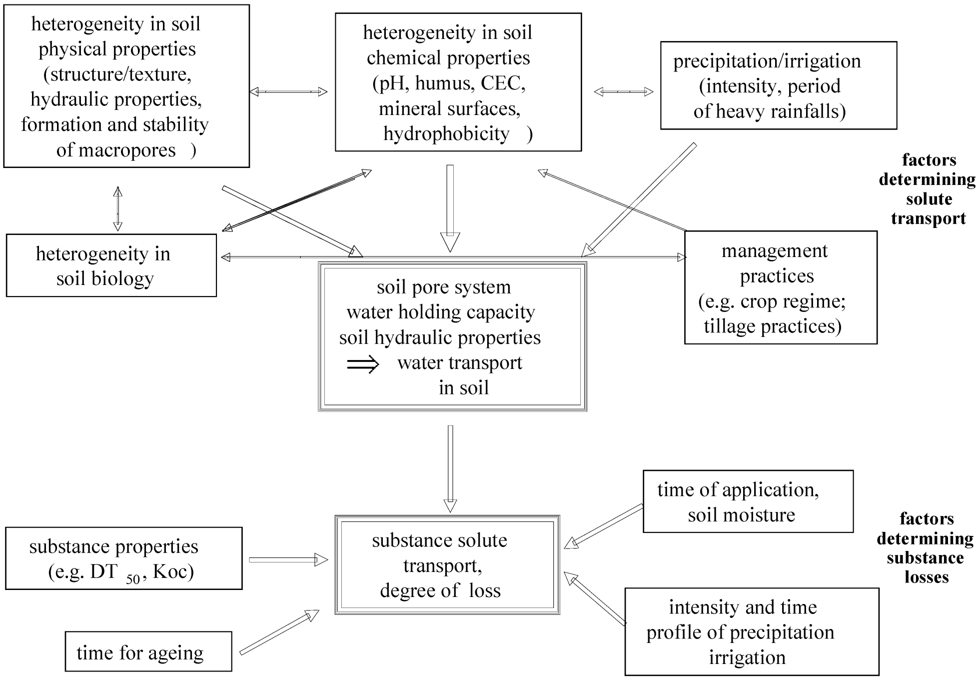


Fig. 1 Factors determining the leaching of substances.

The increase in the number of articles published over the last three decades on the flow of water and solute transport through soil macropores is impressive. An electronic search at Chemical Abstract Services yielded 2 references from the 1970s, 12 from the 1980s, and as many as 218 from the 1990s. The increased research intensity illustrates the growing awareness of the significance of this transport mechanism in soil. Macropore flow is characterized by its velocity due to bypassing the "normal" matrix flow in upper soil horizons. Whereas macropore transport increases the rate of transported material rather than the total amount of conservative and nonadsorbing solutes (e.g., inorganic anions), its potential for diminishing the degradation of organic chemicals of anthropogenic origin may be drastic. Apart from macropore flow, substance movement through the soil is slow and the residence time in the topsoil may be sufficient to allow for dissipation by degradation and adsorption before deeper soil horizons with lower degradation capacities and groundwater are reached. Macropore flow, however, may translocate pesticides to deeper horizons in appreciable quantities. As, in this context, pesticides are the most prominent class of anthropogenic compounds of concern, it is not surprising that research on macropore transport phenomena has mainly concentrated on this class of substance. Since a large proportion of published research papers and almost all contained quantitative information deals with pesticides, this compound class offers the largest database for understanding the phenomenon.

Solute transport through soil via macropores is a highly complex process strongly dependent on a multitude of factors. Not surprisingly, reported losses via macropores are highly variable. Factors commonly assumed to determine the extent of solute transport via macropores include factors determining the abundance and stability of the different kinds of macropores, such as soil texture, organic matter content, actual soil humidity, cultivation practices, previously cultured crops, and many others. Of similar importance are weather phenomena, in particular, frequency, intensity, and time-regime of rainfall, and further factors affecting percolation, such as irrigation and hydraulic conductivity of the horizon beneath the macropores. Finally, properties related to the inherent mobility and persistence of a solute are of relevance for the extent of its transport.

This report does not consider atmospheric deposition, and concentrates on applications according to agricultural practices. After a description of matrix flow and preferential flow in soil, information related to macropores, including their formation and measurement techniques, is presented. Furthermore, the influence of experimental conditions, environmental factors, and solute properties is discussed, based on a statistical evaluation of all published studies including sufficient quantitative information. In a further section, tools for modeling pesticide transport by macropores are presented and critically evaluated. Finally, the significance of the transport via macropores for a contamination of ground and surface water is assessed for pesticides.

2. GENERAL CHARACTERISTICS OF MATRIX AND MACROPORE FLOW

For a discription of soil physical parameter, see Appendix 1.

2.1 Soil hydraulic conductivity

Pore size distribution, and hence water movement in undisturbed soils, strongly depends on soil type and composition. While the total pore volume of different soil types does not differ significantly, there are large differences in pore sizes (Table 1). Clayey soils contain many fine pores, whereas large pores dominate in sandy soils, leading to a pronounced differentiation in saturated hydraulic conductivity (Table 2). Accordingly, water movement in sandy soils is much faster than in silty and clayey soils. The saturated hydraulic conductivities were taken from a textbook showing mean values for silt, clay, and sand.

This explains the large difference between conductivity in sandy and clayey soils. However, the values may significantly differ for native soils depending on soil type, soil formation, and compaction.

Table 1 Distribution of pore volumes [1].

Soil constituents	Total pore volume/%	Fine pores (<0.2 µm)/%	Medium pores <10 µm/%	Large pores >10 µm/%
Sand	~42	~5	~7	~30
Silt	~45	~15	~15	~15
Clay	~53	~35	~10	~8

Table 2 Saturated hydraulic conductivity of soil constituents [1].

Soil type	Saturated hydraulic conductivity/cm d^{-1}
Clay	$\sim 1 \times 10^{-2}$
Silt	~1–4
Sand	$\sim 3 \times 10^{2}$
Preferential flow	$\sim 3 \times 10^{4}$

Pore water in soils is captured by capillary forces and the attraction of the water to the solid surfaces (matrix potential). Consequently, at water-holding capacity, only very large pores are drained and air-filled. In a draining process, the largest pores drain first followed by the smaller ones. The pore space involved in the flow process is constantly decreasing, leading to a considerable reduction in hydraulic conductivity. As the finest pores with their low conductivity are involved minimally in solute movement, their pore water is usually fixed to the soil matrix.

Water flows through the tortuous pathways of the soil pores, interacting with the surface of the solid particles forming the boundaries of the pores. As structured soils are rich in silt and/or clay, they contain only a few large pores, resulting in a slow matrix flow. However, in these soils, matrix flux is usually accompanied by preferential or macropore flow. In structured soils, stable macropores can be formed (see Section 2.2). The volume of macropores depends on several factors that vary in space and time. However, in soils containing high numbers of earthworms, the macropore volume does not exceed a few percent of total porosity (e.g., 0.7–5.7 %) [2]. Schwarz et al. [3] measured about 0.2 % in soil horizons below 40 cm by staining macropores with a dyestuff.

There is no generally accepted definition of macropores. Beven and Germann [4] give a compilation of some definitions of macropores and macroporosity, which is extended by further citations.

The compilation of definitions in Table 3 demonstrates that the term “macropores” covers a wide range of pore sizes, starting with very fine macropores with a diameter of less than 100 µm and ending with biopores of *Lumbricus terrestris* and cracks and fissures of clayey soils in the cm range.

Definitions based more or less on soil types define macropores as pores that drain at least at field capacity of soils. According to German nomenclature, this means at a potential of –6 kPa (equivalent to a 60-cm water column) corresponding to a pore diameter >50 µm (pores of coarse sand without finer fractions). Authors dealing with field experiments define these macropores as “very fine macropores”. However, macropores supporting fast water flux have a diameter of about 1.0 mm and larger.

Table 3 Definitions of macropores.

Reference	Capillary potential/kPa	Equivalent diameter/µm
[1] Scheffer-Schachtschabel (1989)	>–6.0	>50
[4] Beven and Germann (1982)	>–6.0	
[5] Bullock and Thomasson (1979)	>–5.0	>60
[6] Webster (1974)	>–5.0	
[7] Cresswell et al. (1993)	>–1.0	>300
[8] Ranken (1974)	>–1.0	
[9] Luxmoore (1981)	>–0.3	>1000
[10] Beven and Germann (1981)	>–0.1	>3000
[11] Brewer (1964)		5000
coarse macropores		2000–5000
medium macropores		1000–5000
fine macropores		75–1000
very fine macropores		
[11] Reeves (1981)		2000–10 000
enlargeded macrofissures		
macrofissures		200–2000

For the comparison of hydraulic conductivities, the method of measurement has to be taken into consideration. The saturated hydraulic conductivity of sand is measured in the laboratory with a pure sand fraction using short columns. Therefore, in reality, conductivity will not reach the values given in Table 2. Nevertheless, the measured values for total hydraulic conductivity including macropores in undisturbed soils surpass those for matrix flow by 20 to 50 times. The flow velocity also depends on the amount of water supply by heavy rainfall and on the number and diameter of the active macropores, and may reach, for example, 70 cm d^{-1} [12], 100 cm d^{-1} [13], 240 cm d^{-1} [14], and 100–220 cm d^{-1} [15]. Such high flow rates occur only in open-ended macropores. In experiments with large lysimeters, preferential flow was observed to be 100–400 times faster than matrix flow. These values were measured in experiments that allow free drainage of macropores. Flow rates are much lower if macropores end in a subsoil and the overall water conductivity is controlled by homogeneous water transport in the pore system of the receiving soil horizon.

In practice, matrix and macropore flow occur simultaneously during heavy rainfalls. Both processes can overlap and contribute to the total vertical water movement in different ratios depending on rain intensity and duration, infiltration capacity of the soils, macropore characteristics, and inhomogeneities in soil profile.

Matrix flow is most important for sandy soils, because their infiltration capacity is high and macropores are not stable in these soils. However, research has revealed that also in structureless, coarsely textured soils (sandy soils), an infiltrating water front may become unstable, showing a **finger-like preferential flow** pattern [16–18] with flow rates that are much higher than the saturated conductivity of the soil matrix itself. Once a finger has been formed, water and solutes follow the same path during all infiltration events until its "memory", based on the soil moisture characteristic curve, is lost by saturation or drying [19].

Macropore flow is most important for structured (silty, loamy, and clayey) soils, as these do not contain a sufficient amount of large pores like sandy soils and thus have a relativity low hydraulic conductivity by matrix flux. In silty soils, macropores are predominantly formed as biopores by decaying taproots and by earthworm burrows, whereas in clayey soils, macropores are predominantly formed by cracks and fissures during drying. Loamy soils may develop all types of macropores. Caused by the low infiltration capacity of these soils and the occurrence of stable macropores, macropores will become active during heavy rainfalls, transporting water into deeper soil horizons. A well-known phenomenon in drained soils is water flux through macropores that bypass soil segments that are not water-saturated.

After heavy rainfalls, water flux in drain pipes starts long before saturation of the whole soil. Accordingly, the heterogeneity of the macropore system in silty and clayey soils leads to physical and chemical nonequilibrium conditions during periods of water flow and transport of chemicals in soils, combined with pronounced formation of wetting front instabilities. Therefore, water flow through macropores is not uniform, but exhibits highly variable velocities. MacCoy et al. [20] used the term "short-circuit bypass" to indicate this specific form of preferential flow when water bypasses dry soil compartments in large continuous pores (open-ended macropores) in addition to bypassing slow-moving water (matrix flow). For this phenomenon to occur, there must be small nonfilled pores in the vicinity of large pores which contain water.

A further type of fast flow can be described as "**funnel flow**" [21,22]. Funnel flow occurs in inhomogeneous soils, for example, soils of coarse material containing subcompartments of tightly packed fine material. In this case, preferential flow pathways are formed between the edges of materials of different porosity. As macropore flow through fissures and biopores is by far the most important process for fast vertical transport of chemicals, the following parts of the paper focus mainly on this phenomenon.

2.2 Formation of macropores and spatial variance

The formation of macropores and their stability and importance for solute flux depends on soil type, cultivation practices, and climatic conditions. In **clayey soils**, the formation of fissures and cracks built up during soil drying by physical stress is most important. The following description of the formation process of cracks in clayey soils was given by Dexter [23]:

> "When a soil of medium to high clay content dries, it shrinks and vertical desiccation cracks are formed. If the drying is rapid, then the cracks will be closely spaced and will be narrow. If the drying is slow, then the cracks will have greater space and will be wider. These cracks can form important pathways for rapid water infiltration, aeration and for deep penetration of roots though soils horizons, which might otherwise provide mechanical barriers. When these vertical (primary) cracks become wider than about 4 mm, significant convection currents of air can occur within them and drying can then occur from the faces of the primary cracks. This can result in secondary cracks forming at right angles to the primary cracks. In some cases, tertiary cracks can form from the surfaces of the secondary cracks in the same way."

The formation of cracks (i.e., the fragmentation of soil aggregates) can be induced by inclusions of materials of different porosity or composition. Large inclusions are of course more effective in inducing cracking than smaller ones. For aggregates containing multiple inclusions, stress within the elastic deformation zones is additive. Cracks will occur first where inclusions are closest together. Further stressors are roots. As they take water from the soil, soils will dry in the direct neighborhood of large roots. Roots may thus become starting points for cracks.

When soils become wet, they swell and the desiccation cracks close. The rate at which cracks close depends on water flux to and through the cracks and soil characteristics. However, soil will preserve a memory of where former cracks were located. Therefore, after repeated drying, cracks will be formed at the same locations.

In **silty soils**, macropores are mostly created by biological activity, for example, by roots (old root channels) or earthworms [4,24]. Mitchell et al. [25] investigated the formation of biopores upon planting of wheat and alfalfa. Stable macropores were formed by decaying roots of alfalfa, which has a taproot system, whereas wheat with fine, fibrous roots did not produce any macropores. Macropores formed by earthworms can differ significantly in size and depth depending on worm species and abundance. Earthworms have an important impact on the soil structure by releasing soil nutrients, by improving aeration, water-holding capacity, and drainage, and by burying organic matter. An important difference between cracks and biopores is that biopores are stable over longer time periods and coated by the excrements of the earthworms, which contain clay-humus complexes of hydrophobic properties. In swelling soils, the cracks close, but the biopores do not. Therefore, biopores can continue to provide paths for water flux even in fully swollen soils. Table 4 provides an overview of common earthworm species taken from the publications of Fraser et al. [26], Emmerling [27], and Chan [28]. The abundances of the different species vary depending on soil types and cultivation practice. In general, higher abundances were found in organic-rich soil. Total organic carbon (OC) in surface soil generally increases as degree of tillage is reduced by supplementing soil with organic substances (e.g., from residues of crops and cover plants) [29–32].

Table 4 Earthworm activities and abundances.

Species	Depth/cm	Diameter/mm	Abundance/m^{-2}
Lumbricus rubellus	10	6	25–250
Aporrectodea rosea	25	4	<40
Aporrectodea caliginosa	25	5	10–890
Allolobophora clorotica	25	5	<10
Aporrectodea langa	45	8	10–246
Octolasion cyaneum	55	8	<10
Lumbricus terrestris	100	8	5–20

Besides the formation of biopores, cracks, and fissures, cultivation practices that apply deep tillage destroy the soil structure up to a depth of about 60 cm (silty soils), whereas some heavy clay soils can only be ploughed to 20 cm depth. Deep tillage leads to a fast water flow through the produced fissures, which is comparable to a "funnel flow", since the walls of the produced fissures are compacted. After ploughing, the topsoil has a coarse structure with a relatively low density and a high infiltration capacity. This structure, however, will change within a relatively short time-period: after the first heavy rainfalls, the surface of tilled soils may clog and become crusted, which leads to a significantly reduced infiltration capacity and thus to enhanced run-off. Therefore, the inconsistent results of measurements of soil hydraulic and other physical properties under till systems and no-till systems may be due to the transitory nature of the soil structure after tillage, variable soil water content, site history, the time of sampling, and the potential for soil disturbance.

2.3 Measuring macroporosity

In principle, two approaches have been developed to quantify macropores. The first one attempts to determine the influence of macropores by measuring flow characteristics, for example, by plotting breakthrough curves, determining saturated or unsaturated hydraulic conductivity, and using tension infiltrometers. The second procedure is a direct approach that uses methods to determine the actual number, size, area, distribution, and continuity of macropores for various field conditions. The results of the direct approach are useful in developing mathematical models to predict the flow of water and chemicals through the soil profile.

Approach 1

The disc permeameter provides a rapid and convenient in situ method to measure soil hydraulic properties, for example, the sorptivity (S_0) and the hydraulic conductivity (K_0) close to saturation.

If measurements are made under unsaturated supply conditions with disc permeameters of dissimilar radii [35], K_0 may be obtained directly from the unconfined, quasi-steady-state flux densities. For slightly negative supply potentials, the method is particularly attractive, because the variability of soil hydraulic properties is reduced by the exclusion of the larger macropores from the flow. Therefore, the hydraulic conductivity measured under a slightly negative supply potential provides a more appropriate match-point than K_0 when employing ψ_0 to infer the shape of the unsaturated hydraulic conductivity function in field soils [35].

In circular source-point infiltration experiments using tension disc infiltrometers, both the in situ hydraulic conductivity and the sorptivity of an undisturbed soil [34–36] can be determined. In addition, it is possible to estimate different length and time scales characterizing the soil [37], such as the mean pore radius which is hydraulically active for the imposed water tension. Moreover, by using the disc permeameter filled with a tracer such as chloride, it is possible to deduce the effective mobile water content from samples extracted underneath the disc following a period of infiltration [38,39]. Jaynes et al. [40] described a method applying a tension infiltrometer and a sequence of conservative tracers to estimate both the immobile water content and the solute exchange coefficient between the mobile and immobile water domains. This method does not require the assumption made by Clothier et al. [38], presuming negligible solute movement into the immobile zone before sampling.

Before irrigation, further tracers are used, such as ^{18}O-labeled water, ^{15}N-labeled urea, or ^{14}C-labeled pesticides on top of undisturbed soil cores.

Approach 2

To visualize macropores in undisturbed soil cores (lysimeter and field samples), dyestuff is sprayed on the plots followed by water infiltration. Then the distribution of the dyestuff in the soil profile is visualized by excavation and preparation of horizontal and vertical soil segments. A more advanced technique is to generate color digital images of section samples by means of a scanner and analysis with a spectral image analysis system. The spectral intensity values of delineated features are grouped into classes to produce maps of their spatial distribution.

X-ray computer tomography is a further revealing tool for nondestructively measuring bulk density and macroporosity. The method creates an image of the density distribution within a sample. In soil science, computer tomography has been used for several years to measure in detail differences in bulk density, porosity, water content, macropore size, and fracture width [41].

Algorithms based on fractal geometry were developed to estimate soil macropore properties such as macropore size/counts, area porosity, and/or saturated conductivity. Empirical equations were developed to calculate macropore size, count, area porosity, and macropore conductivity based on three levels of available data. These are: soil texture and (1) an arbitrary size (R_x) and pore count above that size (N_x); (2) a measured macropore-saturated hydraulic conductivity (K_{macro}); or (3) an estimated largest macropore radius (R_1).

The form of all regression equations was consistent with equations from fractal geometry. The results indicate that satisfactory estimates of macropore size/counts, area porosity, and saturated conductivity are possible from more readily available macropore data.

The disadvantage of **laboratory methods** for measuring water fluxes is the small size of the soil samples. Macropores may be interrupted by the walls of the test cylinder, and the limited height of the test columns does not allow determination of length of macropores. Therefore, these test methods are of limited relevance for measuring macropore fluxes. However, in repeated experiments, they allow for estimations of the micro-heterogeneity of soils.

Frequently used techniques are porous suction cups or plates and tensiometers. Their advantage is that they are suitable for **field measurements** and can be placed at lower soil depths. The main problem is that the obtained values refer to a single point or rather small volume of soil; the textural and structural heterogeneity of structured soils is not taken into account. If, for example, one suction cup or tensiometer is placed below a macropore, whereas a second one is introduced in a finely structured section without macropores, quite different measurements for water flow or solute concentration will be obtained [42].

Large-scale lysimeters and effluents of drainage provide the most realistic information on substance concentration in the leachate. However, flow patterns may be influenced by free draining of macropores during heavy rainfalls, thus essentially simulating a structured soil over a porous subsoil or bedrocks.

2.4 Water flow and substance transport in soil

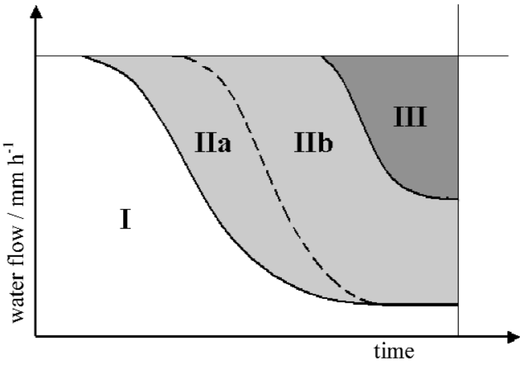
Primary parameters determining the vertical transport of a substance in a soil profile are the water flow (including all parameters that have an influence on the water flow) and substance-related parameters, such as adsorption and desorption processes or degradation kinetics. For transport via matrix flow, these processes are fairly well understood and can even be simulated by mathematical models (see below). If macropore phenomena are involved, water flow and substance transport become much more complicated.

A more quantitative discussion of some of the phenomena described in the following paragraphs is provided on the section "Modeling preferential flow processes".

According to the different hydraulic soil properties, water fluxes in most soils can be divided into the following distinct flow types:

- infiltration into fine to medium matrix pores
- percolation by flow in large matrix pores
- preferential flow in macropores
- plough layer or shallow interflow (subsurface run-off)
- surface run-off
- discharge by drain pipes
- deep seepage

Figure 2 depicts how prevailing flow types change during a rainfall event starting on dry soil and assumed to continue at a constant rate. At the beginning of rainfall, infiltration into matrix pores occurs, followed by percolation via matrix and macropore flow and, if the rainfall continues, by run-off through interflow and surface flow as well as drainage outflow (in case of drained fields). The figure shows generalized possible behavior rather than absolute relationships and describes the different interacting processes in a simple way.



Constant heavy rainfall

I: Matrix flow including uptake into meso- and micropores; decreasing with increasing saturation
IIa: Macropore flow by dead end macropores; decreasing with increasing saturation
IIb: Macropore flow with open ended macropores, e.g. drained fields, nearly constant percolation rate Water flow through IIa and IIb is starting simultaneously; however, water flow through IIa decreases, as subsoil is becoming water-saturated
III: Surface and subsurface run-off

Fig. 2 Time dependence of water flow during a continuing heavy rainfall. *Infiltration and percolation processes.*

The infiltration capacity of dry soils is highest, as the whole spectrum of matrix pores is not water-saturated. During a precipitation (or irrigation) event, the infiltration capacity is reduced, as fine and medium pores are water-saturated and only large pores are still active. If the capacity of matrix flux is exhausted, preferential flow through macropores becomes the dominating path in structured soils. The infiltration capacity strongly depends on soil type, water content of soils, and characteristics of the soil surface. If the soil surface is clogged, the infiltration capacity is significantly lower compared to open structured surfaces (e.g., shortly after cultivation).

Water flow through dead-end macropores ceases with time: At the beginning, water from the macropores is infiltrating the soil matrix. Infiltration strongly decreases when the subsoil is water-saturated. Water flow through open-ended macropores, however, will continue in situations where the flow-event is directly linked with a coarsely structured subsoil, jointed rock, or karstic aquifer, or in drained fields (see Section 4.3).

Surface run-off

Surface run-off starts when the infiltration and percolation capacity of soils, including macropore flux, is exceeded. The pattern of run-off is spatially variable. Its importance is affected by agricultural management, particularly by the cultivation regime, the plant cover, or clogging of the soil surface and crust formation.

