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# Heterogeneous water flow and pesticide transport in cultivated sandy soils

Description of model concepts

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M. Leistra and J.J.T.I. Boesten



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M. Leistra and J.J.T.I. Boesten

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## Abstract

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There is ample experimental evidence that complications in water flow and pesticide transport can occur in cultivated humic-sandy and loamy-sandy soils. As a result, pesticide leaching to groundwater and water courses can be higher than expected. We made an inventory of mechanistic/deterministic model concepts that may be suitable for simulating preferential water flow and pesticide transport in these soils. The convection-dispersion approach, the mobile-stagnant concept, the dual-velocity concept, the explicit description of horizontal diffusion, the soil column approach and a concept of finger flow are discussed. Only for comparatively simple concepts it is feasible to ever obtain the parameter values. Ideally, the data sets to be used for testing the models concepts should be detailed and complete. Discrimination between the validity of the model concepts requires the variation in the measuring results to be limited. Testing of the model concepts under various representative field conditions is needed, to gain confidence in their results.

Keywords: advection, convection, deterministic, diffusion, dispersion, groundwater, leaching, mechanistic, model testing, preferential transport, soil domains.

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**Alterra report 2182**  
Wageningen, May 2011

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# Summary

Humic-sandy and loamy-sandy soils are used on a large scale for agriculture in catchment areas for ground-water and surface water intended to be used for drinking water. There is ample experimental evidence that complications in water flow and pesticide transport can occur in such soils. This can lead to the pesticide concentrations in groundwater and water courses to be higher than expected on the basis of computations with conventional models for the evaluation of leaching risks. Sub-models are needed that simulate the complications in pesticide transport in soil in the computation models.

The heterogeneity of water flow and substance transport in cultivated sandy soils is illustrated by discussing the results of some field experiments. The ranges in volume fraction of water and in concentration of substances measured per depth at the sampling times are very wide. Therefore it can be difficult to select the most appropriate model concept to describe the data. Further, gaps and uncertainties in the measured data can hamper their use in the testing of preferential transport models.

Experiences with the simulation of water flow in sandy soils with the Richards equation, using laboratory-measured hydraulic relationships, are described. Wetting of the soil in the field was found to be irregular and less complete than expected from the moisture retention of completely-wetted soil samples in the lab (based on the water-withdrawal curve).

We made an inventory of model concepts that may be suitable for simulating preferential water flow and pesticide transport in cultivated sandy soils. It should be possible to incorporate the concepts in a mechanistic/deterministic model like the SWAP-PEARL combination. The flexibility of SWAP-PEARL in dealing with the many processes in the field (soil, hydrology, crop, pesticide, management, etc.) should be retained. Comparatively simple concepts are preferred, which require only a few additional parameters that can hopefully be measured.

The concept of enhanced dispersion in a single soil domain for each layer (convection-dispersion approach) does not require modification of the model. Only the input value for the dispersion length needs to be increased to account for preferential transport. The concept corresponds to wave-shaped distributions in soil and breakthrough curves. The dispersion length can be taken to be different for the soil layers (so considering each of them as one soil domain).

The concept of mobile-stagnant water phases is comparatively simple and only requires a few additional parameters. It can explain fast transport of the front part of the concentration distribution and long tailing of the back part. A substantial stagnant water phase for prolonged periods does not seem to be representative for cultivated sandy soils, as movement of weakly-sorbed substances from the top layer is common. The incorporation of variable volume fractions of water in both domains improves the usability of the concept for field soils (drier and wetter periods).

An attractive concept for cultivated sandy soils is the dual-velocity concept with slow-flow and fast-flow water phases, respectively. It allows for a substantial contribution of matrix transport, with an additional contribution of preferential transport. The volume fractions of water in both domains can be simulated to be highly variable, which corresponds to field conditions. However, various parameters and relationships are needed which may be difficult to determine.

The concept of transversal (horizontal) diffusion in a stagnant domain in sandy soils from a mobile domain (vertical transport) has mainly been used as a research tool. It does not allow for the highly variable soil moisture conditions in the field.