Plough layer flow, or shallow interflow

Water may move horizontally within the soil at shallow depths, often in zones of saturation overlying the topsoil/subsoil discontinuity (plough layer), where a "temporary perched" water table occurs.

Discharge by drainpipes

Water may move through the unsaturated zone of the soil to either peripheral or artificial within-field drains. It is the dominant flow in clayey and silty soils that have been drained.

Drainage flow is dominated by macropore flow, as only soils that have low water conductivity or contain hardly water-permeable subsoil horizons are drained. Therefore, drainage pipes are installed to guarantee a sufficient water percolation and to ensure feasible cultivation in autumn and early spring. In addition, drains are installed to control a shallow groundwater table. In drained fields, water flow by macropores is very effective, as macropores are open ending in pathways directly connected to the drainage pipes. Therefore, substance concentrations measured in drainage pipes should be related to possible surface water contamination and not to direct groundwater contamination. The discharge by drainage pipes can be collected and measured quite easily by intercepting the drain lines and installing weirs or similar measuring systems.

Deep seepage

Water may leave the soil at the base of the profile into geological formations in an essentially vertical direction. It is generally assumed that it will continue to move to the groundwater. Deep seepage strongly depends on subsoil characteristics. If subsoils beneath the root zone consist of clayey or silty material, the initially preferential flow will be followed by a slow matrix flux showing characteristics of a water flow in dead-end macropores. If the subsoil beneath the root zone consists of porous material (sandy materials, gravels, or water-permeable parent rocks such as sand or limestone), macropores may drain without a larger depression. For very porous subsoils, water flow velocities by macropores may become similar to those of drained fields. From this it is obvious that the extent of deep seepage largely depends on the hydraulic properties of the subsoil layers. These aspects will be further discussed in Section 4.

Solute transport

Solutes are transported through advection by moving water unless they are retained by adsorption to soil constituents. Other processes like degradation and diffusion are also of importance. Figure 3 illustrates the transport processes assuming a solute deposit on the surface of the soil (e.g., spray applica-

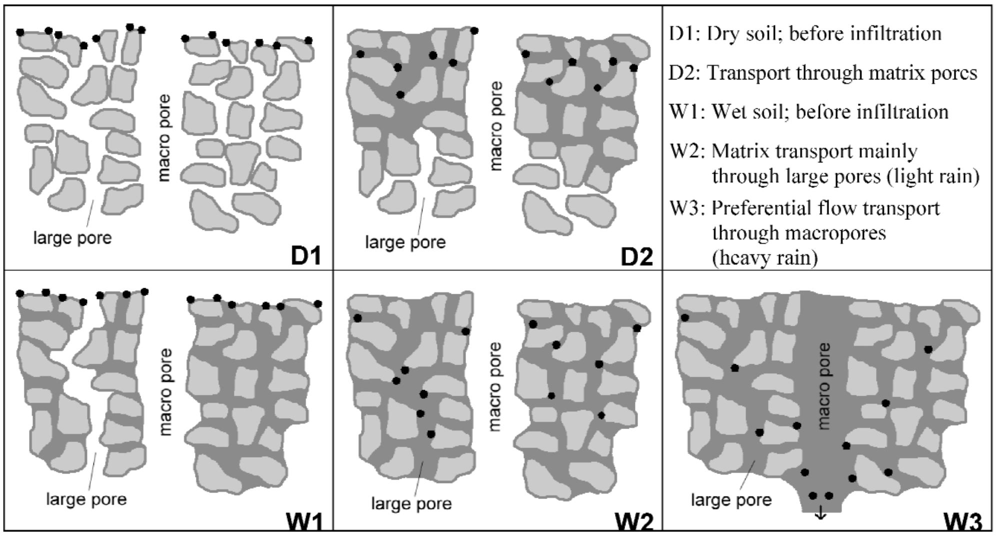


Fig. 3 Transport of solutes in soil.

tion) before the beginning of a rainfall. First, the fine and medium pores will be water-saturated. Then, large pores will become active as well. Solute flux in large pores is much greater than in medium pores. These differences in hydraulic conductivities lead to an uneven distribution of dissolved substances in the soil profile. If rain reaches a wet soil, the solute transport is much faster, since the flow proceeds directly through large pores, bypassing fine pores already filled with rather immobile water.

This effect is even far more pronounced if macropores are activated by a rainfall intensity exceeding the maximum matrix flow. In case of a continuing intense rainfall, macropores may become active even before the matrix pores are fully saturated, as the infiltration process occurs relatively slowly. If the ends of macropores open into drainage pipes or highly permeable subsoils (e.g., karstic rocks or coarse gravel), the overall flow rate and, accordingly, the solute flux are high. This may lead to a significant solute transport through macropores, causing relatively high substance concentrations in the leachate, although the total macropore volume is low. Most significant transport occurs at the beginning of the first flow event after application of the substance on the soil surface, whereas later events transport lower amounts.

Fast water flux through macropores decreases the importance of sorption processes compared to bulk soil due to nonequilibrium conditions which result from a rate of transport exceeding the rate of adsorption. Nevertheless, enhanced adsorption of substances on the walls of biopores has been reported. Edwards et al. [43] found a significant adsorption of alachlor and atrazine within earthworm channels resulting in a reduction of the transport. Stehouwer et al. [44] confirmed this hypothesis by explicit determination of chemical properties of burrow linings as a function of soil depth. The burrow linings consist of earthworm excrements that contain hydrophobic clay-humus complexes. The levels of OC are 2 to 8 times higher in the linings than in the surrounding soil, and the adsorption of atrazine is stronger to burrow lining material. In addition to adsorption, some diffusion of solutes into the soil matrix surrounding a micropore does occur, particularly when the soil matrix is dry. The walls of biopores are colonized with macroorganisms and are well supplied with oxygen and nutrients. Mallawantantri et al. [45] observed increased adsorption and mineralization of 2,4-D, carbofuran and metribuzin in surface linings of macropores and also increased mineralization for 2,4-D and carbofuran.

Contrary to the situation in open-ended macropores, in dead-end macropores the macropore flow and the resulting transport of solutes ceases once the pores are filled. [46]. Further flow is determined by the hydraulic conductivity beneath the macropore zone. Therefore, the transfer of solutes from macropores into the matrix pores of the subsoil horizons is of high importance at the dead ends of macropores. As a consequence, deep seepage of solutes is dependent on the permeability of the subsoil. However, dead-end macropores lead to “hot spots” (i.e., areas of relatively high substance concentrations) around the end of a macropore.

3. EVALUATION OF PUBLISHED RESEARCH PAPERS ON MACROPORE TRANSPORT OF PESTICIDES

This section gives an overview of published papers dealing with quantitative aspects of the transport of solutes through macropore flow and identifies the parameters that predominatly influence the extent of that transport. To this end, we examine whether high amounts of substances in leachates (in the following section, called “losses”) are more frequently related with certain environmental conditions and compound properties than would be statistically expected. Study types used to investigate the transport through macropore flow include measurements in artificially drained fields, lysimeters with structured soils, sampling of soil water with suction cups, and sampling of deeper soil horizons. For IUPAC nomenclature of the pesticides mentioned, see Appendix 2.

3.1 Database

The scientific literature was screened for all pertinent papers that showed clear evidence for macropore flow and that could be evaluated quantitatively. Although there are substantial differences between the suitability of sampling methods for the collection of preferential flow, it was not possible to differentiate among different methods. The main characteristics of transport mechanism through macropores (or other preferential pathways) are the solute concentration peaking at the beginning of a flow event and the maximum concentrations, which strongly decrease from event to event. A prerequisite for a quantitative evaluation is the availability of total losses (i.e., losses in percent of the material present on the soil surface at the beginning of the study). In many papers, these values are reported; in others, they could be derived from the concentrations and the amounts of leachate. To elucidate the influence of environmental and experimental parameters on the losses, sufficient information must be available. Therefore, only papers containing this minimum of experimental information were selected for the evaluation.

Many of the papers report on studies conducted under very artificial, unrealistic conditions such as lysimeter studies involving extreme watering rates shortly after application. As these conditions are inappropriate to draw conclusions of practical relevance regarding the losses via macropores, the selected studies were divided into a subset, including studies run under conditions realistic for moderate climates and a second one with studies run under artificial or otherwise highly atypical conditions, such as highly exaggerated irrigation rates within the first few days after application, or exposure to tropical rains, or forest soils. The validity of the conclusions is, therefore, limited to arable soils in moderate climates.

The selected studies are compiled in Table 12 (realistic conditions) and in Table 13 (unrealistic conditions). The tables include the main experimental and environmental parameters, where available, as well as compound properties.

K_{OC} *(sorption constant related to OC content) and* DT_{50} *(time where 50 % of the original amount has disappeared)*: If reported, values from a particular paper are listed; otherwise, averaged published values* are given as substitutes. Such “generic values” are written in parentheses.

---

*Values were taken from [47] or from [50].

Study description: Includes particularly percolation depths and, in the case of drainage studies, the spacing of drainage pipes (not available in all cases).

Experimental conditions: Include clay and OC content if available, tillage practice, date of application, description of irrigation, and other details about the study deemed important.

Duration: Time period between application of the compound and last flow event, hence includes the entire observation period. Although macropore flow implies a rapid flow event, losses may occur in subsequent flow events over a longer time period, most likely after translocation to deeper soil horizons in the early events.

First event: Interval between application of the compound and the first heavy rain or flow event reported. Although of high potential importance, this parameter is difficult to derive in many cases and is thus uncertain.

C_{max}: Highest concentration reported during the entire study interval (mg/L).

C_{mean}: Mean concentration; calculated under the assumption of the total losses being evenly distributed in the total percolate (mg/L).

Losses: Sum of all losses (i.e., material detected in the outflow of the test system) of the solute during the entire study interval, expressed in % of the applied material.

3.2 General observations

In many studies, researchers attempted to investigate the importance of specific factors. For example, by comparison of neighboring plots drained at different spacing of drainage pipes, the influence of the distance between drainage pipes was derived. Other investigations aimed at elucidating the effect of different tillage systems by keeping other variables as constant as possible. Or, attempts were made to find out about the dependencies on compound properties by joint application of two or more compounds. Can such investigations yield generally valid results? A closer look at the investigations summarized in Tables 12 and 13 shows that this is rarely the case. Factors that dominate in one study do not in others. For example, in [49] dependence of losses on spacing of drainage pipes is reported, whereas in [50] no such influence was observed. While in [51] metolachlor losses were below those of atrazine, in [50] a reversed order was observed despite identical conditions for both substances. Lower losses are reported [52] in 1990 compared to 1989 for atrazine, cyanazine, and alachlor as expected from lower precipitation, lower percolate, and a longer interval to the first leaching event; carbofuran, however, strongly increased from 1989 to 1990 under the same study conditions.

These examples indicate that total losses via macropore flow cannot be attributed to factors in a straightforward manner, nor does one study allow drawing any *general* conclusion. Rather, the available set of results is characterized by a pronounced diversity and inhomogeneity, demonstrating that the numerous factors interact and counteract in an unpredictable manner. Nevertheless, some rough conclusions can be drawn from the studies compiled in Tables 6 and 7:

- Compounds with very high soil adsorption constants ($K_{\mathrm{OC}} > 1000$ cm^3 g^{-1}) are found in the seepage water in very small concentration, if it all.
- Very high precipitation or irrigation shortly after application increases the losses through macropores.
- Soil horizons of a thickness of less than 40 cm are not suitable for investigating transport phenomena via macropores under practical field conditions.

In the following section, a closer, statistically supported look will be made on the influence of parameters that may be of importance.

3.3 Influence of environmental parameters

Losses that could be used for the comparison are highlighted bold in Table 6. As a certain percolation of rain or irrigation water is a precondition for any parameter to influence the losses, experiments that did not show any percolation of water were not considered (e.g., [54]). In order to avoid overweighting of some studies, identical replicates were averaged (remark in the last column, e.g., [49,52]). For the final evaluation, there were 174 results available from 31 studies conducted with 33 different pesticides at 23 sites.

Comparison technique

Losses for individual compounds do not show a direct correlation with any of the environmental parameters. The number of results per compound is too low, and the variability among the results is too high due to the dependence on many parameters. To have at least a rough statistical evaluation, despite the complex and variable dependence on the various factors, all parameters were examined individually as to whether they favor higher or lower losses. To this end, suitable binary designators were attributed to the losses ("high" or "low") and to each of the potential impact parameters (derived from a ranking of the values, see following paragraphs). The statistical evaluation was done by a simple statistical examination on whether the binary variables correlate (i.e., whether high losses occur more frequently in the subsets "high" or "low" for each of the parameters).

Because the *losses*, expressed in % of the applied material, are to some extent dependent on compound properties (see next section), these had to be eliminated. To this end, the assignment to the subsets was done individually for each compound by comparing each result with the compound-specific median value and transforming it into the comparative "loss parameter" with the values "+" (above median), "–" (below median), or "0" (equal median). The "loss parameter" so defined merely depends on environmental factors.

Accordingly, the other parameters were assigned to two groups for each parameter. For the "descriptive" ones, the groups were formed as follows:

Type of investigation: "drainage" or "lysimeter"; the few studies of other types were not assigned to either group.

Season: "spring" or "autumn", depending on the date of application of the pesticide (i.e., the start of the observation period). "Spring" studies started between March and June, most often in May; "autumn" studies started between October and February, most often in November.

Tillage: "deep" or "no", depending on whether the tillage system involved deep or no ploughing.

To all quantitative parameters, a value "+", or "–" was attributed to each study, depending on whether the nominal value was "high" (= "+") or "low" (= "–"), e.g., "high clay content" or "low clay content". The group limits were selected such as to form similarly sized study subsets for this parameter. If no value was reported for a given parameter, the study was not used to examine the influence of that parameter.

In addition to these directly observed parameters, the total percolate expressed as a fraction of the total rainfall or irrigation was calculated. The derived parameter is expected to be higher for rain falling on wet soil and might therefore be relevant for the extent of losses.

The base set of data consists of 174 loss results. They are expressed in "+", "–", or "0" along with the descriptive parameters mentioned above. The correlation between the loss and any environmental parameter was derived by counting the numbers of the combinations +/+, +/–, –/+, and –/– for the pair of variables in question, i.e., it was examined how many of the "high" and "low" losses were linked with either subgroup of a given parameter. The values "0" were assigned in half to both the "high" and "low" losses. The statistical comparison of the numerical values connected with the distributions "+/+":"+/–" and "–/+":"–/–" (or similar for other groups such as "spring/autumn") allows the decision on whether the correlation is significant or not. Statistical testing was done with the χ^2-test. Values for $\chi^2 > 3.8$ prove two distributions to be significantly different at a probability level of 95 %; for details, see textbooks on statistics.

Table 5 Group limits for different parameters.

Parameter	Group limits	
	"–"	"+"
Percolation depth/cm	<95	≥95
Spacing of pipes/m (for drainage studies only)	<10	≥10
Duration/d (observation period)	≤120	>120
Organic carbon/mass %	≤1.4	>1.4
Clay/mass %	≤17	>18
Total rainfall or irrigation/mm	<350	≥350
Total percolate/mm	<70	≥70
First event/d	<10	≥10
Ratio percolate/rain	<0.24	>0.24

To derive the influence of the season upon the losses, for example, the distributions "S/+(loss)":"S/–(loss)" and "A/+(loss)":"A/–(loss)" are evaluated: the distributions are 51.5:54.5 and 39.5:28.5, hence showing a slightly increased frequency for autumn losses being higher than spring losses; the χ^2 value of only 1.5 suggests, however, that the difference is close to randomness.

The procedure was also used to examine the relationships between any other variables. Such comparisons are used in the next chapter to support the validity of conclusions by checking the plausibility of dependencies.

Discussion

The statistical procedure used allows determination of whether the frequency distribution of the losses is statistically linked to that of experimental or environmental parameters. As "correlation" does not necessarily mean causality, it has to be examined further whether any correlation between losses and any parameter is a simple consequence of a causal link to another parameter. Taking into consideration general experience and knowledge as well, the plausibility of conclusions with regard to correlations can be further substantiated.

Table 6 shows the detailed frequency distribution of the subgroups "high losses" and "low losses" for the subgroups of the other parameters, illustrating the influence of the parameters on the losses. For example, high clay content is related to high or low losses, whereas % OC shows a positive correlation (i.e., a tendency for higher losses in soils with a higher OC content). In Table 7, the interrelations between most other parameters are listed in a generalized form (the parameter "tillage" was omitted, as the low number of no-tillage experiments results in erratic correlations). Relation arrows are put in parentheses where a correlation between two parameters is apparent rather than causal. For example, the significant correlation in Table 7 between the study duration and % clay has no causal significance, but is simply due to the fact that the longer studies happened to be carried out more frequently on soils richer in clay. As the clay content did not turn out to significantly influence the losses (see below), this bias has no consequences for the outcome of the evaluation. Hence, some relations between different parameters are accidental and due to the limited number of available investigations, whereas others are as expected, for example, the higher total rainfall in studies starting in autumn. Such relations confirm the applicability of the statistical approach.

Table 6 Dependence of losses on several environmental parameters.

	Type		Depth		Spacing		Duration		Tillage		Season		% oc		% clay		Rain		Percol.		1st event	
	D	L	+	–	+	–	+	–	d	n	S	A	+	–	+	–	+	–	+	–	+	–
Loss +	68.5	20.5	54.5	36.5	43	24.5	47	43	57.5	8.5	51.5	39.5	41	35	31	29	45.5	46.5	45	33.5	36	28
Loss –	68.5	13.5	36.5	46.5	39	24.5	41	44	64.5	5.5	54.5	28.5	28	47	32	34	36.5	39.5	32	39.5	33	27
χ^2 value	1.2		4.4		0.07		0.28		0.93		1.5		4.2		0.13		0.88		2.4		0.02	

Table 7 Relations between any parameter.

	Depth	Spacing	Duration	Season	% oc	% clay	Rain	Percol.	Percol./rain	1st event
Type	↑L	—	—	—	—	—	(↑L)	↑L	↑L	—
	Depth	↑	—	—	—	—	—	(↑)	(↑)	—
		Spacing	—	—	↓	↓	—	—	—	(↓)
			Duration	↑S	—	(↑)	↑	↑	—	(↑)
				Season	—	—	↑S	—	↑A	↑S
					% oc	↑	—	↑	—	(↑)
						% clay	(↑)	↑	—	(↑)
							Rain	↑	↑	(↑)
								Percol.	↑	(↑)
									Percol./rain	—

χ^2:	<3.8	>3.8	
	—	↑	(positive correlation)
		↓	(negative correlation)

In parentheses: apparent (noncausal) correlation

Study types and design

Type of investigation

There is a slight tendency toward higher losses in lysimeter studies compared to drainage studies. This is not surprising, because in lysimeters the percolation is similar over the entire cross-section of the soil, whereas in drainage studies there is some dissimilarity due to a variable distance from the surface to the drainage pipes. It is therefore plausible that in drained fields the collected amount of percolating water is lower than in lysimeter studies, which results in the tendency for higher total amounts of percolate in lysimeter studies (Table 7). Although this is partly due to the random tendency to more rainfall in the lysimeter studies (correlation type/rain in Table 7), the explanation is further supported by the ratio percolate/total precipitation (i.e., the fraction of the total precipitation that percolated). The 90-percentile of the ratio is 0.43 for lysimeter studies (i.e., 43 % of total precipitation percolated during the entire observation period), whereas it is only 0.33 for drainage studies. This is confirmed by a clear dependency of type vs. percolate/rain in Table 7. Therefore, it is evident that the low difference in the losses between drainage and lysimeter studies is reasonable, and it can be assumed that the influence of the other parameters is similar for both study types. It is thus justified to combine the results of all study types for the evaluation.

Percolation depth

Contrary to what might be expected, the group of studies with a deeper percolation depth (>95 cm) shows clearly higher losses. Although this finding confirms that macropore flow bypassing the soil matrix was measured in the studies under evaluation, the conclusion that losses generally increase with depth would, of course, be misleading. The finding may indicate that drainage pipes at a depth of more than 1 m more efficiently drain the *entire* fields (most studies were done on drained fields!). A lower depth would require much narrower spacing to obtain a similar efficiency. This conclusion is supported by a similar inverse correlation between the percolation depth and the total percolate: a χ^2 value of 6.1 proves that the draining efficiency is higher in fields with deeper drainage pipes.

The fact that all lysimeter studies are in the subgroup ">95 cm" has not biased the result. The unexpected dependence is even more pronounced for drainage studies only. For this study type, as expected, the depth is strongly correlated with the spacing ($\chi^2 = 50$), reflecting that the spacing is wider with increasing drainage depth (spacing vs. depth in Table 7).

Therefore, it seems that the correlation of the losses with the percolation depth is due to the higher drainage efficiency in the studies with larger depths, hence rather indirect than causal.

Duration (observation period)

Losses are not significantly dependent on the observation period. This finding is in agreement with the fact that losses are dominated by the first events after application. Losses occurring later are of minor importance, so that the extension of the observation period does not increase the losses significantly. The early occurrence of the losses is another characteristic of macropore transport that is correctly reflected in the evaluation of the studies. The observed dependence of the total precipitation and the total amount of percolate on the observation period are plausible, as both are increasing with increasing study duration.

Agricultural factors

Tillage

There is no significant difference between no-tillage and conventional tillage. The slightly higher number of higher losses in no-till studies is in the range of randomness.

This finding may be surprising in view of the many papers describing a strong influence of tillage practices on soil porosity. It was observed that tillage sequences had an effect on the aeration porosity, which was significantly higher for the minimum tillage. The effect was mainly due to the increase of the pores >300 µm diameter (aeration pores), (e.g., [7,30,61]). Moreover, tillage practices have a strong impact on bulk density and, consequently, on water flow. Edwards et al. [62] noted that the bulk density of a no-till soil was about 1.6 t m^{-3}. If conventionally tilled, the bulk density of the horizon decreased to about 1.0 t m^{-3} shortly after tillage and reconsolidated to about 1.3 t m^{-3} during the growing season. Moreover, the ability of soils to absorb and transmit water is affected by the structural stability of the soil pores and by the moisture conditions of the soil at the time of measurement; both soil conditions are usually modified by tillage practices [63] and strongly dependent on weather conditions and sampling period after cultivation.

Therefore, it appears that the influence of tillage on macropore transport is very complex, and the various factors may, on the whole, average out, resulting in the observed absence of appreciable effects between tillage and no-tillage. Moreover, the total number of no-tillage studies (12) may be just too low to allow meaningful conclusions to be drawn.

Season of application

In agreement with the general experience, a slight tendency to higher losses of autumn-applied pesticides can be observed. However, the difference is low, and the slight trend does not allow for generalization by concluding that losses in autumn are clearly higher than in spring. Table 7 reveals that total percolation (which influences the losses significantly, see below) on average is not higher in autumn than in spring. The higher percolation/rainfall ratio in autumn is obviously outweighed by more intensive rainfalls in spring. This conclusion does, of course, only apply to macropore flow. Without doubt, the matrix flow is higher in autumn as a consequence of a higher water saturation of the soil in the colder season in Europe and North America.

Soil parameters

Organic carbon content: The influence of the content in OC is significant: the higher the OC content, the higher the losses. As the macroporosity of the soil and the stability of the macropores increases with the content in OC, the dependence of the losses on % OC reflects the higher macroporosity, hence the higher leaching. This conclusion is supported by the equally high dependence of the total percolate on the OC content (χ^2 value = 5.8). It also demonstrates that sorption processes are of less importance for preferential transport than for homogeneous transport.

Clay content

The clay content of the topsoils does not appear to be among the factors that dominate the solute transport via macropore flow. This is surprising, as macroporosity is generally higher in heavy soils and might be related to the fact that the present survey was limited to studies where macropore flow occurred (i.e., to silty and clayey soils). Although formation and flow characteristics may differ in clayey and silty soils (see Section 2.2), rapid solute transport will occur in both soils, leading to comparable results.

There are many studies illustrating that macropore flow and macropore transport are much more important for structured soils (i.e., soils rich in clay and/or silt). Bergström and Jarvis [53], for example, compared losses of dichlorprop and bentazon in lysimeters with different soils. Whereas clayey soils, and (even more so) peat, showed relatively high losses, losses were low in a sandy soil. Flury et al. [64] reported losses of triasulfuron, terbuthylazine, and atrazine through macropores of a loamy soil, whereas there was no leaching down to 40 cm in a sandy soil.

Factors related to rainfall, irrigation, and percolation

Total precipitation and total percolate

The total amount of precipitation or irrigation appears to be of minor importance. More important is the amount that percolates. A tendency toward higher losses is indeed observed for higher amounts of percolates. It may appear surprising that the influence of the percolation is not more pronounced. However, percolation depends on many factors that have not usually been recorded in the published papers, such as the humidity status at the beginning of the rainfalls, the extent of shrink fissures, and the duration of saturated percolation conditions.

First rainfall or drainage event

It is surprising that the delay of the first heavy rainfall or drainage event appears to be of no significance. According to experience, pesticides are more available for off-site transport shortly after application than after aging. This is corroborated in the many studies under unrealistic conditions summarized in Table 6, which show high losses upon very heavy rainfall or irrigation within the first three days. Why does this factor not manifest itself in the total losses? One reason may be due to the fact that aging of residues does not depend on the elapsed time only. For example, aging is slower on dry soils, because migration into micropores and to adsorption sites requires some mobile soil water, which is true for many degradation processes. In addition, moderate rainfalls, which do not lead to drainage events, will lead to a distribution of mobile and moderately mobile pesticides in the upper soil layer. This distribution in a broader soil layer causes lower concentrations in the pore water of the soil, which will be transported through macropores by heavy rainfalls. Thus, there may be several factors significantly influencing the losses. Moreover, the actual delay of the first event is difficult to abstract from the study, as comprehensive weather records are rarely provided. So, the delay listed in Table 6 has a relatively high uncertainty in many cases. This may explain why the delay of the first percolation event has no clear effect on the losses, except for the drastic examples shown in Table 6. The somehow erratic and uncertain nature of this parameter is underlined by the fact that there are various noncausal correlations with other parameters (Table 7).

Total losses vs. maximum concentrations in macropore flow

In the same way as described for the total losses, the maximum concentrations were statistically analyzed. No statistically significant correlation could be derived with any environmental parameter. Even more than the total losses, the maximum concentrations depend on factors that are neither controlled nor recorded. They are assumed to be much more determined by the intensity of the first rainfall than by its duration. And, perhaps the fact most responsible for the impossibility to meaningfully interpret maximum concentrations, the number of sampling points over the first percolation event is highly variable throughout the studies. Accordingly, as high sample sizes average out peak concentrations, maxima of different studies are hardly comparable.

3.4 Influence of compound properties

It is known that adsorption to soil organic matter or other soil constituents as well as aging and degradation decrease the concentration of a substance in a soil solution and, thus, its mobility. The chemical properties of a solute that govern these processes consequently determine its availability for transport through macropore flow. Solutes investigated can be divided into inorganic anions, metal ions, and organic molecules.

Common *inorganic anions* are hardly adsorbed, and they are not degradable with a few exceptions, such as nitrate ion, which is reduced under anaerobic conditions. In agreement with their persistence and low adsorptivity, the behavior of inorganic anions in a macropore flow situation is different from organic molecules or inorganic cations. As a consequence of the low retention, the amount transported under realistic precipitation regimes is one to two orders of magnitude higher than that of the most mobile pesticides [53–56] (Tables 12 and 13). Shortly after application, losses of pesticide inorganic anions are similarly high. Upon aging, losses of pesticides strongly decrease, whereas losses of the nonsorbing, nonreactive inorganic anions remain high due to their stability and low tendency for adsorption to soil constituents [57,58].

For *metal ions*, the adsorption to soils seems to play an important role. Strontium showed lower losses than bromide ion and even less than atrazine [59]. This strong retention is assumed to be caused by cation exchange on negatively charged silicate and aluminate sites of soils as well as by chelate formation with soil organic matter.

Among *organic molecules*, pesticides are by far the best-investigated class of compounds. The many studies published on pesticides allow a more comprehensive discussion of the influence of compound properties. The conclusions that can be drawn are, however, valid for other organic molecules as well. The disappearance time (acronym DT_{50}), the water solubility, and the equilibrium constant of adsorption to soil organic material (K_{OC}) are assumed to be the most important properties that may have an impact on the magnitude of losses. A quick look through Tables 6 and 13 reveals the importance of the influence of the adsorption constant K_{OC}, at least for extreme values. Compounds with very high K_{OC} values, such as trifluralin and deltamethrin with a K_{OC} of 8000 and 50 000, show clearly lower losses via macropore flow than compounds with a low K_{OC} value [54,59]. However, fluctuations are significant, resulting from the combined impacts of other structure-related and environmental factors. Therefore, no conclusions regarding the influence of specific compound properties can be drawn from data reflecting the combined influence of compound-related and environmental factors. To elucidate the influence of compound properties, the only results from useable studies are those that include the combined application of two or more pesticides. In these cases, the influence of environmental parameters is identical for *all* compounds involved in a given study, and differences in the losses have to be attributed to properties of the compounds.

All results that were usable to derive compound-related influences are highlighted in italics in Tables 12 and 13. A total of 282 results, for 55 different pairs of compounds, were obtained from 18 studies conducted at 12 sites. They are compiled in Table 14 along with the relevant properties of the compounds, and the results are summarized from the statistical evaluation (see below).

Comparison technique

A comparison was made with all possible results for any two compounds that had been applied at the same time in the same study. Contrary to the above discussion about the influence of various parameters on the losses, the results obtained in studies carried out under unrealistic conditions were taken into account here, provided that two or more compounds had been exposed to identical conditions (Tables 12 and 13). For each compound, losses expressed as concentrations were scaled by division by the rate of application, according to

$$\text{loss}\left(i\right)=\frac{\text{mass concentration}\left(i\right)}{\text{rate}\left(i\right)}$$

Where possible, the mean concentrations over the entire observation period were used, otherwise the maximum concentrations were applied.

In each study, the differences in the losses were calculated for any two pairs and scaled by dividing by the mean. As a prerequisite for usability, at least one compound of a given pair must have been detected in the leachate.

$$\Delta\left(\text{loss}\right)=\frac{\left(\text{loss }\ 2-\text{loss }\ 1\right)\times 2}{\left(\text{loss }\ 2+\text{loss }\ 1\right)}$$

Upon scaling, Δ (loss) is between –2 and +2. Values are positive if loss 2 > loss 1, and negative if loss 1 > loss 2.

Similarly, the differences in the possibly relevant compound properties were translated into the term Δ (property), with property being *solubility*, soil adsorption constants K_{OC}, and disappearance time DT_{50}.

$$\Delta\left(\text{property}\right)=\frac{\left(\text{value }\ 2-\text{value }\ 1\right)\times 2}{\left(\text{value }\ 2+\text{value }\ 1\right)}\ \text{ for property = solubility, } K_{\text{OC}},\ \text{DT}_{50}.$$

As experience suggests, DT_{50} and K_{OC} exert a combined effect on the environmental behavior of a substance, the GUS index* was also used for comparison. The differences in the GUS indices S_{GUS} were not scaled, as they are already derived values within a relatively narrow range (approx. –1 to 5), hence

$$\Delta = S_{\text{GUS}} = S_{\text{GUS}}\ 2 - S_{\text{GUS}}$$

The pairs Δ (loss) vs. Δ (property) were plotted to visualize the extent of the influence of each property (Figs. 2a–d). For this plot, the order of compounds 1 and 2 was selected in such a way that Δ (property) is positive (value 2 > value 1). For a given pair, assignment to 1 or 2 may therefore be different depending on the direction of the differences in that property. Consequently, for the same pair of results Δ (loss) may be positive for one property and negative for another.

For a more quantitative investigation of the influence of compound parameters on the losses, a procedure similar to that described for the environmental parameters was used. To this end, a binary variable *slope* was defined according to

$$slope=\text{sgn}\left(\frac{\Delta\ (loss)}{\Delta\ (property)}\right)\ \text{with } slope = + \text{ or } -$$

and averaged over all pairs of results. The observed distribution "positive:negative" was compared by means of a χ^2 test with the 1:1 distribution which would be expected if the property has no influence. Additionally, subsets "low" and "high" were formed for each property by dividing the entire dataset into two subsets of equal size, one comprising the pairs with larger Δ (property), the other comprising those with the smaller Δ (property). The distributions "positive:negative" in the two subsets were compared,

---

*GUS index (= **g**roundwater **u**biquity **s**core) $S_{\text{GUS}} = \lg(\text{DT}_{50}/\text{d})\ [4 - \lg(K_{\text{OC}}/\text{cm}^3\ \text{g}^{-1})]$ [60].

and the χ^2 test conducted. This comparison allows conclusions as to the significance of the influence of each parameter, under the assumption that all other compound properties on average are similar for both subsets (Table 8).

Table 8 Dependence of frequency distributions of Δ (loss) upon Δ (parameter).

Slope	Δ (Solubility)			Δ (K_{OC})			Δ (DT_{50})			Δ (S_{GUS})		
	Total	Low	High	Total	Low	High	Total	Low	High	Total	Low	High
Positive	69	28	41	35	11	23	71	33	38	108	42	66
Negative	72	43	29	100	52	48	69	34	35	33	26	7
χ^2 test	0.03	5.2		16.6	3.9		0.01	0.1		21.5	16.0	

Discussion

The results for all pairs of substances are summarized in Table 14: The assignment of the substances to compound 1 and 2 as well as the order was selected according to descending Δ (S_{GUS}) values. For some other Δ (parameter) to be positive, the assignment of the substances is reversed, these cases are highlighted in italics.

Solubility

Many published papers describe the assumption that losses through macropores increase with the *solubility*. This assumption—although apparently confirmed in some studies—is not confirmed by considering the totality of the studies. Figure 4a shows that there is no obvious correlation between Δ (loss) and Δ (solubility). This conclusion is in agreement with the result of the statistical evaluation: In 69 cases, the losses increased with the solubility, whereas in 72 cases a decrease was observed. However, there is a significantly higher abundance of increased losses among the pairs with high Δ (solubility) than in the subset with lower values of Δ (solubility), see Table 8, suggesting that there is a weak but existing correlation with solubility.

Adsorption

A major influence of K_{OC} can be observed: Although in Fig. 4c, the data points are scattered over the entire area, a higher abundance is obvious in the region of lower Δ (loss) and higher Δ (K_{OC}). And in Table 9, the distribution "positive:negative" deviates significantly from the 1:1 ratio, proving a statistically significant tendency for lower losses of substances with higher K_{OC} values. From a thermodynamic point of view, it is not surprising that the correlation, although linked, is more pronounced with K_{OC} than with the solubility. Both properties actually being equilibrium constants are determined by the difference of the chemical potential of the solute in the aqueous phase and the chemical potential of the pure phase (solubility) and that in the adsorbed state (K_{OC}). Whereas hardly any pure phase of the solute is present in the practical concentration range in the soil/water-system, the soil adsorption sites are present and adsorption does take place. Independent of the complexity of the solute–soil interactions, which may be very low, they do exist and are taken into account by K_{OC} values. Therefore, this property is more relevant for real environmental processes in soil than the solubility.

Degradation (DT_{50} values)

There is no correlation between losses and DT_{50} values. Even though this conclusion is surprising, it is the clear outcome of the analysis of the available dataset. Figure 4b neither exhibits any systematic distribution pattern of the data points, nor does the distribution of the slope parameter in Table 8 show a shift in abundances caused by DT_{50} values. This inexpected outcome may be the consequence of several factors. First of all, when there is no correlation, this does not necessarily mean that there is no influence. However, it may indicate that the influence of other factors is more important and, therefore, hides the influence of DT_{50}. With the lowest DT_{50} being 7 days and the highest 110 days, the range of

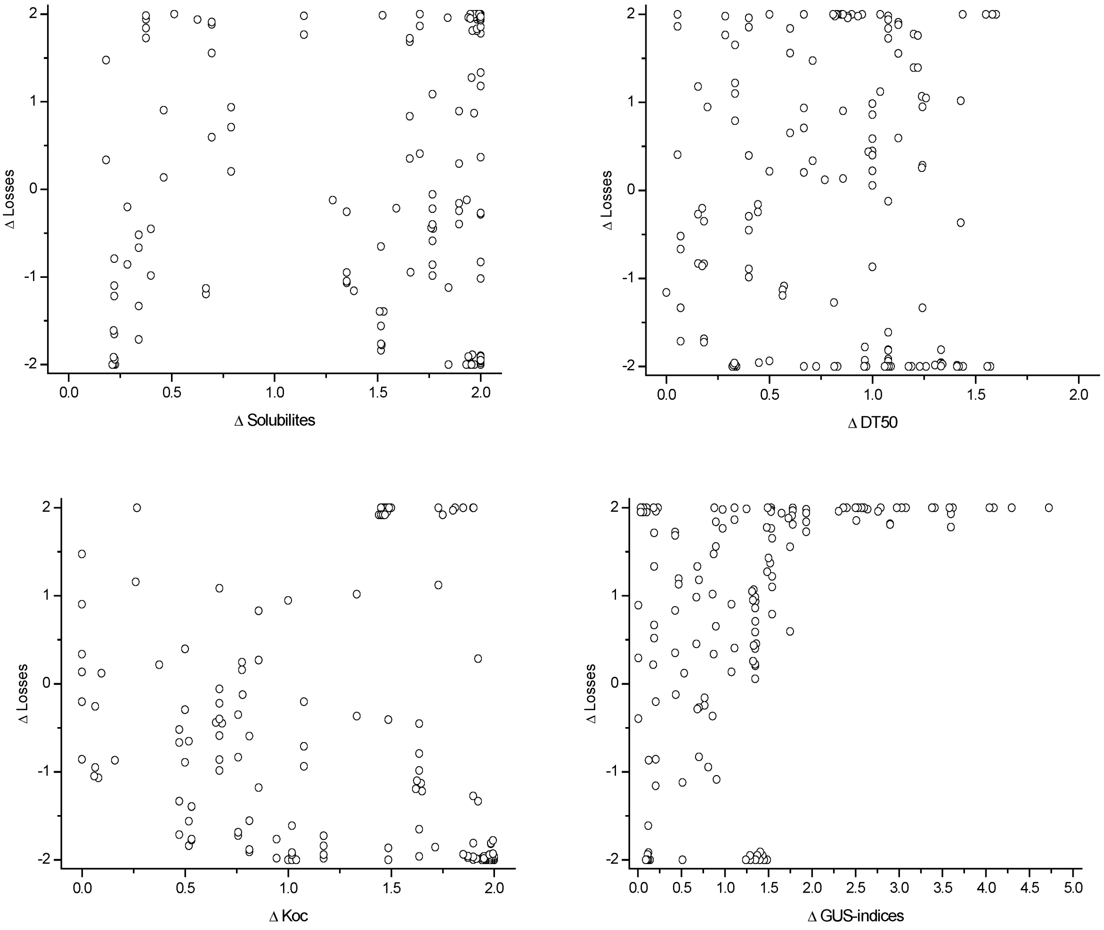


Fig. 4 (a): Δ (Loss) vs. Δ (solubility); (b): Δ (loss) vs. Δ (DT_{50}); (c): Δ (loss) vs. Δ (K_{OC}); (d): Δ (loss) vs. Δ (S_{GUS}).

DT_{50} values is moderate. Moreover, most of the values were not determined on-site, but are published mean values. Therefore, the actual local DT_{50} value may deviate quite significantly from the value applied in our study (even though only four out of the seven pairs for which the DT_{50} values were determined on-site behaved as expected, i.e., they showed a positive slope, whereas for the other three the more persistent compound showed more leaching).

The most pronounced relationship is seen in the GUS index. In Fig. 4d, a systematic pattern is obvious, and the data in Table 8 confirms the highly significant dependence on the GUS indices. This particularly applies for the high differences in the values. In all cases where $\Delta S_{GUS} > 1.5$, there is no deviation from the expected increase in loss with increasing GUS index, whereas out of the slopes for the subset with $\Delta S_{GUS} < 0.8$, 21 are negative and 27 are positive. It may, therefore, be hypothesized that values of $\Delta S_{GUS} < 1.5$ are erratic as a consequence of high uncertainties in K_{OC} and DT_{50} values. Nevertheless, among the investigated parameters the GUS index is the best-suited parameter to describe the influence of compound properties on the losses through macropore flow.

3.5 Range and distribution of total losses

All losses expressed in % of the totally applied amount that were obtained in studies conducted under realistic conditions are described in detail in Table 14. A summary is given in Table 9. The data reveals that for all compounds the observed losses spread out over a certain range with compound-specific frequency distributions. Whereas the largest number of values is close to zero, the median and highest values depend on K_{OC} and DT_{50}, hence on the GUS index. This observation is illustrated with the reported findings for atrazine and isoproturon, the two compounds for which the largest number of results are available (Fig. 5).

Table 9 Statistical key figures of losses by macropore flow.

Compound	# Results	# Studies	Losses of applied material/%	Median	GUS
Clopyralid	3	2	0.0004, 0.008, 1.5	0.008	5.16
Dicamba	2	1	0.09, 0.46	0.28	4.24
Diclofop	2	1	0.007, 0.009	0.008	4.22
Carbofuran	9	3	0.12, 0.125, 0.135, 0.22, 0.53, 0.66, 0.88, 1.08, 1.1	0.53	4.07
Triasulfuron	2	2	0.30, 5.1	2.70	3.96
MCPA	10	3	0, 0, 0, 0, 0, 0, 0, 0.01, 0.025, 0.117	0	3.77
Mecoprop	7	4	0, 0.001, 0.006, 0.015, 0.032, 0.08, 0.292	0.015	3.57
Atrazine	24	10	0.02, 0.038, 0.05, 0.05, 0.055, 0.06, 0.065, 0.065, 0.09, 0.1, 0.155, 0.16, 0.28, 0.32, 0.39, 0.45, 0.45, 0.6, 0.9, 0.975, 1.55, 1.7, 1.8, 3.6	0.220	3.56
Metribuzin	3	1	0.41, 1.02, 1.3	1.02	3.56
Metamitron	1	1	0	–	3.54
Simazine	1	1	0.37	–	3.39
Aldicarb	1	1	0.043	–	3.34
Fluroxypyr	6	1	0, 0, 0, 0, 0.01, 0.04	0	3.25
Bentazon	3	2	0, 0.01, 0.07	0.010	3.21
Terbuthylazine	2	2	0.19, 0.20	0.195	2.74
2,4-D	4	2	0, 0.022, 0.044, 0.06	0.030	2.70
Chlorotoluron	1	1	0.68	–	2.54
Linuron	6	1	0, 0, 0, 0.005, 0.01, 0.1	0.003	2.49
Chloridazon	1	1	0	–	2.48
Isoproturon	24	10	0.002, 0.005, 0.009, 0.013, 0.024, 0.03, 0.035, 0.037, 0.038, 0.058, 0.08, 0.09, 0.18, 0.28, 0.35, 0.35, 0.36, 0.48, 0.55, 0.75, 0.82, 0.94, 1, 2.5	0.135	2.37
Dichlorprop	5	2	0, 0.02, 0.04, 0.2, 0.4	0.040	2.33
Cyanazine	8	2	0.01, 0.015, 0.015, 0.02, 0.02, 0.03, 0.03, 0.12	0.020	2.31
Dimethoate	7	2	0, 0, 0, 0, 0, 0, 0.001	0	2.28
Metolachlor	12	6	0.08, 0.13, 0.15, 0.17, 0.2, 0.3, 0.4, 0.59, 0.625, 0.7, 0.82, 2.3	0.35	2.21

(*continues on next page*)

Table 9 (*Continued*).

Compound	# Results	# Studies	Losses of applied material/%	Median	GUS
Alachlor	11	3	0.001, 0.01, 0.01, 0.01, 0.01,0.01, 0.01, 0.01, 0.05, 0.07, 0.15	0.010	2.08
Fonofos	2	1	0.0005, 0.012	0.006	2.04
Bromoxynil	2	1	0.012, 0.015	0.013	1.72
Prochloraz	1	1	0	–	1.31
Tri-allate	2	1	0, 0	0	1.19
Pendimethalin	4	2	0, 0, 0, 0.027	0	0.59
Trifluralin	5	3	0, 0, 0.0006, 0.0028, 0.1	0.0006	0.17
Chlorpyrifos	2	1	0, 0	0	–0.66
Deltamethrin	1	1	0.003	–	–0.91

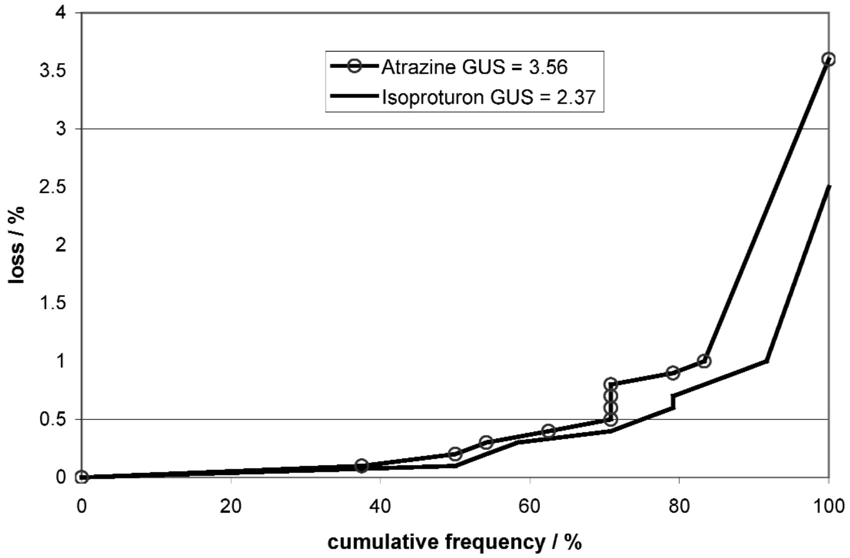


Fig. 5 Frequency distribution of atrazine and isoproturon losses.

In Fig. 6, all losses are plotted vs. the GUS indices S_{GUS}. The distribution of the measured values illustrates the conclusions drawn above: the range of losses is higher with higher GUS indices. A direct relationship between GUS indices and losses cannot be derived. However, the data points shown in Fig. 6 as well as the above considerations suggest a relationship between GUS indices and a given percentile of the losses for each compound. With the assumption of a proportionality of the slopes loss vs. S_{GUS}, the values for the proportionality factor F can be determined to be 0.014, 0.14, 0.28, 0.38, and 0.49 for the 50-, 80-, 90-, 95-, and 97.5-percentile, respectively. Based on this equation, estimates can be made for the losses of a given substance. For example, for a substance with a GUS value of 3, the losses though macropore flow are below 0.042 % in 50 % of the cases, below 0.84 % in 90 % of the cases, etc. The gray line in Fig. 6 ($F = 0.49$) gives approximately the 97.5-percentile of the losses.