The soil columns approach (without transversal interaction) is mainly used for the simulation of plots in the field, e.g. with different hydraulic properties. Leaching from the whole field is calculated from the leaching contributions for each of the soil columns, computed with the one-dimensional model (no model modification needed).

The concept of finger flow in a water-repellent intermediate layer (no horizontal interaction) was derived from experiments for a sand soil with permanent grass cover. Water flow and substance transport in the wettable layers above (top layer) and below (subsoil) the intermediate layer are assumed to be rather uniform. This concept seems to be too extreme for cultivated sandy soils, which are less water-repellent. Consideration of two flow domains in the intermediate layer (fingers and between-fingers) may increase the usability of the concept.

We made an inventory of experiences with the modelling of preferential flow and transport in soils with macropores, as far as they seem relevant for cultivated sandy soil. In the calibration of two-domain computations against measurements, the estimation of parameters is most feasible if the transport behaviour deviates substantially from convection-dispersion behaviour (wave shape). Calibration is facilitated if the variation in measuring results is comparatively small. The difference in transverse equilibration between non-sorbed tracers and sorbed pesticides by diffusion needs further investigation.

Various requirements for sub-models dealing with preferential flow and transport, to be used in the evaluation of leaching risks, are discussed. Well-defined scenarios are needed, that are often derived from specific detailed field experiments. The combination of sub-model and input data must have been tested under various representative field conditions, to gain confidence in the results.

# 1 Introduction

Plant protection compounds (pesticides) applied to crops in the field have to be evaluated with respect to the risk of environmental contamination and effects. After spraying in the field, pesticides are subjected to transport with the water flow in the soil profile. Dependent on the strength of adsorption to soil and the rate of transformation in soil, there may be a risk of leaching to groundwater and water courses (e.g. via tube drains). This may cause residues in water intended to be used for drinking water supply. Further, there may be effects on the aquatic organisms in water courses. In the pesticide registration procedures, the concentrations that can be emitted from agricultural soils to other environmental compartments have to be evaluated.

Soils in the field can be very heterogeneous. Sedimentation may have resulted in a complex pattern of materials of different textural classes. Soil forming processes (e.g. transport of clay, organic matter, iron hydroxides) often have modified the build-up of the soil profile. Biological activity has resulted in root channels, wormholes, etc. The preparation of the land for agriculture may have involved digging trenches for tube drainage, subsoil loosening, filling-up depressions/ditches, etc. Further, the regular soil cultivations affect the heterogeneity of the soils. The result is a highly complex system of soil pores available for water flow and transport of substances.

The classical idea is that water flows rather uniformly through the whole soil body. Flow rate in the various soil pores is then assumed to be somewhat different, with an average value and a variation around the average. A substance is then transported in soil as a wave (chromatographic transport), which widens by hydrodynamic dispersion during transport. More and more experimental results obtained in the last decennia showed that these concepts are invalid for various soil, weather and irrigation conditions.

Water flow and substance transport in loamy/clayey soils with macropores have been the subject of much research in the past decennia. The macropores (e.g. shrinkage cracks, earthworm burrows, root holes, voids between blocky structures) are often clearly visible at the soil surface and in the soil profile. Water from intensive precipitation can flow directly into the macropores, thus moving substances quickly to greater depths in soil. Reviews on water flow and substance transport in loamy/clayey soils with macropores, and on the modelling of these processes, have been presented by e.g. Jarvis (2007) and Köhne et al. (2009a, 2009b). Macropores up to the soil surface can also occur in more sandy soils that are not cultivated regularly, e.g. perennial grassland, orchard soils and no-tillage arable soils. The complications in water flow and substance transport in soils with macropores up to the soil surface are outside the scope of the present study. Nevertheless, some of the model concepts used for loamy/clayey soils can also be used for cultivated humic-sandy and loamy-sandy soils, so these will be included here.

Computation models are important tools in the assessment of the risk of pesticide leaching through soils to groundwater and water courses. About a decade ago, Boesten (2000) characterised the possibilities and limitations of these models. In some model tests, it was found that the movement of the bulk of a pesticide in sandy soils could be described reasonably well by convection-dispersion transport models. Preferential fast transport of a fraction of the pesticide in sandy soil could not be described adequately yet. Different concepts were used in preferential transport models, which required a series of input data. Obtaining the input data for such models in an independent way (not by calibration) was considered to be a stubborn problem.