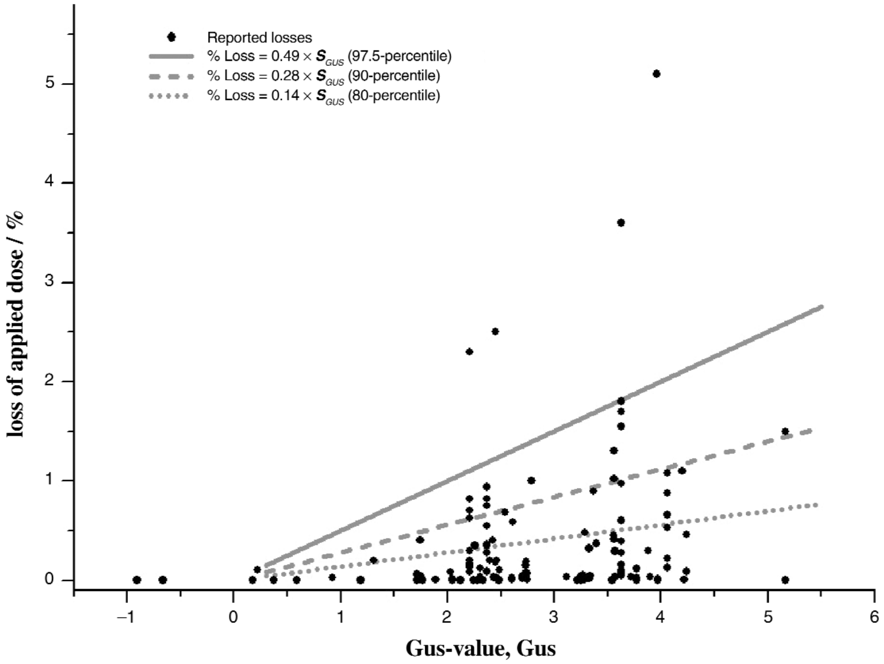


Fig. 6 Dependence of measured losses by macropore flow on GUS values.

The formula derived above is empirical and describes the available data. Only the conclusion that K_{OC} and DT_{50} combined in GUS values determine the influence of compound properties is justified. It is not more than a probabilistic interpretation of the entire set of data from the literature about transport through macropores. As such, it may be used to empirically predict macropore losses of unknown compounds. Its validity is limited to agricultural areas of moderate climate. However, it reflects a worst-case selection in that it may be assumed that hardly any macropore flow data has been published for years with no relevant rainfall events.

4. MODELING PREFERENTIAL FLOW PROCESSES

4.1 Simulating preferential flow

The convection dispersion equation that has been derived already in the 1950s by various workers currently is the most widely used approach to model solute transport in subsurface environments [65]. Based on Darcy's law, water flow is assumed to be describable as the product of a hydraulic gradient and soil hydraulic conductivity, which varies with the soil–water content. The hydraulic conductivity K is a soil property that describes how easy water can move through pore spaces or fractures. It depends on the intrinsic permeability of the material and on the degree of saturation. Saturated hydraulic conductivity describes water movement through saturated media. The hydraulic gradient is a vector at each point in the flow path. Sometimes, it is also called the Darcy slope, because it determines the quantity of a Darcy flux.

It is assumed that physical convection and molecular diffusion combine to displace a solute in porous media:

$$\frac{\partial A}{\partial t} = \frac{\partial}{\partial z}\left(D \; m \frac{\partial c}{\partial z} - qc \right) - \sum Ui$$

A	*total* solute content in the liquid and solite phase ($\mathbf{ML^{-3}}$)
c	mass concentration of solute in liquid phase ($\mathbf{ML^{-3}}$)
Θ_m	volume fraction of mobile water in soil matrix ($\mathbf{1}$)
q	water flow velocity ($\mathbf{LT^{-1}}$)
D	dispersion coefficient ($\mathbf{L^2\,T^{-1}}$)
U_i	source or sink term ($\mathbf{ML^{-3}\,T^{-1}}$)
z	soil depth ($\mathbf{L}$)
t	time ($\mathbf{T}$)

Note: The boldface sans serif symbols in parentheses after the explanations of the symbols, here and in subsequent explanations, are the dimensions of the quantities. **M** = mass, **L** = length, **T** = time, **1** = dimensionless.

The equation implies that the flow is perpendicular to the surface of a planar, infinite soil sample (z-direction), and that the properties over an x-y plane are averaged through use of the volume fraction of mobile water. The sink term U_i in this equation may represent different processes, such as uptake by the crop, degradation or lateral leaching losses to drains. The application of this equation to soils aimed initially to represent experimental results mathematically both in the field and in the laboratory [66]. Unfortunately, the early experiments showed that the convection dispersion equation did not perform well in structured soils containing cracks. It became clear that the substances moved through the soil in localized pathways rather than as a uniform front. These localized movements are not taken into account by the convection–dispersion equation, since this equation assumes that solute dispersion is a Fickian process driven by concentration gradients in the soil matrix only.

It is important to note that a general analytical solution to the convection–dispersion equation is not possible. Under certain conditions (constant D, $U = 0$), an approximate solution can be found. Otherwise, approximate numerical solutions must be carried out.

The situation was even more complicated when experimental studies showed that, depending on soil type and soil structure, different types of preferential flow have to be taken into account to develop a theoretical approach.

As the convection–dispersion equation does not adequately describe fast flow processes in soil, other methods have been developed to cover these transport phenomena at different levels of accuracy.

The **pathway-level approaches** describe transport processes at the scale at which preferential flow pathways occur [67–70], as these approaches describe the soil profile not only by integrating parameters (matrix potentials, moisture contents), but also by considering the microscopy of the soil structure (micrometer). The soil structure is represented by a large number of different microscopic cells each described by physically based parameters (e.g., hydraulic conductivity) only. Therefore, these descriptions are always multidimensional even if the final result may be a one-dimensional concentration. Though the solution of pathway-level descriptions is computationally intensive, the approach principally represents best the multiple effects of preferential flow pathways. However, the validation of these models is limited to conditions for which the pathway models were developed. For example, the model of Montas et al. [69,70] was able to simulate the transport of nonsorbing solutes through a homogeneous soil under saturated flow conditions. However, these conditions imply a degree of control over experimental parameters that can be obtained only under laboratory conditions and on relatively small soil cores.

The **multi-continuum approach** is currently the most popular alternative to the convection dispersion equation. The soil is divided into a number of regions of different porosity including macropores in which given transport equations apply. Models with a large number of regions have been developed [71–73], but a methodology for obtaining their numerous parameters is still pending. Additionally, most of these models are complicated and provide little insight into the critical processes governing the transport of chemicals through preferential flow paths.

Two-region models have been successful in describing laboratory-scale transport, but a number of parameters used in these models (e.g., "fraction of macropores") are difficult to obtain independently [74] and vary in a complex way with flow conditions. These models are based on the assumptions of the convection–dispersion equation, but the micropores and macropores operate as semi-independent interacting flow regions, each characterized by the degree of saturation (soil–water content), the conductivity, and the flux. However, in order to adequately describe transient unsaturated water flow, they require accurate description of two hydraulic functions

- the relationship between the water content Θ and the soil–water pressure head Ψ
- the hydraulic conductivity K dependence on the water content Θ

A problem is that for the macropore regions (soil moisture above Θ_b, the boundary water content, see Fig. 7) the water potential Ψ is difficult to measure. Additionally, the predicted hydraulic conductivity $K(\Theta)$ is extremely sensitive to small changes in soil moisture.

In the micropore region, the necessary function can be estimated with satisfactory quality using the equation of van Genuchten [75] or Brooks and Corey [76] [water release characteristic $\Psi(\Theta)$], and Mualem [77] [hydraulic conductivity $K(\Theta)$].

Presently, the computer program MACRO developed by Jarvis [78,79] is the most widely used dual-porosity/dual-permeability model. The model uses a simple linear function to estimate the water potential in the macropore region, when the soil moisture is between the boundary water content Θ_b and the saturated water content Θ_s. If the soil moisture is below Θ_b, only transport through the soil matrix (no macropore flow) is considered.

$$\Psi = \Psi_b \frac{\Theta_s - \Theta}{\Theta_s - \Theta_b} \tag{1}$$

Ψ	soil water pressure head ($\mathbf{L}$)
Ψ_b	boundary soil water pressure head ($\mathbf{L}$)
Θ	volume fraction of water ($\mathbf{L^3\ L^{-3}} = \mathbf{1}$)
Θ_s	volume fraction of water under saturated conditions ($\mathbf{L^3\ L^{-3}} = \mathbf{1}$)
Θ_b	volume fraction of water under boundary conditions ($\mathbf{L^3\ L^{-3}} = \mathbf{1}$)

The hydraulic conductivity $K(\Theta)$ is estimated in MACRO by using a power law function assuming simply gravity flow of water (Fig. 7).

$$K = K_b + \left(K_s - K_b\right)\left(\frac{\Theta - \Theta_b}{\Theta_s - \Theta_b}\right)^{n*} \tag{2}$$

K	hydraulic conductivity ($\mathbf{LT^{-1}}$)
K_b	boundary hydraulic conductivity ($\mathbf{LT^{-1}}$)
K_s	saturated hydraulic conductivity ($\mathbf{LT^{-1}}$)
n^*	pore size distribution index for macropores ($\mathbf{1}$)

In addition to the information required by computer models that consider a single flow domain only (chromatographic models), MACRO employs additional parameters that cannot be measured directly. Examples are the fraction of macropores (related to total soil porosity), the tortuosity factor for the macropores, and further, the ratio of pesticide degradation rates in micro- and macropores.

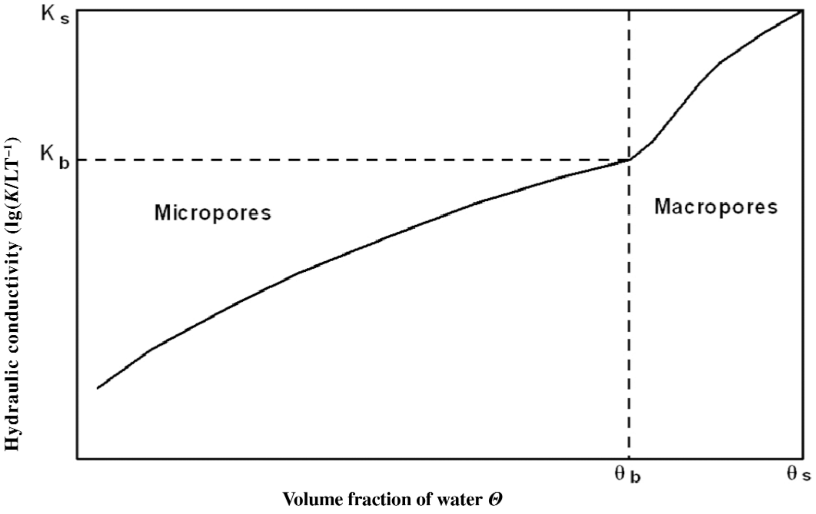


Fig. 7 Hydraulic conductivity function as a function of the soil–water content.

When simulations are performed, MACRO first calculates vertical water and solute fluxes in the micropore domain. In the next step, updated values of water storage are used to determine the excess amount of water routed to the macropores. Water fluxes originating from the macropores are then calculated, and finally the solute concentrations in both domains that solve the solute balance are derived.

MACRO has been tested in several field and lysimeter studies using a number of pesticides including dichlorprop and bentazon [81]; simazine, methabenzthiazuron, and metamitron [80]; alachlor [82], chlorsulfuron [83], and bentazon [84]. MACRO was also used to describe preferential flow processes under various European conditions including Sweden (e.g., [81,83]), Germany [85], the United Kingdom [82,86], and Spain [87,88].

The results of the validation studies clearly demonstrate that prediction of the transport of solutes using the MACRO model remains problematic. Without additional calibrations of the soil hydrology, the variations in the model performance can be rather high. Consequently, these validation studies are mostly based on initial calibrations, usually done stepwise. The common practice is to cut the experimental percolate information and use the first period of the experimental data for calibration and the second period for the validation exercise. In this sense, the model cannot be considered to be predictive, but at best explanatory.

Considering the difficulties in simulating preferential flow processes using deterministic modeling techniques, **Monte Carlo approaches** could be a suitable tool to describe the transport of solutes in soils under preferential flow conditions. The deterministic models previously mentioned work with deterministic variables and parameters averaged over a macroscopic domain. However, Monte Carlo techniques would be able to consider not only the averaged numbers, but also the distribution of the key parameters driving nonequilibrium transport processes. Studies calculating the transport of solutes considering the traditional convection–dispersion equation (chromatographic flow conditions) have been performed already [89,90]. However, a combination of Monte Carlo tools and deterministic nonequilibrium modeling by taking up the ideas of Grant, who had developed a simple stochastic model of infiltration simulating “macropore” soil water flow by 1991 [91], is still lacking. A combination of Monte Carlo tools with more sophisticated preferential flow models would, therefore, be highly desirable.

4.2 Performance of preferential flow models

As already mentioned, the currently used preferential flow models need parameters that cannot be measured independently. For example, the pore size distribution in the macropore region is expressed by an (empirical) index and has to be found by expert judgment or calibration. Similarly, for two-region models (e.g., MACRO), accounting for diffusive and convective exchange of solute between the flow regions by mass transfer must be calculated by parameters obtained also by pure calibration. However, these parameters can be extremely sensitive toward pesticide leaching, as they control whether water (and pesticide) flows from macropores to micropores or the other way round. Further sensitive parameters that have to be set by calibration are the fraction of pesticide that equilibrates with the water in the macropores and the fraction that equilibrates with the micropore liquid.

When all these parameters are considered, it becomes obvious that meaningful predictions of the fate of pesticides in structured soil are hardly possible without an initial calibration phase. However, to be able to test the performance of preferential flow models in an objective manner, calibration should follow a reasonable procedure. Unfortunately, it is often unclear in published literature which procedure has been used to parametrize preferential flow models. Vanclooster et al. [92] recommend a multistage validation in which the different components of the pesticide emission models (hydrology, heat transport, and pesticide transport) are validated separately in a sequential process. The idea is to consider calibration as a parameter estimation technique. During calibration, an object function is optimized in a way that the difference between model-calculated and observed pesticide concentration is minimized. In a second phase, the ability of the model to extrapolate or to predict is assessed. During this phase, no readjustment of the model parameters should be done, and the whole model with calibrated parameter values is tested against experimental data. First results using this approach show that the experimental datasets available are usually not sufficiently detailed to objectively perform such a sophisticated approach. This may be the reason why, in model validation studies that followed the protocol, the results were more dependent on the modeling expert performing the simulations than the model he was using [96,97].

To summarize current experiences with model validation projects, it can be concluded that reasonable predictions using macropore flow models can only be expected where long-term historical field data are available and where—before starting simulations to predict other time periods—this information has been used to calibrate the model in a well-conceived way, as suggested by Vanclooster et al. [92].

In addition to the information required by computer models that consider a single flow domain only (chromatographic models), MACRO employs additional parameters that cannot be measured directly. Examples are the fraction of macropores (related to total soil porosity), the tortuosity factor for the macropores, and further, the ratio of pesticide degradation rates in micro- and macropores.

When simulations are performed, MACRO first calculates vertical water and solute fluxes in the micropore domain. In the next step, updated values of water storage are used to determine the excess amount of water routed to the macropores. Water fluxes originating from the macropores are then calculated, and finally the solute concentrations in both domains which solve the solute balance are derived.

4.3 Preferential flow models in the pesticide registration procedure

From a scientific point of view, a simulation model should preferably need only independently measurable parameters, such as soil particle distribution, instead of using empirical parameters that always need site-specific (and sometimes even time-dependent) calibration. Unfortunately, apart from the pathway-level approaches, all preferential models do need extensive calibration, as they all need parameters that cannot be directly measured in experiments. The prediction of preferential flow is therefore practically impossible for sites that have not been intensively investigated before.

For registration purposes, however, this is not the most important criterion. The simulations usually performed under the scope of registration are based on a limited number of realistic worst-case scenarios. In the past 10 years, chromatographic leaching models have been implemented in the registration procedure (PELMO in Germany, PESTLA and PEARL in the Netherlands).

However, the European FOCUS group went one step further by suggesting also the computer model MACRO be used within the European pesticide registration procedure [95] to estimate the leaching of pesticides under preferential flow conditions. The FOCUS group (*FO*rum for the *C*o-ordination of pesticide fate models and their *US*e) was set up by the European Commission (DG-SANCO) with conscious knowledge that there was no agreed methodology for exposure modeling. FOCUS has published general guidance documents and reports on the use of mathematical models for predicted environmental concentrations (PECs) in groundwater, surface water, and soil.

Due to the problems in calibrating the soil hydrology under preferential flow conditions, FOCUS defined only a single scenario (Châteaudun, France) for MACRO. However, it is important to note that neither the nine chromatographic flow scenarios nor the one preferential flow scenario were really defined to estimate concentration in real groundwater. The objective of the FOCUS project was to estimate the overall 80th percentile of the substance concentration leaching below 1 m depth. The hydrologic condition at about 1 m depth is very important (e.g., existence of drainage systems and/or impermeable soil layers), especially for the preferential flow situation where pesticides can be transported into the soil to depths of 1 m extremely rapidly. It will determine whether pesticide concentrations simulated or measured at that soil depth have any relevance for deeper groundwater layers.

Table 10 shows sample results of MACRO simulations of the leaching behavior of seven pesticides using the above FOCUS scenario. The pesticides were selected to cover the full range of typical adsorption and desorption properties. The structures of the pesticides have not been released by the FOCUS group. The simulations were performed for 20 different years with annual applications of 1 kg/ha.

Table 10 Annual pesticide concentrations in the percolate (80th percentile in $\mu g\ L^{-1}$) and losses (80th percentile in % of applied dose) for the FOCUS scenario "Châteaudun" after spring and autumn applications. Results of simulations with FOCUS MACRO 2.2.1

Pesticide	GUS index S_{GUS}	Spring app.[a] (maize) conc./$\mu g\ L^{-1}$ predicited	Autumn app[b] (winter cereals) conc./$\mu g\ L^{-1}$ predicited	Spring app[a] (maize) loss/% predicted	Autumn[b] (winter cereals) loss/% predicted	Calc. loss/% based on GUS index (80th percentile) cf. Fig. 4
A	–0.41	0.000	0.000	0	0.000	0
B	1.72	0.0023	0.00568	0.0024	0.00106	0.24
C	2.37	0.0065	1.11	0.24	0.27	0.33
D	2.89	0.427	1.02	0.18	0.28	0.40
E	3.32	4.84	14.0	1.19	4.64	0.46
F	3.56	3.56	5.1	1.49	1.11	0.50
G	5.16	42.7	90.1	18.4	22.49	0.72

[a] Irrigated.
[b] Nonirrigated.

Depending on the season of application, MACRO simulates pesticide concentrations in the percolate up to 10 times above the respective simulations with chromatographic models [94]. However, if compounds are sorbed weakly to the soil, the differences in the predictions between both types of models become smaller, as movement through the soil matrix then is the dominating migration process of these substances.

Table 1 presents the 80th percentile of the annual concentrations, the standard output for simulations performed in the pesticide registration procedure required in the European Union. As the leaching of pesticides can be highly event-driven—especially if preferential flow is involved—annual concentrations have been selected as the basis for decision-making.

However, for a comparison of simulated results with experimental data, the losses are more suitable. In the following, two figures on the annual losses are presented for the same scenario (Châteaudun) as shown in Table 1.

4.4 Comparison of model-predicted losses with experimental data

For predictions by MACRO to be considered reliable, the results should lie within the range observed so far in real field experiments (i.e., in the range presented in Fig. 6). The reported results are of very different origin and have been generated under various, but realistic, conditions. For this reason, they can be assumed to reflect “reality”. On the other hand, MACRO-generated data, if applied with input data that are realistic, generate data for situations that are possible in reality, hence they should overlap to some extent with measured data. Even though such a comparison cannot be considered a validation in the strict sense, it can, however, be taken as a strong plausibility test.

For four out of seven investigated pesticides (A, C, D, F), the simulated losses are in agreement with the experimental data. The data points in Fig. 8 (spring) and Fig. 9 (autumn) are within the 97.5th percentile of the measured losses (straight line in Figs. 8 and 9), although losses predicted are significantly below the observed values for compounds with GUS indices S_{GUS} below 3. Two compounds, however, partially (compound E) or even completely (compound G) exceed this experimental threshold curve. These two compounds exhibit very low K_{OC} values. The results of the comparison thus suggest that MACRO underestimates the losses for compounds with low or medium GUS indices, i.e., with low inherent mobility properties (pesticide B). On the other hand, MACRO appears to overestimate the losses for compounds with very low K_{OC} values (pesticide G). Pesticide A is not shown in the figures due to its low GUS index of $S_{\mathrm{GUS}} = -0.41$.

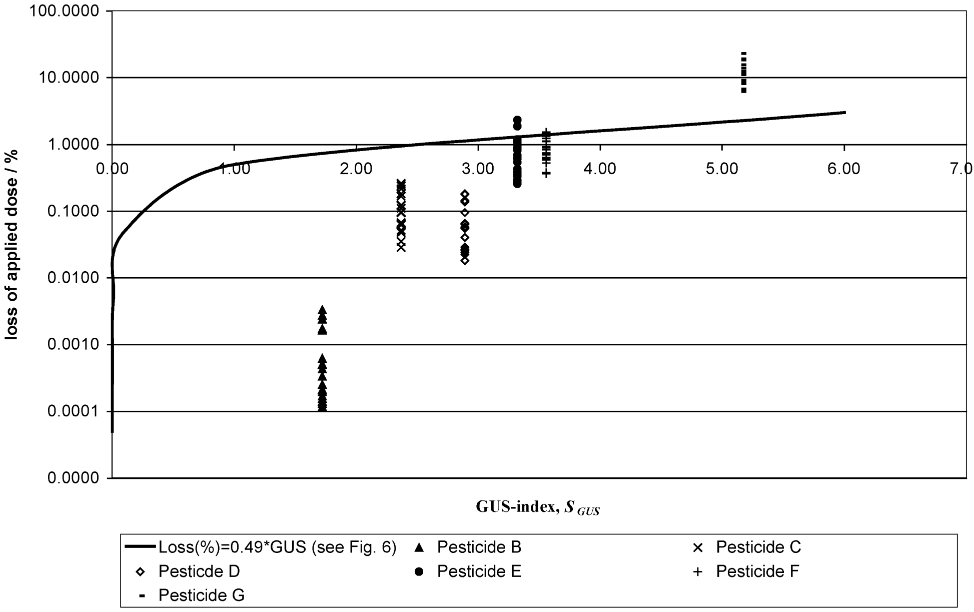


Fig. 8 Dependence of simulated losses on GUS indices S_{GUS} (FOCUS MACRO simulation), 20 annual applications (Châteaudun, maize, spring application).

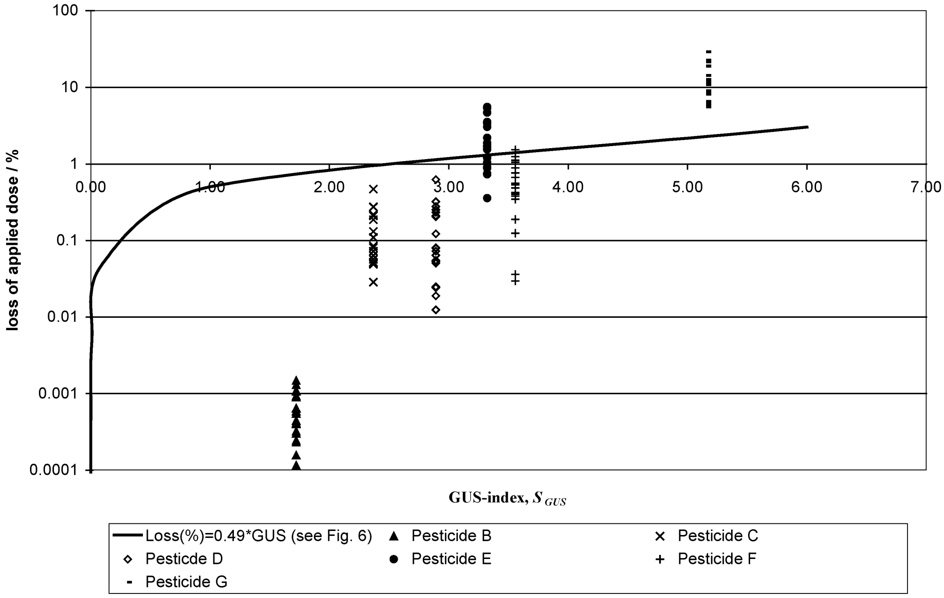


Fig. 9 Dependence of simulated losses on GUS indices S_{GUS} (FOCUS MACRO simulation), 20 annual applications (Châteaudun, winter cereals, autumn application) .

It is important to consider that the figures do not represent comparisons of experimental data and respective MACRO simulations. Instead, experimental data are compared with MACRO simulations using a constant (standard) scenario that has been suggested by the FOCUS group (Châteaudun scenario). Nevertheless, it is obvious that the Châteaudun simulations performed with MACRO showed significant underestimation of compounds with low or medium GUS indices and some overestimation of compounds with high GUS indices.

If we neglect the influence of the given scenario and concentrate on possible limitations of the model, two factors may contribute to the deviations. First, transport of solutes adsorbed to dispersed microparticles or dissolved organic matter is not taken into account by models. Although little is known about their extent, there are reports describing some importance of such factors, in particular for strongly adsorptive compounds (e.g., [59,96]). Transport in the adsorbed phase would, of course, explain the underestimation for compounds with low GUS indices. This is in line with observations by Kördel et al. [97], who could explain the transport of pendimethalin through macropores only by considering transport of this strongly sorbing substance via dissolved OC or suspended soil particles.

Secondly, the considerable overestimation of the losses for compounds with a low K_{OC} may be related to the fact that, contrary to what is assumed in model calculations, adsorption/desorption is not just a simple and reversible equilibrium. Rather, aging processes are important and the actual adsorption is higher than suggested by the batch equilibrium K_{OC}. As the conclusion is justified that such aging effects would be relevant for weakly adsorbing compounds, it is not surprising that the tendency to overestimate the losses increases with decreasing K_{OC}.

4.5 Limitations and challenges

The situation of modeling preferential flow can be summarized as follows:

- Preferential flow models usually need parameters that cannot be independently measured, but have to be found by expert judgment or calibration. Unfortunately, these parameters can be extremely sensitive toward pesticide leaching, as they control key flow processes.

- At present, meaningful predictions of the fate of pesticides in structured soil are hardly possible without an initial calibration phase. However, to be able to test the performance of preferential flow models in an objective manner, calibration should follow a "reasonable procedure".
- The present experiences with model validation projects demonstrate that reasonable predictions using macropore flow models can be expected only where long-term historical field data are available and where—before starting with simulations to predict other time periods—this information has been used to calibrate the model in a well-conceived way.
- It is not clear whether the development of improved estimation procedures for macropore flow parameters will ever lead to a more robust and accurate model suitable for management purposes. When more than 20 years of research on the different types of nonequilibrium flow processes is considered, it seems that the complex geometry of soils makes it impossible to model solute transport at a macroscopic level based on a deterministic description of microscopic processes.
- The development of stochastic modeling tools by combining the existing deterministic models with Monte Carlo modules may have promise for a future risk assessment of these substances. Even if the models are not superior in describing the local transport of chemicals, they will be suitable for estimating the regional behavior of agrochemicals from a management point of view.
- The present preferential flow scenario "Châteaudun" defined by FOCUS does not cover the simulation of pesticide concentration in real groundwater. Instead, the transport through the first meter of a structured soil considering macropore flow is considered. Further studies have to be performed in order to calibrate macropore models that are able to simulate the whole passage to the groundwater table.

5. SIGNIFICANCE OF SOLUTE TRANSPORT THROUGH MACROPORES

Measurements of the hydraulic conductivity of soils containing macropores together with the results of the investigations discussed in Section 2 and model calculations suggest that transport through macropores by far exceeds the transport through matrix flow. Transported fractions of neutral molecules can reach or even exceed 1 % of the material present and available on the soil surface. Fractions of persistent and nonadsorbing inorganic anions may be considerably higher than 1 %.

Are the measured losses typical for real situations? The evaluation of the practical significance of macropore transport, for example, for transport of pesticides into surface or groundwater, requires a careful assessment of the measurement techniques used to quantify the transport. All techniques applied so far are based on measurements under conditions of free-flowing, open-ended, macropores, which are comparable to lysimeters or artificially drained fields, and they are valid for all scenarios where these conditions prevail. Therefore, the macropore transport is of high importance for surface waters receiving the outflow of drainage systems. The values referenced in Section 4 can therefore be taken as the best available estimates for losses to **surface water** via subsurface drainage.

Are the measured losses typical for real situations? The evaluation of the practical significance of macropore transport, for example, for transport of pesticides into surface or groundwater, requires a careful assessment of the measurement techniques used to quantify the transport. All techniques applied so far are based on measurements under conditions of free-flowing, open-ended macropores, which are comparable to lysimeters or artificially drained fields, and they are valid for all scenarios where these conditions prevail. Therefore, the macropore transport is of high importance for surface waters receiving the outflow of drainage systems. The values referenced in Section 2 can therefore be taken as the best available estimates for losses to **surface water** via subsurface drainage.

The significance of the data for a transport of solutes to **groundwater** is much lower, however. In most cases, the macropore system is not open-ended, but overlies an unsaturated zone with prevailing matrix flow. These less permeable horizons strongly limit the mass transport in most cases. Once the macropore system is water-saturated, the preferential flow ceases.

The differing situations in open- and dead-ended macropores were simulated in an experiment specifically designed by Kördel et al. [97]. Large outdoor lysimeters of 1.2 m depth and a surface area of 1 m^2, which contained macropores, were partly equipped with suction plates at the bottom and were partly free-flowing. Macropores ending over suction plates roughly simulate dead-end macropores, since the flow of solutes through the fine porous material of the suction plates is restricted. This is clearly shown by the time-dependence of leachate formation. In winter, the leachate is more or less continuously collected by the suction plates, whereas leachate from free drainage is only collected after heavy rainfalls. In these situations, the amount of leachate obtained by free drainage by far exceeds the leachate collected by means of suction plates. Higher substance concentrations in the leachate and higher amounts of leachate by autumn application reveal an attenuation factor of 150–200. Differences in spring application were due to higher concentrations by comparable amounts of leachate (Table 11) (only scarce events of heavy rainfalls resulted in preferential flow).

Table 11 Pesticide losses by suction plates and free drainage (lysimeter experiment).

Substance	Application	Open-ended macropores/%	Dead-ended macropores/%	Attenuation factor
Isoproturon	Autumn 1998	3.0	0.016	188
Isoproturon	Autumn 1999	2.7	0.014	193
Isoproturon	Autumn 2000	0.3	0.002	150
Metolachlor	Spring 1999	0.7	0.023	30
Metolachlor	Spring 2000	0.5	0.009	56
Terbuthylazine	Spring 2001	0.6	0.030	20
Terbuthylazine	Spring 2002	0.4	0.017	24

The losses in the luvisol (loamy silt) by free drainage were much lower ranging from 0.17 to 0.1 %. This soil type did not contain large macropores, but showed a combination of a short-distance macropore flow up to a depth of 20–30 cm followed by matrix flow and subsequent combined macropore and matrix flow in deeper soil layers. This was demonstrated by staining the flow regime at the termination of the study.

The studies elucidate the importance of well-developed and open-ended macropores. If free drainage is hindered, transport is reduced by a factor of up to 100 and more. Therefore, it is justified to conclude that the extent of losses via macropore flow, as derived in Section 4, is significant for groundwater only under conditions where open-ended macropores occur, i.e., where macroporous soil horizons overlie very shallow groundwater or highly permeable subsoil systems, such as coarse sediments, karstic or joint rocks with a direct link to an aquifer.

In real situations, slow matrix flow in deeper soil usually limits the preceding macropore transport of solutes. The macropore flow stops or strongly slows down once the macropore system is saturated so that degradation and immobilization by adsorption and migration into micropores of nonconservative and nonadsorptive compounds continue. The macropore system is even assumed to enhance either process as long as the solute still resides in microbiogically active soil layers. As the macropore system also transports dissolved or dispersed humic matter to deeper soil layers and provides good aeration, a high biological activity can be assumed in the surroundings of macropores. In particular, the walls of biopores are colonized with microorganisms and are well supplied with oxygen and nutrients. For example, Mallawantantri et al. [45] observed an increased adsorption and mineralization of 2.4-D, carbofuran, and metribuzin in surface linings of macropores. They furthermore report increased mineralization for 2,4-D and carbofuran. Accordingly, there is evidence that the degradation capacity is increased in soil areas where transfer from macropores into the soil matrix takes place.

(*Text continues on p. 153*)

Table 12 Published results from preferential flow studies with conditions realistic for moderate climates.

Ref.	Compound	K_{OC}/ $\mathrm{cm^3 g^{-1}}$	$\mathrm{DT_{50}}$/d	*Sol*/ mg $\mathrm{L^{-1}}$	Study description	Experimental conditions	Substudy	Rate kg $\mathrm{ha^{-1}}$	Duration/ d	Rain/ mm	Percol./ mm	1^{st} event/d	C_{max}/ µg $\mathrm{L^{-1}}$	C_{average}/ µg $\mathrm{L^{-1}}$	Loss/%	Remarks
50	Atrazine Metolachlor	(100) (200)	36 20	33 530	Field drainage Depth 1 m Spacing 10–30 m USA (Louisiana)	Clay loam, OC not reported Area 16 ha, maize, normal tillage Appl.: 1987-04-23	Atrazine	1.63	243	1091	133	11	0.99	0.47	***0.038***	No influence of spacing of drainage system
							Metolachlor	2.16	243	1091	133		<0.4	2.1	***0.13***	
98	Fluroxypyr	(66)	(31)	91	Field drainages Depth 2 m Spacing 15 m Sweden (Lanna)	40 % clay, 2.6 % OC Area 0.4 ha; Barley, normal tillage Appl: 1988-05-25		0.19 0.34	98	222	21 17	40	<1 2	<1 <1	**<0.01** **0.01**	Fluroxypyr-meptyl applied
98	Fluroxypyr	(66)	(31)	91	Monoliths Laboratory study Depth 1 m Sweden (Kjettslinge/Uppsala)	Spring barley, normal tillage 20 % clay, 2.6 % OC Watered prior to application; applied 1988-06-2 a) natural precipitation; b) water up to average, first watering 1988-07-04	a)	0.19 0.38	90	136	1 3	32	5 <1	5 <1	**0.04** **<0.01**	Fluroxypyr-meptyl applied
							b)	0.19 0.38	90	216	3 4		<1 <1	<1 <1	**<0.01** **<0.01**	
49	Atrazine Cyanazine Alachlor Carbofuran Chlorpyrifos	91 97 157 41 28 286	(60) (14) (15) (50) (30)	33 170 240 351 0.4	Field drainages Depth 75 cm Spacing 5, 10, 20 m USA (Indiana)	12 % clay, 66 % silt, 0.75 % OC Area 6 ha, continuous maize 1984–1988, normal tillage	5 m 10 m	Atrazine 1.1	360	1189	296	n.r.	10	0.20 0.20	***0.055*** **0.05**	Products used 1984–88, observable period only 1985 due to lacking drainflow in other years
						Appl.: 1985-04-22		Cyanazine 2.3		Total rain Apr. 85– Apr. 86			10	0.16 0.12	***0.02*** **0.015**	
								Alachlor 2.3					2	0.09 0	***0.01*** **0**	Results are average from 2 blocks
								Carbofuran 1.5					150	3.35 2.66	***0.66*** **0.53**	20 m spacing yielded less drainflow and losses of pesticides
								Chlorpyrifos 1.5					0 0	0 0	***0*** **0**	**For comparison of compounds, only 5 m replicates were used**
99	Clopyralid	(6)	(40)	7.85	Field drainages Depth 2 m Spacing 15 m Sweden (Lanna)	40 % clay, 2 % OC area 0.4 ha; barley, normal tillage Appl.: 1988-05-25		0.12 0.24	90	222	22 20	39	0.5 6.0	0.0022 0.096	**0.0004** **0.008**	First heavy rain after dry June No occurrence in drainage with later rainfall events

(*continues on next page*)

Table 12 (*Continued*).

Ref.	Compound	K_{OC}/ cm³g^{-1}	DT$_{50}$/d	*Sol*/ mg L^{-1}	Study description	Experimental conditions	Substudy	Rate kg ha^{-1}	Duration/ d	Rain/ mm	Percol./ mm	1st event/d	C_{max}/ µg L^{-1}	$C_{average}$/ µg L^{-1}	Loss/%	Remarks
100	Atrazine Alachlor	(100) (170)	65 35	3 240	Field drainage Depth 0.95 m Spacing 12 m Canada (Ontario)	Clay loam, OC not reported 3 × 2 plots 1000 m^2 each; maize diff. tilling systems Appl.: 1984-05-11 1985-04-29 1986-05-13	1984 1985 1986	1.8 Atrazine	1 year	828 1052 909	62 199 244	n.r.	n.r.	8.5 3.5 12	***0.28*** ***0.39*** ***1.7***	No effects of tillage systems on surface/subsurface runoff
							1984 1985 1986	2.5 Alachlor		828 1052 909	62 199 244			6 0.6 0.7	***0.15*** ***0.05*** ***0.07***	
101	Mecoprop Simazine 2,4-D	(20) (130) (20)	6.3 63 4.3	500 000 6 20 000	Drainage Depth 1 m Spacing 20 m UK (Rosemaund)	Silty clay, 2–3 % OC, various drained fields of 1-10 ha in one catchment (150 ha); normal tillage	1987	Mecoprop 1	30	n.r.	n.r.	2	11.7	–	**0.08**	% was recalculated to get the total % over all drain events, following the annual applications.
						Application: Mecoprop, 1987-11-17 Simazine, 1988-12-08/1989-02-17 2,4-D 1987-11-26	1988	Simazine 0.6	14/84			7	68		**0.37**	Rates are averages over the treated fields.
							1987 1988	2,4-D 0.6 0.6	20 81			19 n.r.	5.1 <0.01		**0.06** **0**	
53	Dichlorprop Bentazon	32 Hassla 19 Lanna (34)	5 Hassla (5) Lanna 13	350 570	Field lysimeters Depth 108 cm Sweden (Lanna and Hassla)	Lanna clay, 2.2 % OC Hassla silty clay loam, 2.8 % OC Spring barley, normal tillage Appl.: DCP, 1989-06-09 Bentazon, 1990-06-08	Hassla a) b)	1.6 (DCP)	255 255	518 603	50 100	<14 <14	4.5 26.6	1.3 6.4	**0.04** **0.4**	Irrigation to compensate for : a) Uppsala average (554 mm/y) b) Uppsala 75-y worst case (715 mm/y)
							Lanna a) b)		255 255	518 603	120 160	<14 <14	4.8 8.0	2.7 0.20	**0.2** **0.02**	Chloride: 50 % leached
							Lanna a) b)	0.6 (Bentazon)	307 307	583 619	280 290	10 10	0.2 2.0	0.02 0.15	**0.01** **0.07**	No leaching in a sandy soil
102	Isoproturon Mecoprop	(130) (20)	55 4.5	65 500 000	Field mole drainages: Depth 55 cm Spacing 2 m UK (Oxfordshire)	60 % clay, OC not reported 4 plots 0.2 ha each, cereals, no tillage (light harrow) Appl.: 1989-11-15 Isoproturon; 1990-10-08 Isoproturon	IPU 89/90	2.5	105	320	n.r.	30	41		**0.48**	Only mole experiments 1989/90 and 1990/91 could be evaluated.
							IPU 90/91	2.4 2.4	100	115		n.r.	30		**<0.01**	
							MP 90/91		100	115		n.r.	<0.2		**<0.01**	
103	Isoproturon	(130)	30	65	Field mole drainages, Depth 50 cm Spacing 3 m Suction cups (0.5 m) UK (Oxfordshire)	Heavy clay soil, 2.6 % OC (0–5 cm), 0.48 % OC at 40 cm Area 1250 m^2 Cereals, normal tillage Appl.: 1993-02-10	Drainage	2.4	50–52	23	6.9	50	550	355	**1.0** **.**	Wet soil when treated with isoproturon
							Suction cup at 50 cm		56	n.r.	n.r.		240			Concentrations in suction cups decreased after 56 days.
104	Atrazine	(100)	(60)	33	Field drainage Depth 1.22 m Spacing 36.6 m Suction cups (1.5 m) USA (Iowa)	Loamy soil, OC not reported area 0.74 ha, suction cups at 1.5 m No tillage Appl.: 1990-05-02	Drainage	1.68	110 d	660	ca. 300	7	2.9	1.95	**0.45**	Concentrations in groundwater: 3 m: 0.1 µg L^{-1} (May 18) <0.1 µg L^{-1} (June 12)
							Suction cup at 1.5 m						4.7	2.2		

(*continues on next page*)

Table 12 (*Continued*).

Ref.	Compound	K_{OC}/ cm^{3}g^{-1}	DT$_{50}$/d	*Sol*/ mg L^{-1}	Study description	Experimental conditions	Substudy	Rate kg ha^{-1}	Duration/ d	Rain/ mm	Percol./ mm	1st event/d	C_{max}/ µg L^{-1}	$C_{average}$/ µg L^{-1}	Loss/%	Remarks
54	Isoproturon Mecoprop Fonofos Trifluralin	25 (10) 672 6200	(18) (21) (55) (60)	65 500 000 13 0.3	Field mole drainages Depth 55 cm Spacing 1.8 m UK (Northumberl.)	34 % clay, 3.2 % oc Plots A,B,C 0.25 ha each Wheat, normal tillage	Isoproturon									1989/90 was dry year (507 mm) with soil moisture deficit in fall, low winter drainage: 81 mm; 1990/91 was average (684 mm), winter drainage 288 mm; (30-year average 718 mm rain, 275 mm winter drainage);
							1989 autumn	2	30–120	275	75	n.r.	7.0	0.35	***0.013***	
							1990 autumn	2.5	0–120	457	277		4.4	0.52	***0.058***	
						Appl.: Isoproturon and mecoprop: 1989-11-27 and 1990-11 to plot A 1989-11-27 and 1990-11 to plot B 1989-04 and 1990-04 to plot C;	1990 spring	2	0–60	27	3.5		120.7	21	***0.037***	
							1991 spring	2.5	0–60	33	0		0	0	(0)	
							Mecoprop									
							1989 autumn	2.4	30–120	275	75		6.4	0.03	***0.001***	
							1990 autumn	2.4	0–120	457	277		16.4	0.05	***0.006***	Both springs were dry.
						Fonofos: 1990-02 and 1991-02 to plot A	1990 spring	2.4	0–60	27	3.5		60.0	10.3	***0.015***	Bromide ion: 11.5 %
							1991 spring	2.4	0–60	33	0		0	0	(0)	
						Trifluralin: 1989-11-27 and 1990-11 to plot B	Fonofos									% losses in parentheses were not used as these zero values were due to the nonoccurrence of percolation.
							1990 spring	1.4	0–60	88	63		0.2	0.011	**0.0005**	
							1991 spring	1.4	0–60	182	164		3.0	0.10	**0.012**	
						Bromide ion 1990-11-04	Trifluralin									
							1989 autumn	0.96	30–120	275	75		0.15	0.008	***0.0006***	
							1990 autumn	0.96	0–120	457	277		0.12	0.010	***0.0028***	
51	Atrazine Metolachlor	(100) (200)	(60) (20)	33 530	Field drainage Depth 0.95 m Spacing 12 m Canada (Ontario)	Clay loam, OC not reported 3 × 2 plots 1000 m^2 each; maize diff. tilling systems Appl.: 1987-05-12 1988-05-12 1989-05-15 1990-06-01	1987	1.7 Atrazine	1 year	848	200	40	~100	5	***0.6***	Rainfall far above average in May–July 1989
							1988			571	100	130	~100	1.7	***0.1***	
							1989			763	140	14	~100	44	***3.6***	
							1990			1116	230	70	~100	13	***1.8***	No influence of tillage systems observed
							1987	2.5 Metolachlor (2.1 in 1990)		848	200	40	~100	2.5	***0.2***	
							1988			571	100	130	~100	2.0	***0.08***	
							1989			763	140	14	~100	41	***2.3***	
							1990			1116	230	70	~100	6.4	***0.7***	

(*continues on next page*)

Table 12 (*Continued*).

Ref.	Compound	K_{OC}/ cm^{3}g^{-1}	DT$_{50}$/d	*Sol*/ mg L^{-1}	Study description	Experimental conditions	Substudy	Rate kg ha^{-1}	Duration/ d	Rain/ mm	Percol./ mm	1^{st} event/d	C_{max}/ µg L^{-1}	$C_{average}$/ µg L^{-1}	Loss/%	Remarks
105	Bentazon	(130)	(20)	570	Field drainages	Site A: 18 % clay, 1 % OC										
	Chloridazon	(33)	(10)	0.34	Depth 0.7–1 m	Site B: 20 % clay, 1.2 % OC										
	Chlorotoluron	(190)	(30)	7.4	Spacing 10 m.	Normal tillage										
	Dichlorprop	(26)	(8)	0.59	Germany (Westfalia)	Site A (5 ha): sugar beets/3 ha										
	Isoproturon	(130)	(18)	65		1992-04-02										
	MCPA	(20)	(25)	800 000		1992-05-13										
								1.3	200	500	0.4	14	0.15	0.001	**<0.001**	
	Metamitron	(40)	(30)	1700		1992-05-28										
								1.5								
	Metolachlor	(200)	(20)	530												
								2	170	440	0.4	10	0.02	0.001	**<0.001**	
	Pendimethalin	(5000)	(90)	0.275												
						Site A (5 ha): maize/2 ha										
	Terbuthylazine	(220)	(45)	9												
						1992-05-03 Pendimethalin										
								1.6	180	470	0.4	10	<0.01	<0.001	**<0.001**	
						Site A (5 ha): winter wheat										
						1992-11-09 Pendimethalin										
						Isoproturon										
								0.8	140	370	77	6	0.7	0.003	***<0.001***	
						1993-04-21 Bentazon										
								1.0	140	370	77	6	62	4.1	***0.35***	
						Dichlorprop-P										
								1.0	190	550	1.4	13	0.45	<0.01	***<0.001***	
						1993-05-12 MCPA										
								0.7	190	550	1.4	13	<0.05	<0.001	***<0.001***	
								0.75	170	515	1.4	8	<0.05	<0.01	**<0.001**	
						Site A (5 ha): No crop										
						29.10.93 Isoproturon										
						Chlorotoluron										
								1.5	180	480	120	16	280	7.0	***0.55***	
								2.45	180	480	120	16	370	14.2	***0.68***	
						Site A (5 ha): maize										
						1994-05-10										
						1994-06-07 Terbuthylazine										
								0.74								
						Metolachlor										
								1.0	0–300	800	62	2	66	5.5	***0.19***	
								2.0	0–300	800	62	3	54	5.6	***0.17***	
						Site B(1.1 ha): winter barley										
						1992-11-25:										
						Isoproturon										
								0.8	160	290	54	1	0.7	0.01	***<0.001***	
								1.0	160	290	54	1	26.0	1.5	***0.08***	
112	Triasulfuron	9.3	(19)	815	Field studies with soil	5 % clay, 2.1 % OC	Triasulfuron.	0.05	4	90	n.r.	1	32	16	***0.9***	% of applied leached below
	Atrazine	128	(60)	33	core sampling	3 reps, 2 m^2 each; tillage to 20	Atrazine	1.5		90			21	1	***0.2***	80 cm; lower leaching if appl.
	Terbuthylazine	357	(45)	9	Depth 1 m	cm	Terbuthyl-	1.5		90			1.5	0.15	***0.3***	was to dry soil.
					Switzerland (Zürich)		azine									
						Appl.: Sept 1991										No leaching below 40 cm at a
						1,2,3 d after appl. irrigation with										site with sandy soil.
						30 mm water within 8 h, after 4										
						d soil was excavated to 1 m										
						depth.										
107	Isoproturon	81	12	65	Drainages	57 % clay, 3.1 % OC		0.9	0–19	10	0.6	5	290		(0.17)	
					Depth 50 cm	area 600 m^2			19–27	8.8	1.34		130		(0.17)	
					Spacing 3 m	Cereals, normal tillage			27–75	16.5	2.42		8		(0.013)	Only total losses used for
					UK (Oxfordshire)	0.9 kg ha^{-1} on 1994-03-12			0–75	35.3	4.4		290	72	**0.35**	comparison (0–75 days)

(*continues on next page*)

Table 12 (*Continued*).