Heterogeneities in water flow and substance transport in cultivated sandy soils (humic and loamy) have received comparatively little attention. However, there is ample experimental evidence that complications can occur in such soils (Leistra and Boesten, 2010). Non-uniform water flow may be caused by processes in the plant canopy (e.g. stem flow), at the soil surface (e.g. surface depressions) or within the soil (e.g. differences in hydraulic conductivity). Sandy soils are used on a large scale for agriculture in catchment areas for groundwater and surface water intended to be used for drinking water. The question rises how the complications in water flow and pesticide transport in sandy soils can be incorporated into computation models. An extended model could be used as a tool in a more realistic evaluation of the risk of pesticide leaching from sandy soils to groundwater and water courses.

The present study deals with mechanistic-deterministic descriptions of preferential flow and transport processes in heterogeneous soils. The concepts should be applicable to cultivated humic-sandy and loamy-sandy soils. A selection is made of some comparatively simple concepts, for which only a few additional parameters are needed. Somewhat more complex concepts would require several input data which are difficult to estimate. It should be possible to combine the concepts with the SWAP-PEARL combination of models based on the Richards equation for water flow and the convection-dispersion equation for substance transport (Van Dam et al., 2008; Leistra et al., 2001; Tiktak et al., 2000). The differential equations are solved numerically using the finite-difference approach. The capability of SWAP-PEARL to describe a wide range of processes in the field in a flexible way (including various complications) should be retained.

In Chapter 2 an outline is given of experimental results on water flow and substance transport in sandy soils. The examples mainly deal with studies in The Netherlands. Experiences with respect to the simulation of water flow in sandy soils are described in Chapter 3. In Chapter 4, six concepts for the modelling of water flow and substance transport in sandy soils are discussed:

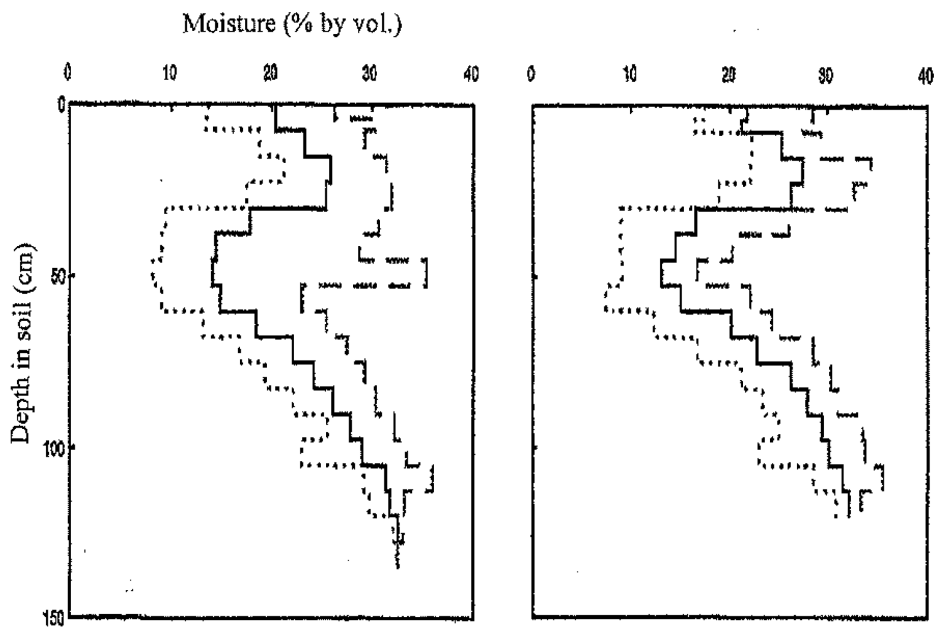
- 1) convection-dispersion,
- 2) mobile-stagnant domains,
- 3) dual-velocity domains,
- 4) transverse diffusion,
- 5) soil column approaches and
- 6) flow fingers in a water-repellent intermediate layer.