Ref.	Compound	K_{OC}/ $\mathrm{cm^3 g^{-1}}$	$\mathrm{DT_{50}}$/d	*Sol*/ mg $\mathrm{L^{-1}}$	Study description	Experimental conditions	Substudy	Rate kg $\mathrm{ha^{-1}}$	Duration/ d	Rain/ mm	Percol./ mm	1^{st} event/d	C_{max}/ µg $\mathrm{L^{-1}}$	C_{average}/ µg $\mathrm{L^{-1}}$	Loss/%	Remarks
108	Isoproturon	86 (A) 140 (B)	63 (A) 127 (B)	65	Field mole drainages: Depth 55 cm Spacing 2 m UK (Oxfordshire)	68 % clay, 5.0 % OC area 2 × 0.24 ha, plot A crop residues chopped, plot B burnt before incorporation; Cereals, normal tillage; Appl.: 1991-10-09, 1992-04-05	Plot A	2.475	135	150	2.5	25	30	9.8	**0.038**	
							Plot B	(autumn)	135				120	35	**0.035**	
											1.4					
							Plot A	1.625	72	ca. 100	0.9		105		n.r.	Lower losses (not reported) in spring than in autumn
							Plot B	(spring)	72				55		n.r.	
109	Atrazine MCPA Isoproturon Dimethoate Aldicarb Carbofuran	(100) (20) (130) (20) (30) (22)	46 5 24 16 21 38	33 800 000 65 39 800 6000 351	Drainage Depth 1 m Spacing 20 m UK (Rosemaund)	Silty clay, 2–3 % OC, various drained fields of 1–10 ha in one catchment (150 ha); normal tillage	Atrazine 91	2.8	183	122	n.r.	27	81.4	–	**0.32**	
							Atrazine 92	1.0	36	23		83	3		**0.02**	
							MCPA	1.68	52	19		4	46.8		**0.01**	
						Application (to var. crops): Atrazine 1991-11, 1992-05 MCPA 1991-02 Isoproturon 1991-10/12, 1992-03 Dimethoate 1990-11 Aldicarb 1992-02, 1992-06 Carbofuran 1991-12	IPU 90	1.3	130	69		27	17.2		**0.009**	
							IPU 91	0.54	153	86		13	6.1		**0.024**	
							Dimethoate	0.3	96	49		27	1.2		**0.001**	
							Aldicarb	1.0	91	54		2	3.15		**0.043**	
							Carbofuran	3.0	177	133		15	264		**1.1**	
59	Trifluralin Deltamethrin Chlorpyrifos Fenpropimorph	(8000) (50 000) (6000) (2000)	200 (20) 66 (54)	0.3 <0.0002 0.4 4.3	Drainage Depth 1 m Spacing 20 m UK (Rosemaund)	Silty clay, 2–3 % OC, various drained fields of 1–10 ha in one catchment (150 ha); normal tillage	Trifluralin	1.1	154	n.r.	n.r.	5	14.1	–	**0.1**	Trifluralin and deltamethrin are particle-adsorbed.
							Deltamethrin	0.005	115			1	1.9		**0.003**	
						Application to winter wheat: Trifluralin 1992-11-06 Deltamethrin 1992-12-15 Chlorpyrifos 1993-03-19 Fenpropimorph 1993-03-19	Chlopyrifos	0.72	21			19	*4.3*		n.r.	Chlorpyrifos and fenpropimorph used for compound comparison
							Fenpropim	0.75	21			19	*1.6*		n.r.	
55	Isoproturon Pendimethalin Carbetamide Dimefuron Bromide ion	(130) (5000) (90) (205)	(18) (90) (18) (60)	65 0.275 3500 16 000	Field drainages Depth 1 m Spacing 13 m Germany (Schleswig-Holstein)	10–20 % clay, OC not reported area 0.5 ha, normal tillage Application 1993-12-15: isoproturon, pendimethalin	1993									Horizontal flow between A/B-horizon toward the trench zone of the drains.
							Isoproturon	0.67	2	n.r.	n.r.	1	*300*		n.r.	
							Pendi-methalin	0.54	2				*12*			
						Application 1994-11-07: Bromide ion carbetamide, dimefuron	1994	1.75	7				*900*			Concentration of bromide ion 32 000 µg $\mathrm{L^{-1}}$ in 1993, 19 000 µg $\mathrm{L^{-1}}$ in 1994.
							Isoproturon	0.88	7			7	*400*			
							Pendi-methalin									

(*continues on next page*)

Table 12 (*Continued*).

Ref.	Compound	K_{OC}/ $cm^3 g^{-1}$	DT_{50}/d	*Sol*/ mg L^{-1}	Study description	Experimental conditions	Substudy	Rate kg ha^{-1}	Duration/ d	Rain/ mm	Percol./ mm	1^{st} event/d	C_{max}/ µg L^{-1}	$C_{average}$/ µg L^{-1}	Loss/%	Remarks
52	Atrazine Cyanazine Alachlor Carbofuran	91 97 157 41	(60) (14) (15) (50)	33 170 240 351	Field drainages Depth 75 cm Spacing 5, 10, 20 m USA (Indiana)	Silt loam (12 % clay, 0.75 % OC) Area ca. 4 ha Continuous maize 1984–1991, normal tillage atrazine 1984–1991 cyanazine 1984–1991 alachlor 1984–1991 carbofuran 1985–1991	5 m/1989 10 m/1989	Atrazine 1.1 Cyanazine 2.3 Alachlor 2.3 Carbofur. 1.5	35	184	18.4	4	n.r.	9.3 3.6 15.0 3.85 traces traces 17.9 11.0	***0.155*** **0.06** ***0.12*** **0.03** ***0.01*** **0.01** ***0.22*** **0.135**	Results are average from 2 blocks 20 m spacing yielded less drainflow and losses of pesticides. **For comparison of compounds, only 5 m replicates were used**
						Appl.: 1989-05-17 1990-05-28 1991-04-30	5 m/1990 10 m/1990	Atrazine 1.1 Cyanazine 2.3 Alachlor 2.3 Carbofur. 1.5	30	114	8.1	9	n.r.	8.8 12.2 5.7 2.8 traces traces 163 200	***0.065*** **0.09** ***0.02*** **0.01** ***0.01*** **0.01** ***0.88*** **1.08**	
							5 m/1990 10 m/1990	Atrazine 1.1 Cyanazine 2.3 Alachlor 2.3 Carbofurane 1.5	29	133	17.7	14	n.r.	3.1 4.0 1.9 3.9 traces traces 10.2 10.6	***0.05*** **0.065** ***0.015*** **0.03** ***0.01*** **0.01** ***0.12*** **0.125**	
56	Isoproturon Linuron Dimethoate MCPA	(130) (400) (20) (20)	(18) (60) (7) (25)	65 81 39 800 800 000	Field lysimeters 1.05 m depth UK	1) 30 % clay, 4 % OC, permanent grassland 3) 10 %, clay, 1.0 % OC, fallow, previously wheat 4) 19 % clay, 1.0 % OC fallow, previously fodder maize	Isoproturon 1) 94/95 95/96 3) 94/95 95/96 4) 94/95 95/96	2.5	1 year	573 555	206 128 214 202 249 161	n.r.	30 80 10 5 30 85	9.1 16.0 3.2 1.1 9.4 5.6	***0.75*** ***0.82*** ***0.28*** ***0.09*** ***0.94*** ***0.36***	Bromide ion: 29 % and 19 % leached in 94/95 and 95/96, respectively.
						Cultivated to 15 cm with a fork, winter wheat planted Treatment 1994-11-18: Isoproturon, Linuron, Bromide ion Treatment 1995-04-20: Dimethoate, MCPA	Linuron 1) 94/95 95/96 3) 94/95 95/96 4) 94/95 95/96	0.74			206 128 214 202 249 161		1.8 <0.2 0.4 <0.2 2.6 <0.2	0.04 <0.2 <0.04 <0.2 0.30 <0.2	***0.01*** ***0*** ***0.005*** ***0*** ***0.1*** ***0***	
						July 27 harvest, then left fallow	Dimethoate	0.68	1 year	as above	as above			<0.2	***0***	Dimethoate and MCPA: no detections in any year and soil
						b) Treatment 1995-10-25: Isoproturon, Linuron, Bromide ion Treatment 1996-03-26: Dimethoate, MCPA	MCPA	1.75	1 year					<0.2	***0***	

(*continues on next page*)

Table 12 (*Continued*).

Ref.	Compound	K_{OC}/ cm^3g^{-1}	DT_{50}/d	*Sol*/ mg L^{-1}	Study description	Experimental conditions	Substudy	Rate kg ha^{-1}	Duration/ d	Rain/ mm	Percol./ mm	1st event/d	C_{max}/ µg L^{-1}	$C_{average}$/ µg L^{-1}	Loss/%	Remarks
110	Metolachlor Atrazine	(200) (100)	(20) (200)	530 33	Field drainages Depth 1–1.5 m USA (Illinois)	Silty clay loam, OC not reported Area 15 ha, normal tillage Appl.: 1997-04-15	Metolachlor Atrazine	2.8 2.1	56	n.r.	n.r.	50	29 28		***0.30*** ***0.45***	
111	Metolachlor	204	35 (1996) 27 (1998)	530	Field drainage Depth 90 cm Spacing 8 m France (Lorraine)	54 % clay, 1.9 % OC Area 1.85 ha, maize, normal tillage Appl.: 1996-05-07 and 1998-05-14	1996	3.05	0–300	655	154	n.r.	131	11.5	**0.59**	Bulk losses in interval 0-25 days
							1998	3.9	0–47	130	7.4		395	213	**0.40**	
112	Prochloraz	1300	(30)	34	Drainage Depth 1.1 m Spacing 10 m Denmark (Jutland)	16 % clay, 1.6 % OC Plot size 25 m^2 Wheat, normal tillage Appl.: 1997-04-07.		0.42	12	105	30	2	24	2.8	**0.2**	Irrigated 4 times at approx. 12 mm/h for 3 h each, (1 prior to appl.)
113	Isoproturon	(130)	15.5 Oct. 19.5 Mar.	65	Drainage Depth 1 m Suction cups (1–5 m) Germany (Westfalia)	19.7 % clay, 1.3 % OC, area 1 ha; normal tillage Appl.: 1997-10-17 Late 1990–03	Autumn Spring	1.5 1.5	150 ca. 90	n.r. n.r.	n.r. n.r.	20 10	0.1 11	– –	**0.002** **0.03**	Lower conc. in suction cups (only sporadically detected), no detections in groundwater at 10 m.
120	Clopyralid	(6)	(40)	7.85	Field drainage and suction cups Spacing 15 m Depths: drains 2 m cups 0.3–1.8 m CDN (Saskatchewan)	Loam soil, 17 % clay, 1.4 % OC barley 1985–1991, normal tillage, Irrigation days 3–21, total 300 mm, Appl.: 1991-09-04	Cups 1.8 m Tile/2 m	0.2	35	300 irrig +14.4 mm rain	83.8	3	<0.05 4.7	<<0.5 3.6	ca. 0.1 **1.5**	
114	Isoproturon Pendimethalin Triasulfuron	112 3380 16.5	(18) (90) (19)	65 0.275 815	Field mole drainages (core plots): Depth 55 cm Spacing 2 m UK (Oxfordshire)	60 % clay, 2.6 % OC 8 plots 0.2 ha each, cereals, normal tillage Appl.: 1993-11-02 Isoproturon; Pendimethalin	1993/94 Isoproturon Pendimethalin	 2.5 2.0	60	n.r.	79	11	n.r.	79 0.68	***2.5*** ***0.027***	
						1994-11-17 Isoproturon Triasulfuron	1994/95 Isoproturon Triasulfuron	 2.5 0.008	66	n.r.	44	17	n.r.	10.2 0.87	***0.18*** ***5.1***	
114	Isoproturon Pendimethalin Triasulfuron Prochloraz Propiconazole	112 3380 16.5 2880 738	(18) (90) (19) (30) (110)	65 0.275 815 34 110	Field mole drainages (pilot plots): Depth 55 cm Spacing 2 m UK (Oxfordshire)	60 % clay, 2.6 % OC 8 plots 0.2 ha each, cereals, normal tillage Appl.: 1993-11-02 Isoproturon, Triasul-furon, Pendimethalin, Prochloraz	1993/94 Isoproturon Triasulfuron Pendimethalin Prochloraz	 2.5 0.008 2.0 0.405	60	n.r.	54	11	n.r.	148 0.67 0.74 0.38	*3.2* *4.8* *0.02* *0.05*	Only "control plots" considered for comparison. Absolute losses are not reliable, therefore considered only for comparison of compounds.
						1994-11-17 Isoproturon, Tria-sulfuron, Propiconazole	1994/95 Isoproturon Triasulfuron Propiconazole	 2.5 0.008 0.25	66	n.r.	39	17	n.r.	<0.3 0.64 0.077	*<0.005* *3.3* *0.012*	

(*continues on next page*)

Table 12 (*Continued*).

Ref.	Compound	K_{OC}/ cm^3g^{-1}	DT_{50}/d	*Sol*/ mg L^{-1}	Study description	Experimental conditions	Substudy	Rate kg ha^{-1}	Duration/ d	Rain/ mm	Percol./ mm	1^{st} event/d	C_{max}/ µg L^{-1}	$C_{average}$/ µg L^{-1}	Loss/%	Remarks
115	Atrazine	(100)	65	33	Field drainage	Clay loam, 1.5 % OC	1992									Only sub-study with open drainages considered.
	Metolachlor	(200)	(20)	530	Depth 0.60 m	3 × 2 plots 1000 m^2 each; maize	Atrazine I	0.55	365	954	314	12	30	2.6	***1.5***	
	Metribuzin	(60)	(40)	1220	Spacing 7.5 m	with/without intercrop	II	0.55			386			2.3	***1.6***	
					Canada (Ontario)	Appl.: 1992-05-14	Metolachlor	0.84			314		60	2.2	***0.84***	
						1993-05-17	II	0.84			386			1.7	***0.80***	Replicate I: ploughed without intercrop
						1994-05-13	Metribuzin I	0.25			314		10.5	0.65	***0.82***	
						(tank-mixes applied)	II	0.25			386			0.79	***1.22***	
																Replicate II: ploughed with intercrop (ryegrass)
							1993									
							Atrazine I	0.55	365	728	104	22	20	3.4	***0.65***	
							II	0.55			132			5.3	***1.3***	**For comparison, averages of replicates were used.**
							Metolachlor	0.84			104		30	3.2	***0.40***	
							II	0.84			132			5.4	***0.85***	
							Metribuzin I	0.25			104		11	2.0	***0.85***	
							II	0.25			132			3.3	***1.75***	Most losses occurred during first 2 months of the year.
							1994									
							Atrazine I	0.55	365	610	204	47	9	0.44	***0.16***	
							II	0.55			201			0.42	***0.16***	
							Metolachlor	0.84			204		10.5	0.64	***0.15***	
							II	0.84			201			0.61	***0.15***	
							Metribuzin I	0.25			204		8	0.49	***0.40***	
							II	0.25			201			0.52	***0.42***	
127	Diclofop	(14)	(30)	0..8	Field drainage	Loam soil, 17 % clay, 1.4 % OC	CT									Applied products:
	Bromoxynil	(190)	(10)	130	Depths 2 m	barley 1985–1994,	Diclofop	0.8	50	220 irrig	62	2	0.52	0.090	**0.007**	Diclofop-methyl ester:
	2,4-D	(20)	(10)	20 000	Spacing 15 m	3.6 ha conventional tillage (CT),	Bromoxynil	0.28					0.39	0.054	**0.012**	(K_{oc} 16 000, DT_{50} 1 d, sol. 0.8
	MCPA	(20)	(25)	800 000	CDN (Saskatchewan)	4.6 ha no tillage (NT) in 1992,	2,4-D	0.425		rain n.r.			0.96	0.15	***0.022***	mg/L
	Dicamba	(2)	(14)	400 000		before CT	MCPA	0.47					1.18	0.19	***0.025***	Bromoxynil-octanoate ester:
	Mecoprop	(20)	(21)	500 000		Irrigation days 3–13, total 220	Dicamba	0.11					0.7	0.16	***0.090***	(K_{oc} 10 000, DT_{50} 1 d, sol. 0.08
	Tri-allate	(2400)	(82)	4		mm,	Mecoprop	1.05					2.46	0.52	***0.032***	mg/L
	Trifluralin	(8000)	(60)	0.3		Application: 1992-09-23	Trifluralin	1.7					traces	traces	***<0.001***	
								0.82					traces	traces	***<0.001***	
							NT									Authors emphasize the uncertainty which K_{oc}/DT_{50} values determine % leaching; therefore results with these substances were not considered to elucidate the influence of compound properties.
							Diclofop									
							Bromoxynil	0.8	50		67	2	0.34	0.11	**0.009**	
							2,4-D	0.28		220 irrig			0.19	0.063	**0.015**	
							MCPA	0.425					0.64	0.28	***0.044***	
							Dicamba	0.47					1.81	0.82	***0.117***	
							Mecoprop	0.11		rain n.r.			1.36	0.76	***0.461***	
							Tri-allate	1.05					8.64	4.58	***0.292***	
							Trifluralin	1.7					traces	traces	***<0.001***	
								0.82					traces	traces	***<0.001***	

Table 13 Published results from preferential flow studies with conditions unrealistic for moderate climates.

Ref.	Compound	K_{OC}/cm³ g^{-1}	DT$_{50}$/d	*Sol* /mg L^{-1}	Study description	Experimental conditions	Substudy	Rate kg ha^{-1}	Duration /d	Rain /mm	Percol./ mm	1st event/d	C_{max}/µg L^{-1}	$C_{average}$/µ g L^{-1}	Loss/%	Remarks
116	Bromacil Napropamide	22.8 245	(60) (70)	700 74	Lysimeter Depth 24 cm UK	35 % clay, 7.3 % OC, no tillage, diam. 23 cm; Chemigation 12 mm a) initially dry; b) initially wet followed by flushing with 125 mm	a)	7.8 (Naprop.)	ca. 1	137 irrig.		0			ca. 100	Extremely exaggerated irrigation rate
							a) b)	2.1 (Bromacil)							85 23	
117	Napropamide	347	(70)	74	Field studies with soil core sampling Depth ≤3 m USA (California)	Loamy sand, <5 % clay, 0.58 % OC Area 0.64 ha, normal tillage Appl. 1982-08-04, 1 h later: 30 mm irrig., sprinkling with 280 mm over 14 d After 14 days, 36 soil cores were taken (0–300 cm), 19 analyzed		2.5	14	280 (irrig.)	230	0.1	n.r.		21 9.8 1.9 0.5 0	60 cm depth 80 cm depth 120 cm depth 160 cm depth 200 cm depth (% leached *below* depth) Irrigation shortly after appl.
57	Atrazine Strontium bromide	(100)	(60)	33	Lysimeter Laboratory study Depth 30 cm USA	Silt loam, OC not reported; 6 blocks (30 × 30 × 30) from no-till area planted with maize for 25 y. Irrigation schema 1: 1 h/5 mm rain 1 h after appl, 0.5 h/30 mm rain 2 d later (A) 0.5 h/30 mm rain 7 d later (B) Irrigation schema 2: 0.5 h/30 mm rain 1 h after appl. 0.5 h/30 mm rain 7 d later (B)	1) Atrrazine Strontium Bromide	7.7 235 428	9	65	7.8	0.1		1.3 mg/l 2.6 130.3	3.10 0.30 3.17	Concentrations expressed in mg/l.
							2) Atrrazine Strontium Bromide		7	60	5.9	0.1		1.9 5.3 114.3	4.66 2.28 6.75	

(*continues on next page*)

Table 13 (*Continued*).

Ref.	Compound	K_{OC}/cm^3 g^{-1}	DT$_{50}$/d	*Sol* /mg L^{-1}	Study description	Experimental conditions	Substudy	Rate kg ha^{-1}	Duration /d	Rain /mm	Percol./ mm	1$^{\mathrm{st}}$ event/d	C_{max}/μg L^{-1}	C_{average}/μ g L^{-1}	Loss/%	Remarks
57	Atrazine Strontium bromide	(100)	(60)	33	Lysismeter Laboratory study Depth 30 cm USA	Silt loam, OC not reported; 6 monoliths (30 × 30 × 30) from a no-till corn field. Irrigation 1 h after application: 1) rain A: 30 mm within 15 min 2) rain A: 30 mm within 30 min 3) rain A: 30 mm within 2 h	1) Atrrazine Strontium Bromide	7.7 25.8 47.2	7	60	12	0.1	2.4 mg/l 4.8 230	4600 6100 42900	7.3 2.9 11.1	A 2 mm/min rain during 15 min has return period of 10 y, shorter 2 mm/h rains are frequent
							2) Atrrazine Strontium Bromide		7	60	9.6		8.1 167 680	3900 7600 44 700	4.8 2.8 9.0	
						1 week later (to all subtrials): rain B: 30 mm within 30 min	3) Atrrazine Strontium Bromide		7	60	7.2		2.1 3.6 227	2300 1060 27 200	2.2 0.3 4.2	
118	Atrazine	(100)	25	33	Field drainage Depth 1 m Spacing 5.5/10.9 m USA (Louisiana)	61 % clay, 1 % OC, sugarcane; Plot A: 0.32 ha, spacing 5.5 m Plot B: 0.65 ha, spacing 10.9 m Appl.: June 19, 1989 1990-12-13	Plot A Plot B	4.48 (spring)	91	489	350 219	2	82 403	20 54	1.6 2.6	Continuous rainfall during entire study period. Days 0–10: 150 mm (spring)
							Plot A Plot B	2.24 (autumn)	95	459	356 170		165 82	11 8.0	1.8 0.6	30 mm (autumn)
58	Atrazine Metribuzin Nitrate ion	340 150	21 spring 14 winter 22 winter	33 1220	Field drainage Depth 1 m Spacing 5.5/10.9 m USA (Louisiana)	61 % clay, 1 % OC, sugarcane; Plot A: 0.32 ha, spacing 5.5 m Plot B: 0.65 ha, spacing 10.9 m Appl.: 1991-06-19 nitrate ion 1991-06-11 atrazine	<u>Spring</u> nitrate ion A B	122	0–89 0–89	653 653	199 85	1	22 300 48 700	5027 4880	8.2 3.4	Heavy rainfall already on the first day after application in summer
							Atrazine A B	2.24 [1]	0–89 0–89	653 653	199 85		114 144	13.7 14.9	1.2 0.57	
							<u>Autumn</u> atrazine A B	2.24 atrazine	0–95 0–95	551 551	334 114	5	81 67	13.6 8.7	*2* *0.44*	
							Metribuzine A B	1.12 metribuzine	0–95 0–95	551 551	334 114		94 52	5.8 3.4	*1.7* *0.33*	

(*continues on next page*)

Table 13 (*Continued*).

Ref.	Compound	K_{OC}/cm³ g^{-1}	DT$_{50}$/d	*Sol* /mg L^{-1}	Study description	Experimental conditions	Substudy	Rate kg ha^{-1}	Duration /d	Rain /mm	Percol./ mm	1st event/d	C_{max}/μg L^{-1}	$C_{average}$/μ g L^{-1}	Loss/%	Remarks
119	Atrazine 2,4-D Dicamba	(100) (20) (2)	(60) (10) (14)	33 500 000 400 000	Field lysimeters with suction cups Depth 105/135 cm USA (Missouri)	2 × 3 plots each 1 m^2, with soybeans, no tillage; equipped pan lysimeters at 1.05 m (3 plots A) or 1.35 m (3 plots B) and with suction cups; Appl. to moist soil: 1992-05-18 irrigated 6 h after appl. 50 mm at 15 mm/h		Atrazine: 1.4 2,4-D: 1.46 Dicamba: 0.84	0–187 0–187 0–187	520 rain+irr.		0.2		0.05–0.3 ≤0.05 0.05–0.2	*8/2* *2.6/2.9* *6/10*	Concentrations expressed in mg/l
121	Chlorotoluron Methabenzthiazuron	(190) (250)	(30) (90)	7.4 59	Soil columns Depth 85 cm Germany (Lower Saxony)	19 % clay, 1.3 % OC Normal tillage 5 lysimeters (diameter 30 cm) Start at field capacity. After appl. 3 irrigations for 1 h at 25 mm/h, 48 h interval inbetween	Chlorotoluron Methabenz	10 14	3	65	40	0	43 n.r.	25	0.1 <0.1	Chlorotoluron detected in 2 of 5 lysimeters, MBT in 1 of 5
122	Picloram Atrazine Simazine	(10) (100) (130)	(90) (60) (60)	200 000 33 6	Field with suction cups Depth 0.3–1.1 m New Zealand	Silt loam, 1.7 % OC; area 225 m^2, no vegetation, no tillage Application (herbicides and bromide ion): in Nov. 1993 Irrigation in summer (Nov./March), no details given	Picloram Atrazine Simazine (Suction cup at 1.1 m)	22 22 22	360	874	Not known		*1200* *12* *45*	n.r.	n.r.	Over the following year matrix superimposed (change preferential → matrix flow at lower depths Bromide ion: 80 000 μg/l after application of 20 kg/ha

Table 14 Dataset with concurrently applied pesticides.

Pair no.	Compound 1					Compound 2					Solubility/slope			DT$_{50}$/slope			K_{OC}/slope			S_{GU}/slope			Ref.
		Sol/mg L^{-1}	K_{OC}/cm^3 g^{-1}	DT$_{50}$/ d	GUS		*Sol*/mg L^{-1}	K_{OC}/cm^3 g^{-1}	DT$_{50}$/ d	GUS	Δ	pos.	neg.	Δ	pos.	neg.	Δ	pos.	neg.	Δ	pos.	neg.	
1	Chlorpyrifos	0.4	**28 300**	30	–0.67	Carbofuran	351	**41**	50	4.06	2.00	1	0	0.50	1	0	*1.99*	0	1	4.72	1	0	49
2	Chlorpyrifos	0.4	**28 300**	30	–0.67	Atrazine	33	**91**	60	3.63	1.95	1	0	0.67	1	0	*1.99*	0	1	4.30	1	0	49
3	Trifluralin	0.3	8000	60	0.17	Dicamba	400 000	2	14	4.24	2.00	2	0	*1.24*	0	2	*2.00*	0	2	4.07	2	0	123
4	Trifluralin	0.3	8000	60	0.17	MCPA	800 000	20	25	3.77	2.00	2	0	*0.82*	0	2	*1.99*	0	2	3.60	2	0	123
5	Trifluralin	0.3	**6200**	60	0.37	Mecoprop	600 000	10	21	3.97	2.00	2	0	*0.96*	0	2	*1.99*	0	2	3.60	2	0	54
	id.	0.3	8000	60	0.17	*id.*	600 000	20	21	3.57	2.00	2	0	*0.96*	0	2	*1.99*	0	2	3.40	2	0	123
6	Tri-allate	4	2400	82	1.19	Dicamba	400 000	2	14	4.24	2.00	2	0	*1.42*	0	2	*2.00*	0	2	3.05	2	0	123
7	Chlorpyrifos	0.4	**28 300**	30	–0.67	Cyanazine	170	**97**	14	2.31	1.99	1	0	*0.73*	0	1	*1.99*	0	1	2.97	1	0	49
9	Trifluralin	0.3	**6200**	60	0.37	Isoproturon	65	**25**	18	3.27	1.98	2	0	*1.08*	0	2	*1.98*	0	2	2.90	2	0	54
10	Chlorpyrifos	0.4	**28 300**	30	–0.67	Alachlor	240	**157**	15	2.12	1.99	1	0	*0.67*	0	1	*1.98*	0	1	2.79	1	0	49
11	Prochloraz	34	**2880**	30	0.80	Triasulfuron	815	**16.5**	19	3.56	1.84	1	0	*0.45*	0	1	*1.98*	0	1	2.76	1	0	114
12	Pendimethalin	0.275	**3380**	90	0.92	Triasulfuron	815	**16.5**	19	3.56	2.00	1	0	*1.30*	0	1	*1.98*	0	1	2.64	1	0	114
13	Tri-allate	4	2400	82	1.19	MCPA	800 000	20	25	3.77	2.00	2	0	*1.07*	0	2	*1.97*	0	2	2.59	2	0	123
14	Trifluralin	0.3	8000	60	0.17	2,4-D	500 000	20	10	2.70	2.00	2	0	*1.43*	0	2	*1.99*	0	2	2.53	2	0	123
15	Simazine	6	130	60	3.35	Picloram	200 000	10	90	5.86	2.00	1	0	0.40	1	0	*1.71*	0	1	2.51	1	0	122
16	Tri-allate	4	2400	82	1.19	Mecoprop	600 000	20	21	3.57	2.00	2	0	*1.18*	0	2	*1.97*	0	2	2.38	2	0	123
17	Atrazine	33	100	60	3.56	Picloram	200 000	10	90	5.86	2.00	1	0	0.40	1	0	*1.64*	0	1	2.31	1	0	122
18	Alachlor	240	**157**	15	2.12	Carbofuran	351	**41**	50	4.06	0.38	1	0	1.08	1	0	*1.17*	0	1	1.93	1	0	49
	id.	240	**157**	15	2.12	*id.*	351	**41**	50	4.06	0.38	3	0	1.08	3	0	*1.17*	0	3	1.93	3	0	52
19	Pendimethalin	0.275	5000	90	0.59	Isoproturon	65	130	18	2.37	1.98	2	0	*1.33*	0	2	*1.90*	0	2	1.78	2	0	105
	id.	0.275	5000	90	0.59	*id.*	65	130	18	2.37	1.98	1	0	*1.33*	0	1	*1.90*	0	1	1.78	1	0	55
	id.	0.275	**3380**	90	0.92	*id.*	65	**112**	18	2.45	1.98	2	0	*1.33*	0	2	*1.87*	0	2	1.53	2	0	114
20	Cyanazine	170	**97**	14	2.31	Carbofuran	351	**41**	50	4.06	0.69	1	0	1.13	1	0	*0.81*	0	1	1.75	1	0	49
	id.	170	**97**	14	2.31	*id.*	351	**41**	50	4.06	0.69	3	0	1.13	3	0	*0.81*	0	3	1.75	3	0	52
21	Prochloraz	34	**2880**	30	0.80	Isoproturon	65	**112**	18	2.45	0.63	1	0	*0.50*	0	1	*1.85*	0	1	1.65	1	0	114
22	2,4-D	500 000	20	10	2.70	Dicamba	400 000	2	14	4.24	*0.22*	0	2	0.33	2	0	*1.64*	0	2	1.54	2	0	119
	id.	500 000	20	10	2.70	*id.*	400 000	2	14	4.24	*0.22*	0	2	0.33	2	0	*1.64*	0	2	1.54	2	0	123
23	Alachlor	240	**157**	15	2.12	Atrazine	33	**91**	60	3.56	*1.52*	0	4	1.20	4	0	*0.53*	0	4	1.51	4	0	49
	id.	240	170	**35**	2.73	*id.*	33	100	**65**	3.63	*1.52*	0	3	0.60	3	0	*0.52*	0	3	0.89	3	0	100
24	Tri-allate	4	2400	82	1.19	2,4-D	500 000	20	10	2.70	2.00	2	0	*1.57*	0	2	*1.97*	0	2	1.51	2	0	123
25	Terbuthylazine	9	**357**	45	2.39	Triasulfuron	815	9.3	19	3.88	1.96	1	1	*0.81*	1	1	*1.90*	1	1	1.48	1	1	106

(*continues on next page*)

Table 14 (*Continued*).

Pair no.	Compound 1	*Sol*/mg L^{-1}	K_{OC}/cm³ g^{-1}	DT$_{50}$/ d	GUS	Compound 2	*Sol*/mg L^{-1}	K_{OC}/cm³ g^{-1}	DT$_{50}$/ d	GUS	Solubility/slope Δ	pos.	neg.	DT$_{50}$/slope Δ	pos.	neg.	K_{OC}/slope Δ	pos.	neg.	S_{GU}/slope Δ	pos.	neg.	Ref.
26	Isoproturon	65	130	18	2.37	MCPA	800 000	20	25	3.77	2.00	0	6	0.33	0	6	*1.47*	6	0	1.41	0	6	56
27	Metolachlor	530	200	20	2.21	Atrazine	33	100	60	3.56	*1.77*	0	1	1.00	1	0	*0.67*	0	1	1.35	1	0	110
	id.	530	200	20	2.21	*id.*	33	100	60	3.56	*1.77*	0	3	1.00	3	0	*0.67*	0	3	1.35	3	0	115
	id.	530	200	20	2.21	*id.*	33	100	60	3.56	*1.77*	0	4	1.00	4	0	*0.67*	0	4	1.35	4	0	51
	id.	530	200	**20**	2.21	*id.*	33	100	**36**	3.11	*1.77*	1	0	0.57	0	1	*0.67*	1	0	0.90	0	1	50
28	Metolachlor	530	200	20	2.21	Metribuzin	1220	60	40	3.56	0.79	3	0	0.67	3	0	*1.08*	0	3	1.35	3	0	115
29	Cyanazine	170	**97**	14	2.31	Atrazine	33	**91**	60	3.63	*1.35*	0	1	1.24	1	0	*0.06*	0	1	1.32	1	0	49
	id.	170	**97**	14	2.31	*id.*	33	**91**	60	3.63	*1.35*	0	3	1.24	3	0	*0.06*	0	3	1.32	3	0	52
30	Linuron	81	400	60	2.49	MCPA	800 000	20	25	3.77	2.00	0	3	*0.82*	3	0	*1.81*	3	0	1.29	0	3	56
31	Propiconazole	110	**738**	110	2.31	Triasulfuron	815	**16.5**	19	3.56	1.52	1	0	*1.41*	0	1	*1.91*	0	1	1.25	1	0	114
32	Isoproturon	65	**112**	18	2.45	Triasulfuron	815	**16.5**	19	3.56	1.70	3	0	0.05	3	0	*1.49*	0	3	1.11	3	0	114
33	2,4-D	500 000	20	10	2.70	MCPA	800 000	20	25	3.77	0.46	2	0	0.86	2	0	0.00	-	-	1.07	2	0	123
34	Terbuthylazine	9	**357**	45	2.39	Atrazine	33	128	60	3.37	1.14	2	0	0.29	2	0	*0.94*	0	2	0.97	2	0	106
35	Dichlorprop	0.59	26	8	2.33	Bentazon	570	34	20	3.21	2.00	1	0	0.86	1	0	0.27	1	0	0.88	1	0	105
36	2,4-D	500 000	20	10	2.70	Mecoprop	600 000	20	21	3.57	0.18	2	0	0.71	2	0	0.00	-	-	0.87	2	0	123
37	2,4-D	500 000	20	10	2.70	Atrazine	33	100	60	3.56	*2.00*	1	1	1.43	1	1	1.33	1	1	0.86	1	1	119
38	Chlorpyrifos	0.4	6000	**66**	0.40	Fenpropimorph	4.3	2000	54	1.21	1.66	0	1	*0.20*	1	0	*1.00*	1	0	0.81	0	1	59
39	Atrazine	33	**340**	**14**	1.68	Metribuzin	1220	**150**	**22**	2.45	1.89	0	2	0.44	0	2	*0.78*	2	0	0.77	0	2	58
	id.	33	100	60	3.56	*id.*	1220	60	40	3.56	1.89	2	1	*0.40*	1	2	*0.50*	1	2	0.003	2	1	115
40	Isoproturon	65	**25**	18	3.27	Mecoprop	600 000	**10**	21	3.97	2.00	1	2	0.15	1	2	*0.86*	2	1	0.70	1	2	54
41	Atrazine	33	100	60	3.56	Dicamba	400 000	2	14	4.24	2.00	1	1	*1.24*	1	1	*1.92*	1	1	0.68	1	1	119
42	Mecoprop	600 000	20	21	3.57	Dicamba	400 000	2	14	4.24	*0.40*	0	2	*0.40*	0	2	*1.64*	0	2	0.67	2	0	123
43	Metolachlor	530	200	20	2.21	Terbuthylazine	9	220	45	2.74	*1.93*	0	1	0.77	1	0	0.10	1	0	0.53	1	0	105
44	Atrazine	33	**128**	60	3.37	Triasulfuron	815	9.3	19	3.88	1.84	0	2	*1.04*	2	0	*1.73*	2	0	0.51	0	2	106
45	MCPA	800 000	20	25	3.77	Dicamba	400 000	2	14	4.24	*0.67*	0	2	*0.56*	0	2	*1.64*	0	2	0.47	2	0	123
46	Atrazine	33	91	60	3.63	Carbofuran	351	41	50	4.06	*1.66*	1	0	0.18	0	1	0.76	0	1	0.43	1	0	49
	id.	33	91	60	3.63	*id.*	351	41	50	4.06	*1.66*	3	0	0.18	0	3	0.76	0	3	0.43	3	0	52
47	Carbetamide	3500	90	18	2.57	Dimefuron	16 000	205	60	3.00	*1.28*	0	1	1.08	0	1	0.78	0	1	0.43	0	1	55
48	Dimethoate	39 800	20	7	2.28	Linuron	81	400	60	2.49	*1.99*	0	3	1.58	3	0	1.81	3	0	0.20	3	0	56
49	Mecoprop	600 000	20	21	3.57	MCPA	800 000	20	25	3.77	*0.29*	0	2	0.17	0	2	0.00	-	-	0.20	0	2	123
50	Simazine	6	130	60	3.35	Atrazine	33	100	60	3.56	*1.38*	0	1	0.00			0.26	1	0	0.20	0	1	122
51	Alachlor	240	157	15	2.12	Cyanazine	170	97	14	2.31	*0.34*	0	1	0.07	0	1	0.47	0	1	0.19	1	0	49
	id.	240	157	15	2.12	*id.*	170	97	14	2.31	*0.34*	0	3	0.07	0	3	0.47	0	3	0.19	3	0	52
52	Isoproturon	65	130	18	2.37	Chlorotoluron	7.4	190	30	2.54	*1.59*	0	1	0.50	1	0	0.38	1	0	0.17	1	0	105
53	Propiconazole	110	**738**	110	2.31	Isoproturon	65	**112**	18	2.45	*0.51*	1	0	*1.44*	1	0	*1.47*	1	0	0.14	0	1	114
54	Isoproturon	65	130	18	2.37	Linuron	81	400	60	2.49	0.22	0	6	1.08	0	6	1.02	0	6	0.12	0	6	56
55	Prochloraz	34	**2880**	30	0.80	Pendimethalin	0.275	**3380**	90	0.92	*1.97*	1	0	1.00	0	1	0.16	0	1	0.12	0	1	114
56	Dimethoate	39 800	20	7	2.28	Isoproturon	65	130	18	2.37	*1.99*	0	6	0.88	6	0	1.47	6	0	0.09	6	0	56
											Total	*69*	*72*	*Total*	*71*	*69*	*Total*	*35*	*100*	*Total*	*108*	*33*	

Bold: Values measured with soil from the experimental site

Moreover, increased adsorption of solutes on the walls of biopores has been reported. Edwards et al. [43] found a significant adsorption of alachlor and atrazine in earthworm channels resulting in a reduction of transport. Stehouwer et al. [44] confirmed this hypothesis by the explicit determination of chemical properties of burrow linings as a function of soil depth. The burrow linings consist of excrements of the earthworms containing hydrophobic clay-humic complexes. The level of OC is 2 to 8 times higher in the burrow linings than in the surrounding soil, and the adsorption of atrazine is stronger to lining material of burrows. Further to adsorption, solutes may diffuse into the soil matrix surrounding macropores, particularly when the soil matrix is dry.

Therefore, there seems to be sufficient evidence to conclude that the relevance of macropore transport of solutes is much lower for groundwater. The measured values suggest that the attenuation factor ranges between 20 and 200. However, when performing groundwater modeling, it has to be considered that losses even less than 0.1 % of the applied amount can lead to values above 0.1 μg L^{-1}.

6. CONCLUSIONS

- In well-structured, fine-textured soils, preferential flow is more the rule than the exception. There is strong experimental evidence that macropore transport by far exceeds matrix transport. Consequently, the transport of solutes through macropore flow is of utmost importance for pesticides.
- As matrix transport is slow, degradation as well as equilibrium and nonequilibrium adsorption including aging is fully effective during the whole percolation process. For rapid macropore transport, however, substance properties are much less important.
- Nevertheless, the significance of macropore transport increases with increasing persistence and inherent mobility of the compound. The extensive research that has been conducted over the past years clearly demonstrates that:
  - Significant amounts of all substances with GUS values S_{GUS} above 1 may be transported via macropore flow in structured soils.
  - Beyond this prerequisite, the inherent mobility of a compound has an impact on the amount that is transported rather than on the retention.
  - In addition to compound properties, macropore flow is strongly affected by many environmental parameters, like soil texture, weather conditions and soil biology, that determine the amount, design (e.g. length, diameter, form), properties, stability and distribution of macropores.
  - Organic matter and micro inhomogeneities act as starting points for macropore formation.
  - Soil moisture and precipitation/irrigation regime strongly influence the amount of pesticide losses. Heavy rainfalls occurring shortly after pesticide application lead to high losses, as degradation and aging are prevented. Therefore, studies with unrealistic watering rates shortly after application were excluded.
  - Management practices and changes in the structure of the soil surface affect the amount and stability of macropores and their permeability from the soil surface to deeper soil horizons, and thus the infiltration capacity of soils and the overall macropore flow.
- The density, size and structure of macropores are highly variable within time and space. The variability and unpredictability are even more pronounced considering weather conditions causing macropore flow.
- Macropore transport to groundwater is measured by means of techniques and under conditions of free flowing, i.e., open-ended macropores. The results are, therefore, only valid for real situations where such conditions prevail. The measured losses only apply for scenarios where macropores directly open into a coarsely structured subsoil, jointed rock, or karst aquifer. Less permeable subsoils prevent the continuous macropore flow of water. This applies for most regions.

- Drainage and lysimeter experiments are of utmost importance for surface waters receiving the outflow of drainage systems.
- As groundwater pollution by macropore transport depends on multiple site-specific factors, such as soil characteristics, climatic conditions, permeability of subsoils, groundwater level, and management practices, an assessment of groundwater contamination based on pesticide properties is impossible. As losses via macropore transport may considerably exceed losses via matrix transport at a specific site, a site-specific assessment is urgently needed.
- Contrary to chromatographic models, the present macropore models need additional parameters that cannot be independently measured in the laboratory. Therefore, meaningful predictions of transport of chemicals through macroporous soil that are solely based on soil characterization are not possible. Reasonable predictions using macropore flow models can only be expected when long-term historical field data is available. A further prerequisite is that such information was used to calibrate the model in a well-conceived way before starting with simulations for predictions of other time periods.

7. REFERENCES

1. P. Schachtschabel, H.-P. Blume, G. Brümmer, K.-H. Hartge, U. Schwertmann. *Lehrbuch der Bodenkunde*, 12th ed., F. E. Verlag, Stuttgart (1989).
2. F. Binet, V. Hallaire, P. Curmi. *Soil Biol. Biochem.* **29**, 577 (1997).
3. R. C. Schwartz, K. J. Mc Innes, A. S. R. Juo, C. E. Cervantes. *Soil Sci.* **164**, 561 (1999).
4. K. Beven, P. Germann. *Water Resour. Res.* **18**, 1311 (1982).
5. P. Bullock, A. J. Thomasson. *J. Soil Sci.* **30**, 391 (1979).
6. J. Webster. North Westland, Master's thesis, University of Canterbury, New Zealand (1974).
7. H. P. Cresswell, D. J. Painter, K. C. Cameron. *Soil Sci. Soc. Am. J.* **57**, 816 (1993).
8. D. W. Ranken. Master's thesis, Oregon State University, Corvallis (1974).
9. R. J. Luxmoore. *Soil Sci. Soc. Am. J.* **45**, 671 (1981).
10. K. Beven, P. Germann. *J. Soil Sci.* **32**, 15 (1981).
11. (a) R. Brewer. *Fabric and Mineral Analysis of Soils*, John Wiley, New York (1964); (b) M. J. Reeves. *Eng. Geol.* **14**, 231 (1981).
12. B. Bejat, E. Perfeet, V. L. Quisenberry, M. S. Coyne, G. R. Haszler. *Soil Sci. Soc. Am. J.* **64**, 818 (2000).
13. W. Kördel, H. Klöppel, M. Klein, P. Dreher. UBA Report, FKZ: 126 05 204 (2003).
14. J. Vanderborgh, A. Timmermann, J. Feyen. *Soil Sci. Soc. Am. J.* **64**, 1305 (2000).
15. P. Germann, K. Beven. *J. Soil Sci.* **32**, 1 (1981).
16. D. E. Hill, J.-Y. Parlange. *Soil Sci. Soc. Am. Proc.* **36**, 697 (1972).
17. P. A. C. Raats. *Soil Sci. Soc. Am. Proc.* **37**, 681 (1973).
18. J. S. Selker, T. S. Steenhuis, J.-Y. Parlange. *Soil Sci. Soc. Am. J.* **56**, 1346 (1992).
19. Y. Liu, J.-Y. Parlange, T. S. Steenhuis. *Water Resour. Res.* **31**, 2263 (1995).
20. E. L. Mac Coy, C. W. Boast, C. W. Stehouwer, E. J. Kladivko. In *Soil Processes and Water Quality. Adv. Soil Sci.*, R. Lai, B. A. Stewart (Eds.), pp. 303–348, Lewis Publications, Ann Arbor, MI (1994).
21. K.-J. S. Kung. *Geoderma* **46**, 51 (1990).
22. K.-J. S. Kung. *Geoderma* **46**, 59 (1990).
23. A. R. Dexter. *Water Resour. Res.* **29**, 1859 (1993).
24. W. Ehlers. *Soil Sci.* **119**, 242 (1975).
25. A. R. Mitchell, T. R. Ellsworth, B. Meek. *Soil Sci. Plant Anal.* **26**, 2655 (1995).
26. P. M. Fraser, P. H. Williams, R. J. Haynes. *Appl. Soil Ecol.* **3**, 49 (1995).
27. C. Emmerling. *Appl. Soil Ecol.* **17**, 91 (2000).
28. K. Y. Chan. *Soil Tillage Res.* **57**, 179 (2001).