Chapter 5 describes general experiences with preferential transport modelling. The requirements for the use of computation models in the evaluation of leaching risks are discussed (Chapter 6). Finally, the general discussion, conclusions and recommendations are presented in Chapter 7.

## 2 Nature of experimental results

In the comparison of computations and measurements for water and substances in the soil profile, usually averaged values of the measurements per depth were used. The computed distribution with depth in the soil is then compared with the distribution of the average of the measured values per depth. Preferably, a confidence interval of the measurements is also given. For a thorough understanding of what actually happens, however, more attention is needed for the spatial variation in the measurements. The heterogeneity in the transport processes in sandy soils is illustrated here, using first of all the results of a field study for humic-sandy soil in The Netherlands.

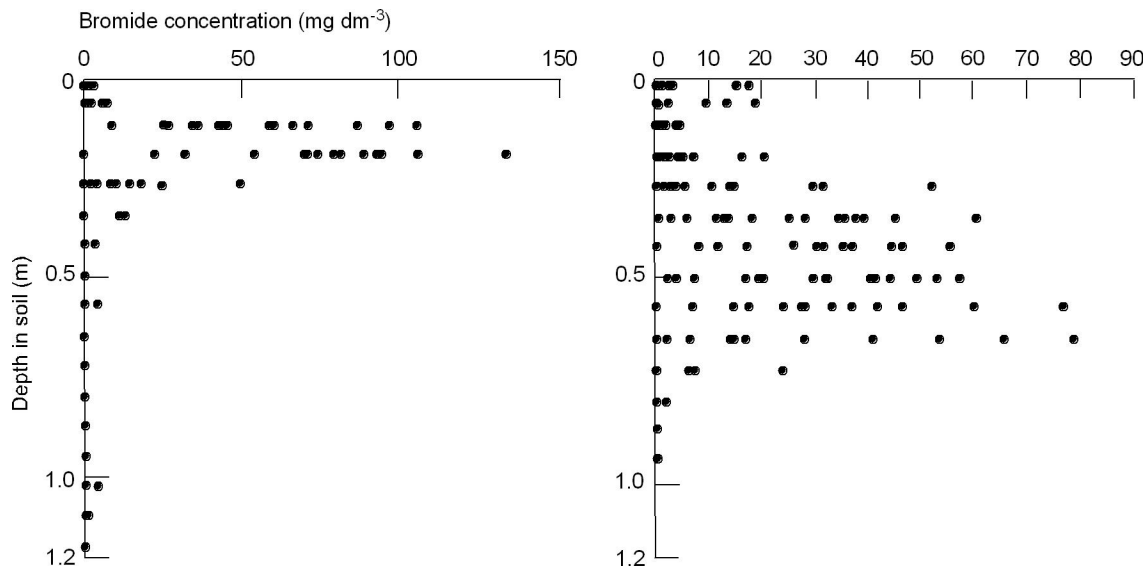
The volume percentages of water in a humic-sandy soil used for arable farming (Vredepeel, The Netherlands), as measured by Hamminga et al. (1994), are presented in Figure 1. Besides the averaged values per depth, the ranges of measured volume percentages are given. The situations deal with November/December, a period in which the soil profile is gradually wetted due to the increasing rainfall surplus. Wetting of the soil takes place in a very heterogeneous way. The hydraulic conductivity of soils is strongly dependent on the volume fraction of water, so the spatial differences in conductivity will be enormous. It can be expected that water from further rainfall is conducted mainly via the wetter places in soil.



**Figure 1**

*Volume percentages of moisture as a function of depth in the Vredepeel humic-sandy soil on 23 November (left) and 14 December (right) (Hamminga et al., 1994). Average values (solid line), minimum values (dotted line) and maximum values (dashed line).*

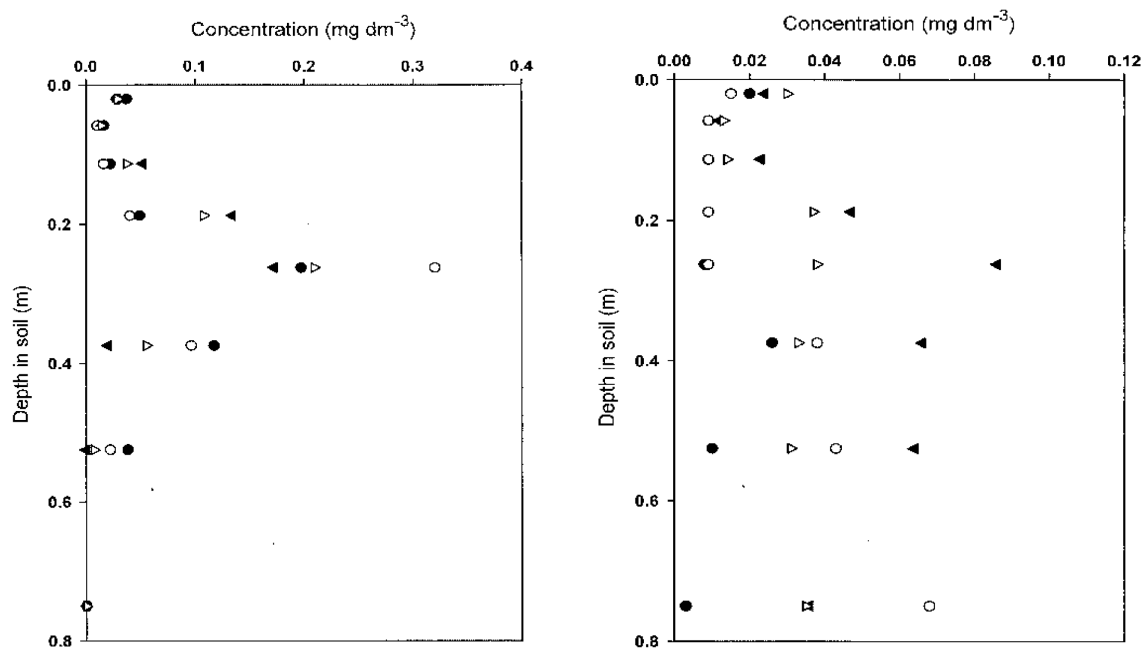
The water tracer bromide ion moved roughly in a wave through the soil profile, but the differences in the concentration per depth were very large (Hamminga et al., 1994; Figure 2). At some places in the soil profile, bromide concentration was (almost) zero, although the depth was well within the range of the main wave of bromide ion. The wetter places in soil contained higher concentrations of bromide ion than the drier places. The spreading in the bromide concentration per depth was greater than the spreading in the bromide applied at the soil surface. This indicates that there was a lateral (horizontal) transport component in the upper part of the soil profile, followed by localised more vertical transport. Incidental concentrations of bromide ion were measured in the upper groundwater in the period before the main wave arrived.



**Figure 2**

*Concentrations of bromide ion (applied on 22 November) in the Vredepeel humic-sandy soil measured on 14 December (left) and 3 January (right) (Hamminga et al., 1994).*

The individual concentrations of bentazone measured in the Vredepeel humic-sandy soil were reported by Van der Pas (1993). The herbicide was measured in four soil samples, each composed of the four subsamples per layer and per field section (16 cores per time for the whole field). The measured concentrations are given in Figure 3. The concentration of bentazone showed a very wide range of values at most of the sampling depths, in spite of the combination of the four subsamples per field section.



**Figure 3**

Concentrations of bentazone (applied on 22 November) in the profile of the Vredepeel humic-sandy soil on 3 January (left) and 5 March (right) (from tables in: Van der Pas, 1993).

Besides the concentrations in soil, Van der Pas (1993) also reported concentrations of bentazone measured in the upper groundwater of the Vredepeel field. In one of the four field sections (lowest soil surface; shallowest water table), bentazone showed up comparatively early (at 103 days after application in the autumn) and its concentration increased to substantial levels at the end of the experiment (at 474 days). In a second field section, bentazone appeared in the groundwater after 474 days. In the other two field sections (highest soil surface; deepest groundwater table), concentration of bentazone in the groundwater remained below detectable level in the experimental period (474 days). The differences in bentazone concentration in groundwater seem to be too great to make the data set suitable for the testing of leaching models for the whole (averaged) field.