29. M. R. Carter, P. M. Mele. *Aust. J. Soil Res.* **30**, 493 (1992).
30. A. J. Franzluebbers, F. M. Hans, D. A. Zuberer. *Soil Sci. Soc. Am. J.* **58**, 1639 (1994).
31. P. J. Haines, N. C. Uren. *Aust. J. Exp. Agric.* **30**, 365 (1990).
32. R. Lal, A. A. Mahboubi, N. R. Fomsey. *Soil Sci. Soc. Am. J.* **58**, 517 (1994).
33. K. R. J. Smettern, B. E. Clothier. *J. Soil Sci.* **40**, 563 (1989).
34. K. M. Perroux, I. White. *Soil Sci. Soc. Am. J.* **52**, 1205 (1988).
35. J. L. Thony, G. Vachaud, B. E. Clothier R. Angulo-Jaramillo. *Soil Technol.* **4**, 111 (1991).
36. M. D. Ankeny, M. Ahmed, T. C. Kaspar, R. Horton. *Soil Sci. Am. J.* **55**, 467 (1991).
37. I. White, M. J. Sully. *Water Resour. Res.* **23**, 1514 (1987).
38. B. E. Clothier, M. B. Kirkham, J. E. McLean. *Soil Sci. Am. J.* **56**, 733 (1992).
39. B. E. Clothier, L. Heng, G. N. Magesan, I. Vogeler. *Aust. J. Soil Res.* **33**, 397 (1995).
40. D. B. Jaynes, S. D. Logsdon, R. Horton. *Soil Sci. Soc. Am. J.* **59**, 352 (1995).
41. P. A. Olsen. *Soil Tillage Res.* **44**, 1 (1997).
42. A. L. Armstrong, P. B. Leeds-Harrisson, G. L. Harris, J. A. Catt. *Soil Use Manage.* **15**, 2406 (1999).
43. W. M. Edwards, M. J. Shipitalo, W. A. Dick, L. B. Owens. *Soil Sci. Soc. Am. J.* **56**, 52 (1992).
44. R. G. Stehouwer, A. Dick, S. J. Traina. *J. Environ. Qual.* **22**, 181 (1993).
45. A. P. Mallawatantri, B. G. McConkey, D. J. Mulla. *J. Environ. Qual.* **25**, 227 (1996).
46. M. Burghardt. *Feldversuche zur Erfassung des Transportverhaltens vvon gelösten und partikulären Tracern mittels Multitracing-Technik in einem schluffigen Boden*. Jülich, Forschungszentrum, Zentralbibliothek (2003).
47. R. D. Wauchope, T. M. Buttler, A. G. Hornsby, P. W. M. Augustinjn-Beckers, J. B. Burt. *Rev. Environ. Contamin. Toxicol.* **123**, 1 (1992).
48. R. J. Hance, C. R. Worthing. *The Pesticide Manual*, 9th ed., British Crop Protection Council, London (1991).
49. E. J. Kladivko, G. E. Van Scoyoc, E. J. Monke, K. M. Oates, W. Pask. *J. Environ. Qual.* **20**, 264 (1991).
50. L. M. Southwick, G. H. Willies, R. L. Bengston, T. J. Lormand. *J. Irrig. Drainage Eng.* **116**, 16 (1990).
51. J. D. Gaynor, D. C. MacTavish, W. I. Findlay. *J. Environ. Qual.* **24**, 246 (1995).
52. E. J. Kladivko, J. Grochulska, R. F. Turco, G. E. Van Scoyoc, J. D. Eigel. *J. Environ. Qual.* **28**, 997 (1999).
53. L. F. Bergström, N. J. Jarvis. *Weed Sci.* **41**, 251 (1993).
54. (a) C. D. Brown, R. A. Hodgkinson, D. A. Rose, J. K. Syers, S. J. Wilcockson. *Pestic. Sci.* **43**, 131 (1995); (b) C. D. Brown, D. A. Rose, J. K. Syers, R. A. Hodgkinson. *BCPC Monograph* **62**, 93 (1995).
55. S. M. Kamra, J. Michaelsen, W. Wichtmann, P. Widmoser. *Water Sci. Technol.* **40**, 61 (1999).
56. C. D. Brown, J. M. Hollis, R. J. Bettinson, A. Walker. *Pest Manag. Sci.* **56**, 83 (2000).
57. M. J. Shipitalo, W. M. Edwards, W. A. Dick, L. B. Owens. *Soil Sci. Soc. Am. J.* **54**, 1530 (1990).
58. L. M. Southwick, G. H. Willis, D. C Johnson, H. M. Selim. *J. Environ. Qual.* **24**, 684 (1995).
59. A. B. Turnbull, R. M. Harrison, R. J. Williams, P. Matthiessen, D. N. Brooke, D. A. Sheahan, M. Mills. *J. Chart. Inst. Water Environ. Manage.* **11**, 24 (1997).
60. D. J. Gustafson. *Environ. Toxicol. Chem.* **8**, 339 (1989).
61. M. J. Shipitalo, W. A. Dick, W. M. Edwards. *Soil Tillage Res.* **53**, 267 (2000).
62. W. M. Edwards, L. D. Norton, C. E. Redmond. *Soil Sci. Soc. Am. J.* **52**, 483 (1988).
63. M. Flury. *J. Environ. Qual.* **25**, 25 (1996).
64. M. Flury, H. Flühler, W. A. Jury, J. Leuenberger. *Water Resour. Res.* **30**, 1941 (1994).
65. M. Th. Van Genuchten. In *Hydrological Interactions Between Atmosphere, Soil and Vegetation*, pp. 169–183, Proceedings of the Vienna Symposium, August 1991, *IAHS Publ.* No. 204, Wallingford, Oxfordshire, UK (1991).

66. J. S. Aronofsky, J. P. Heller. *AIME Petr. Trans.* **210**, 345 (1957).
67. J. Skopp, W. R. Gardner. *Soil Sci. Soc. Am. J.* **56**, 1680 (1992).
68. W. M. Edwards, R. R. van der Ploeg, W. Ehlers. *Soil Sci. Soc. Am. J.* **43**, 851 (1979).
69. H. J. Montas, J. D. Eigel, B. A. Engel, K. Haghighi. *Trans. ASAE* **40**, 1245 (1997).
70. H. J. Montas, J. D. Eigel, B. A. Engel, K. Haghighi. *Trans. ASAE* **40**, 1257 (1997).
71. J. L. Hutson, R. J. Wagenet. *Soil Sci. Soc. Am. J.* **59**, 743 (1995).
72. J. P. Gwo, P. M. Jardine, G. V. Wilson, G. T. Yeh. *J. Hydrol.* **164**, 21 (1995).
73. T. S. Steenhuis, J.-Y. Parlange, M. S. Andreini. *Geoderma* **46**, 193 (1990).
74. S. Koch, H. Flühler. *Water, Air, Soil Pollut.* **68**, 275 (1993).
75. M. Th. A. van Genuchten. *Soil Sci. Soc. of Am. J.* **44**, 892 (1980).
76. R. H. Brooks, A. T. Corey. *Hydrology Paper* **3**, Colorado State University, Fort Collins, Colorado (1964).
77. Y. Mualem. *Water Resour. Res.* **12**, 513 (1976).
78. N. J. Jarvis. *Report & Dissertation* **9**, Dept. Soil Sci., Swed. Univ. Agric. Sci. Uppsala (1991).
79. N. J. Jarvis. *Report & Dissertation* **19**, Dept. Soil Sci., Swed. Univ. Agric. Sci. Uppsala (1994).
80. N. J. Jarvis. *Ecol. Model.* **81**, 97 (1995).
81. N. J. Jarvis, M. Stähli, L. Bergström, H. Johnsson. *J. Environ. Sci. Health, A* **29**, 1255 (1994).
82. N. J. Jarvis, M. Larsson, P. Fogg, A. D. Carter. In: *Proc. BCPC Symposium "Pesticide movement to water"*, A. Walker, R. Allen, S. W. Bailey, A. M. Blair, C. D. Brown, P. Günther, C. R. Leake, P. H. Nicholls (Eds.), pp. 161–170, Warwick, UK (1995).
83. L. Bergström. *Pestic. Sci.* **48**, 37 (1996).
84. M. Larsson. Diss., Swedish University of Agricultural Sciences, Uppsala (1999).
85. I. Bärlund. Diss., Universität Karlsruhe *IHW Publikation* **63** (1998).
86. A. Armstrong, A. Karin, N. Amraoui, B. Diekkrüger, N. Jarvis, C. Mouvet, P. Nicholls, C. Wittwer. *Agric. Water Manage.* **44**, 85 (2000).
87. L. Andreu, F. Moreno, N. J. Jarvis, G. Vachaud. *Agric. Water Manage.* **25**, 71 (1994).
88. L. Andreu, N. J. Jarvis, F. Moreno, G. Vachaud. *Soil Use Manage.* **12**, 109 (1996).
89. H.-J. Franke, G. Teutsch. *Ecol. Model.* **75/76**, 529 (1994).
90. M. Klein. *J. Pesticide Sci.* **24**, 55 (1999).
91. S. A. Grant, J. D. Jabro, D. D. Fritton, D. E. Baker. *Water Resour. Res.* **27**, 1439 (1991).
92. M. Vanclooster, J. J. T. I. Boesten, M. Trevisan, C. D. Brown, E. Capri, O. M. Eklo, B. Gottesbüren, V. Gouy, A. M. A. van der Linden. *Agric. Water Manage.* **44**, 1 (2000).
93. A. Tiktak. *Agric. Water Manage*. **44**, 119 (2000).
94. J. J. T. I. Boesten. *Agric. Water Manage*. **4**4, 389 (2000).
95. FOCUS. Report of the FOCUS Groundwater Scenarios Workgroup, *EC Document* Reference Sanco/321/2000 (2000).
96. W. Kördel, M. Dassenakis, J. Lintelmann, S. Padberg. *Pure Appl. Chem.* **69**, 1571 (1997).
97. Kördel, H. Klöppel, M. Klein, P. Dreher. *UBA-Report,* FKZ 126 05 204 (2003).
98. L. F. Bergström, A. S. McGibbon, S. R. Day, M. Snel. *Pestic. Sci.* **29**, 405 (1990).
99. L. F. Bergström, A. S. McGibbon, S. R. Day, M. Snel. *Environ. Toxicol. Chem.* **10**, 563 (1991).
100. J. D. Gaynor, D. C. MacTavish, W. I. Findlay. *Arch. Environ. Contam. Toxicol.* **23**, 240 (1992).
101. P. Matthiessen, C. Allchin, R. J. Williams, S. C. Bird, D. Brooke, P. J. Glendinning. *J. Inst. Water Environ. Manage.* **6**, 496 (1992).
102. G. L. Harris, P. H. Nicholls, S. W. Bailey, K. R. Howse, D. J. Mason. *J. Hydrol.* **159**, 235 (1994).
103. (a) A. H. Haria, A. C. Johnson, J. P. Bell, C. H. Batchelor. *J. Hydrol.* **163**, 203 (1994); (b) A. C. Johnson, A. H. Haria, C. L. Bhardwaj, C. Völkner, C. H. Batchelor, A. Walker. *J. Hydrol.* **163**, 217 (1994).
104. K. Jayachandran, T. R. Steinheimer, L. Somasundaram, T. B. Moorman, R. S. Kanwar, J. R. Coats. *J. Environ. Qual.* **23**, 311 (1994).

105. (a) U. Traub-Eberhard, W. Klein, W. Kördel, R. Winkler. *Z. Umweltchem. Ökotox.* **7**, 168 (1995); (b) W. Kördel, I. Rönnefahrt, R. Winkler. *Gesunde Pflanzen* **49**, 163 (1997).
106. M. Flury, J. Leuenberger, B. Studer, H. Flühler. *Water Resour. Res.* **31**, 823 (1995).
107. (a) A. C. Johnson, A. H. Haria, V. L. Cruxton, C. H. Batchelor, R. J. Williams, K. Heppell, T. Burt. *BCPC Monograph* **62**, 105 (1995); (b) A. C. Johnson, A. H. Haria, C. L. Bhardwaj, R. J. Williams, A. Walker. *Pestic. Sci.* **48**, 225 (1996).
108. A. J. Beck, G. L. Harris, K. R. Howse, A. E. Johnston, K. C. Jones. *J. Agric. Food Chem.* **43**, 1368 (1995).
109. R. J. Williams, D. N. Brooke, P. Matthiessen, M. Mills, A. Turnbull, R. M. Harrison. *J. Inst. Water Environ. Manage.* **9**, 72 (1995).
110. L. E. Gentry, M. B. David, K. M. Smith-Starks, D. A. Kovacic. *J. Environ. Qual.* **29**, 232 (2000).
111. S. Novak, J.-M. Portal, M. Schiavon. *Chemosphere* **42**, 235 (2000).
112. K. G. Villholth, N. J. Jarvis, O. H. Jacobsen, H. de Jonge. *J. Environ. Qual.* **29**, 1298 (2000).
113. E. W. Gatzweiler, B. Schmidt, M. Feyerabend. *Hum. Environ. Exposure Xenobiot.*, Proc. 11th Symp. Pestic. Chem., A. A. M. Del Re (Ed.), **11**, 305 (2000).
114. R. L. Jones, G. L. Harris, J. A. Catt, R. H. Bromilow, D. J. Mason, D. J. Arnold. *Brighton Crop Prot. Conf.* – Weeds 1995, 489 (1995).
115. J. D. Gaynor, C. S. Tan, C. F. Drury, H. Y. F. Ng, T. W. Welacky, I. J. van Weesenbeeck. *J. Environ. Qual.* **30**, 361 (2001).
116. R. E. White, J. S. Dyson, Z. Gerstl, B. Yaron. *Soil Sci. Soc. Am. J.* **50**, 277 (1986).
117. W. A. Jury, H. Elabd, M. Resketo. *Water Resour. Res.* **22**, 749 (1986).
118. L. M. Southwick, G. H. Willis, H. M. Selim. *J. Agric. Food Chem.* **40**, 1264 (1992).
119. J. A. Tindall, W. K. Vencill. *J. Hydrol.* **166**, 37 (1995).
120. J. Elliott, A. J. Cessna, K. B. Best, W. Nicholaichuk, L. C. Tollefson. *J. Environ. Qual.* **27**, 124 (1998).
121. C. F. Stange, B. Diekkrüger, H. Nordmeyer. *Pestic. Sci.* **52**, 241 (1998).
122. M. E. Close, L. Pang, J. P. C. Watt, K. W. Vincent. *Geoderma* **84**, 45 (1998).
123. J. A. Elliott, A. J. Cessna, W. Nicholaichuk, L. E. Tollefson. *J. Environ. Qual.* **29**, 1650 (2000).
124. IUPAC. *Compendium of Chemical Terminology*, 2nd ed. (the "Gold Book"), compiled by A. D. McNaught and A. Wilkinson, Blackwell Science, Oxford (1997). XML on-line corrected version: <http://goldbook.iupac.org> (2006–) created by M. Nic, J. Jirat, B. Kosata; updates compiled by A. Jenkins.
125. OECD. Chemicals Testing Monographs No. 22: Testing and Assessment: Guidance Document for the Performance of Outdoor Monolith Lysimeter Studies, Organization for Economic Cooperation and Development, Paris.

APPENDIX 1: SHORT DESCRIPTION OF SOIL PHYSICAL PARAMETERS AND EQUATIONS

hydraulic conductivity, K SI unit: m s^{-1}

Property of soil or rock that describes the ease with which water can move through pore spaces or fractures.

Note 1: It depends on the intrinsic permeability of the material and on the degree of saturation. Saturated hydraulic conductivity, K_o or K_{sat}, describes water movement through saturated media.

Note 2: Hydraulic conductivity is the proportionality constant in Darcy's law, which states that the volume of water flowing through an aquifer divided by the cross-sectional area of the aquifer is proportional to the gradient of hydraulic head, i.e.,

$$Q = K(\mathrm{d}\psi/\mathrm{d}l) \qquad \text{(Darcy's law)}$$

where

Q: volume of water percolating through an element of area in an element of time [volume/(area × time) **LT^{-1}**]
ψ: overall potential which is the sum of capillary, gravity and osmotic potential (length **L**)
l: length of the flow path (length **L**)
K: hydraulic conductivity (length/time **LT^{-1}**)
$d\psi/dl$: change of the hydraulic head within an element of length of the flow path (dimensionless **1**)

It can be measured by creating a hydraulic gradient between two points and measuring the flow rate and area of cross-section between the two points.

Note 3: Shepherd (1989) derived an empirical formula for approximating hydraulic conductivity from grain-size analyses:

$$K = a(D10)^b$$

where a and b are empirically derived terms based on the soil type, and D_{10} is the diameter of the 10th percentile grain size of the material.

capillary potential, ψ_{cap} SI unit: m
matrix potential (synonym)
soil water pressure head (synonym)
Height of water resulting from capillary rise in soils.

Note: Capillary potential is a measure of how strongly soil water is attracted to soil solids, and depends on soil type and soil moisture. For fine pores, it is much higher than that for large pores. ψ_{o} designates the capillary potential close to saturation.

osmotic potential, ψ_{osm} SI unit: m
Height of water in soils caused by differences in salt concentrations across semipermeable regions and leading to water enrichment in saline zones of soils.

gravity potential, ψ_z SI unit: m
Height of water subject to gravitational force and of most importance close to water saturation.

pore volume, V_{P} SI units: m^3
Volume of water required to replace water in a given volume V of a saturated porous medium.

Note 1: For example, if the total volume of the medium is $V = 10$ m^3 and the effective porosity is $n_{\mathrm{e}} = 0.4$, the pore volume equals 4 m^3 of water. ($V_{\mathrm{P}} = n_{\mathrm{e}}\, V$). The effective porosity n_{e} is the quotient of the pore volume to the total soil volume considered ($n_{\mathrm{e}} = V_{\mathrm{P}} / V$).

pore size SI unit: m
See Section 2.1.

tensiometer
Device used to determine matrix water potential ψ_{m} in the vadose zone (unsaturated zone above the groundwater), and consisting of a glass or plastic tube with a porous ceramic cup filled with water.

Note: By applying different suction pressures, the pore water removable at that specific pressure can be measured. Tensiometers are grouped according to their forms as suction cups or suction plates.

tension disc infiltrometer or **disc permeameter**

Device used to measure in situ infiltration. A disc permeameter comprises a nylon mesh supply membrane (with a very small diameter around 10–40 µm), a water reservoir, and a bubbling tower. The bubbling tower is connected to the reservoir and is open to air. The bubbling tower controls the potential applied to the membrane by adjusting the water height in the air-inlet tube.

Note 1: Single- and double-ring infiltrometers measure flow only under ponded (saturated) conditions, and when used in soil with distinct macropores, preferential flow will dominate the flow. This does not reflect infiltration under rainfall or sprinkler irrigation. Therefore, many authors attempt to create a negative potential (tension) on the water flow to exclude macropores in the flow process, and hence measure only the soil matrix flow.

lysimeter

Laboratory column of selected representative soil or a protected monolith of undisturbed field soil with which it is possible to sample and monitor the movement of water and substances [124].

Note: In practice, a monolith lysimeter consists of an undisturbed soil block or cylinder, embedded in an inert container (e.g., stainless or galvanized steel or Fiberglas) with a bottom permeable to drainage water or leachate (e.g., a perforated bottom, or quartz sand filter bottom). A sampling device allows for collection of the leachate. A minimum surface area of the soil core of 0.5 m^2 is recommended. The height of the soil sample is usually in the range 0.1 to 1.3 m [125].

APPENDIX 2: COMMON AND IUPAC NAMES OF PESTICIDES MENTIONED IN THIS REPORT

Common name	IUPAC name	CAS No.
2,4-D	(2,4-dichlorophenoxy)acetic acid	94-75-7
alachlor	2-chloro-*N*-(2,6-diethylphenyl)-*N*-methoxymethylacetamide	15972-60-8
aldicarb	(*EZ*)-2-methyl-2-(methylsulfanyl)propanal *O*-methylcarbamoyloxime	116-06-3
atrazine	6-chloro-*N*-ethyl-*N*'-propan-2-yl-1,3,5-triazine-2,4-diamine	1912-24-9
bentazon(e)	3-propan-2-yl-1*H*-2,1,3-benzothiadiazin-4(3*H*)-one 2,2-dioxide	25057-89-0
bromacil	(*R,S*)-5-bromo-3-butan-2-yl-6-methyluracil	314-40-9
bromoxynil	3,5-dibromo-4-hydroxybenzonitrile	16118-49-3
carbetamide	(*R*)-1-(ethylcarbamoyl)ethyl phenylcarbamate	15663-66-2
carbofuran	2,3-dihydro-2,2-dimethylbenzofuran-7-yl methylcarbamate	1696-60-8
chloridazon	5-amino-4-chloro-2-phenylpyridazin-3(2*H*)-one	15545-48-9
chlorotoluron	*N'*-(3-chloro-4-methylphenyl)-*N,N*-dimethylurea	2921-88-2
chlorpyrifos	*O,O*-diethyl *O*-3,5,6-trichloropyridin-2-yl phosphorothioate	1702-17-6
clopyralid	3,6-dichloropyridine-2-carboxylic acid	21275-46-2
cyanazine	2-(4-chloro-6-ethylamino-1,3,5-triazin-2-ylamino)-2-methylpropanenitrile	52918-63-5
deltamethrin	(*S*)-cyano-(3-phenoxyphenyl)methyl (1*R*,3*R*)-3-(2,2-dibromoethen-1-yl)-2,2-dimethylcyclopropanecarboxylate	1918-00-9
dicamba	3,6-dichloro-2-methoxybenzoic acid	120-36-5
dichlorprop	(*R*,*S*)-2-(2,4-dichlorophenoxy)propanoic acid	40843-25-2
diclofop	(*R*,*S*)-2-[4-(2,4-dichlorophenoxy)phenoxy]propanoic acid	34205-21-5

dimefuron	*N*′-[4-(5-*tert*-butyl-2-oxo-1,3,4-oxadiazol-3(2*H*)-yl-3-chlorophenyl]-*N*,*N*-dimethylurea	60-51-5
dimethoate	*O*,*O*-dimethyl *S*-methylcarbamoylmethyl phosphorodithioate	67564-91-4
fenpropimorph	(*R*,*S*)-*cis*-4-[3-(4-*tert*-butylphenyl)-2-methylpropyl]-2,6-dimethylmorpholine	69377-81-7
fluroxypyr	4-amino-3,5-dichloro-6-fluoropyridin-2-yloxyacetic acid	66767-39-3
fonofos	(*R*,*S*)-*O*-ethyl *S*-phenyl ethylphosphonodithioate	34123-59-6
isoproturon	*N*,*N*-dimethyl-*N*'-(4-propan-2-ylphenyl)urea	330-55-2
linuron	*N*'-(3,4-dichlorophenyl)-*N*-methoxy-*N*-methylurea	94-74-6
MCPA	(4-chloro-2-methylphenoxy)acetic acid	7085-19-0
mecoprop	(*R*,*S*)-2-(4-chloro-2-methylphenoxy)propanoic acid	41394-05-2
metamitron	4-amino-3-methyl-6-phenyl-1,2,4-triazin-5(4*H*)-one	1869-97-9
methabenzthiazuron	benzothiazol-2-yl-*N*,*N*′-dimethylurea	512 18-45-2
metolachlor	2-chloro-*N*-(6-ethyl-2-methylphenyl)-*N*-[(1*R*,*S*)-2-methoxy-1-propan-2-yl]acetamide	21087-64-9
metribuzin	4-amino-6-*tert*-butyl-3-methylsulfanyl-1,2,4-triazin-5(4*H*)-one	15299-99-7
napropamide	(*R*,*S*)-*N*,*N*-diethyl-2-(1-naphthyloxy)propanamide	40487-42-1
pendimethalin	*N*-(1-ethylpropyl)-2,6-dinitro-3,4-dimethylaniline	1918-02-1
picloram	4-amino-3,5,6-trichloropyridine-2-carboxylic acid	67747-09-5
prochloraz	*N*-propyl-*N*-[2-(2,4,6-trichlorophenoxy)ethyl]imidazole-1-carboxamide	60207-90-1
propiconazole	(2*R*,*S*,4*R*,*S*;2*R*,*S*,4*S*,*R*)-1-[2-(2,4-dichlorophenyl)-4-propyl-1,3-dioxolan-2-ylmethyl]-1*H*-1,2,4-triazole	122-34-9
simazine	6-chloro-*N*,*N*′-diethyl-1,3,5-triazine-2,4-diamine	5915-41-3
terbuthylazine	*N*′-*tert*-butyl-6-chloro-*N*-ethyl-1,3,5-triazine-2,4-diamine	2303-17-5
triallate	*S*-(2,3,3-trichloroprop-2-en-1-yl) *N*,*N*′-dipropan-2-yl(thiocarbamate)	82097-50-5
triasulfuron	*N*′-[2-(2-chloroethoxy)phenylsulfonyl]-*N*-(4-methoxy-6-methyl-1,3,5-triazin-2-yl)urea	1582-09-8
trifluralin	2,6-dinitro-*N*,*N*-dipropyl-4-trifluoromethylaniline	1689-84-5