The herbicide bentazone was applied in summer on a barley crop grown on an undisturbed loamy-sand-on-sand soil (1 m deep) in a lysimeter. In dry periods (Sweden), rainfall was supplemented by irrigation. The behaviour of bentazone in the soil was simulated with the MACRO model, using the option of a single matrix-flow domain (only micropores) (Jarvis et al., 1994). First of all, the simulation of water flow in the lysimeter soil was calibrated. Using the single-domain option, it was not possible to simulate the early start of bentazone leaching from the lysimeter in the autumn. It was concluded that preferential water flow and herbicide transport occurred in the sandy soil.

Sarmah et al. (2004) described experiences with the testing of pesticide-behaviour models for agricultural soils in New Zealand. The field experiments used for testing the models yielded uncertain results. The pesticides arrived earlier in deeper suction cups than in shallower cups, which shows that the latter had been by-passed. The authors presumed that preferential transport of the pesticides in soil was missed by soil coring. The measuring results for the pesticides per depth and time combination were highly variable. When compared, suction-cup samples and soil-core samples can give conflicting results. In various cases, no site-specific adsorption and transformation-rate data were available as input when testing the models. In other cases,

there was a great discrepancy between the processes in the lab and in the field. The differences between model results and experimental results were often large. In view of the uncertainties in the data sets, the authors expected difficulties in their use for the testing of preferential transport models.

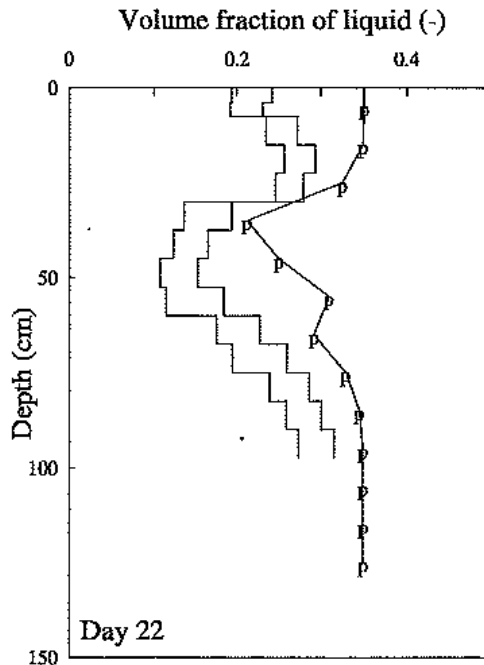
The brief survey in this chapter shows that the differences in the volume fractions of water measured per depth in soil at each sampling time were great. Consequently, the differences in hydraulic conductivity will be also great. The substance concentration measured per depth showed wide ranges. Further, these concentrations are dependent on the method of sampling, e.g. suction sampling of soil solution versus soil coring. It is difficult to measure preferential transport in soil via profile sampling, local pathways with high concentrations can be easily missed. The processes in case of pesticides can be expected to even more complex than those with inert tracers. The adsorption and rate of transformation of pesticides in the field soil may deviate from that measured in the laboratory. Further, adsorption and transformation rate may show a wide variability with location in the field soil. In this chapter only a few examples are given on the nature of the results of measurements for moisture and substances in sandy soils. A more comprehensive review of the complications in water flow and substance transport in sandy soils, and of their causes, has been presented by Leistra and Boesten (2010).



### 3 Experiences with simulating water flow

There are various reasons why water flow through sandy soils can be non-uniform. Precipitation water falling on the crop canopy follows special pathways to the soil surface, by stemflow and leafdrip. Infiltration into the soil surface may show differences due to variation in soil structure and possible water repellency. At high precipitation intensities, water is redistributed over the soil surface and flows to (micro)depressions where it infiltrates. Hydraulic conductivity within the soil profile differs due to differences in texture, in structure and in volume fraction of water. A comprehensive review of the causes of the variation in water flow in soils with location and time has been given by Leistra and Boesten (2010). In this Chapter, experiences with the simulation of water flow using computation models are discussed. Such experiences provide further information on the nature of water flow, as a carrier for substance transport in soil.

Water flow in the humic-sandy soil profile of the Vredepeel (The Netherlands) experimental field was simulated by Van den Bosch and Boesten (1994) and Van den Bosch et al. (1999), using the SWACROP-PESTLA combination of models. When using the moisture retention curves measured in the laboratory, the volume fractions of water in the field were over-estimated (Figure 4). The moisture retention curves for the three soil layers had to be lowered to obtain a reasonable description of water distribution in soil (calibration). The hydraulic conductivities had to be increased for two layers (Van den Bosch et al., 1999), to improve the description of water redistribution in the soil profile in wet and dry periods.



**Figure 4**

*Computed and measured soil moisture profiles in the humic sandy soil of the Vredepeel experimental field on 14 December (Van den Bosch and Boesten, 1994).*

Water flow in an arable loamy-sand soil was described by the mobile-stagnant concept (Larsson et al., 1999). Water flow in the mobile domain was described by using the Richards equation. The fraction of soil water containing mobile water was obtained by calibration: it ranged from 0.77 in the top layer to 0.85 in the subsoil to 0.7 m depth. The volume fraction of water as a function of depth in soil was described reasonably well. On the contrary, the one-region model (all water mobile) over-estimated the volume fraction of water. The fraction of the soil water being mobile tended to increase in the course of the winter-half-year, as the soil became wetter by the rainfall surplus.

Attempts were made to describe water flow in the humic-sandy soil at Vredepeel (The Netherlands) with the PESTLA model (Boesten and Gottesbüren, 2000). When using hydraulic relationships measured in the laboratory (both for the field and from a data base) the volume fractions of water in soil were over-estimated. The moisture retention curves for the soil layers had to be calibrated to obtain a reasonable description of the soil moisture profiles. The calibrated moisture retention curves indicated that moisture retention in the soil layers was substantially lower than derived from the lab measurements.

Eighteen model users selected one or two models (from a total of ten models) to simulate water flow in the Vredepeel humic-sandy soil (Vanclooster and Boesten, 2000). The data set on the Vredepeel experiment was provided by Boesten and Van der Pas (2000). The models were based on the Richards equation or on the capacity approach for the description of water flow. The modelling efficiency for water flow was low when the models were not calibrated (Vanclooster and Boesten, 2000). The hydraulic relationships measured in the laboratory had to be adjusted to improve the correspondence of the simulations with the soil moisture profiles measured in the field.

In summary, it was found to be difficult to simulate water flow in field soils on the basis of the hydraulic relationships measured in the laboratory. Moisture retention in the field is lower than expected, which indicates that the soils are incompletely/non-uniformly wetted. The soil between the main flow paths is expected to be gradually wetted, with a lateral flow component. The moisture retention curve may be more critical for an acceptable description of the soil moisture profile than the hydraulic conductivity curve.

## 4 Modelling substance transport

### 4.1 Introduction

The aim of this chapter is to discuss some concepts that may be suitable for modelling heterogeneous pesticide transport in cultivated humic-sandy and loamy-sandy soils. A selection is made from the concepts presented in the literature. The concepts should be simple, because models based on somewhat more complex concepts require several input data presenting difficulties in estimation. Further it should be possible to combine the concepts with the SWAP-PEARL combination of models. This combination is based on the Richards equation for water flow and the convection-dispersion equation for substance transport. The processes are described in one dimension (vertical). The differential equations are solved numerically using the finite-difference approach. The flexibility of the SWAP-PEARL model in describing the wide range of relevant processes in the field should be retained. The selected concepts are mechanistic-deterministic in nature, like the SWAP-PEARL model.

In the following sub-chapters, six concepts for modelling heterogeneous transport in sandy soils are described:

- 1) the convection-dispersion approach for one soil domain, using enhanced values of the dispersion length (dispersivity);
- 2) the soil system is divided into two domains with mobile and stagnant water, respectively;
- 3) the soil system is divided into two domains with comparatively fast and slow water flow, respectively;
- 4) transversal (horizontal) diffusion from a mobile region in a stagnant region is simulated explicitly;
- 5) the soil of a field is divided into independent soil columns with different water flow velocities, etc.;
- 6) flow and transport through a set of fingers in an otherwise water-repellent intermediate soil layer between wettable layers.

### 4.2 Convection-dispersion in one soil domain

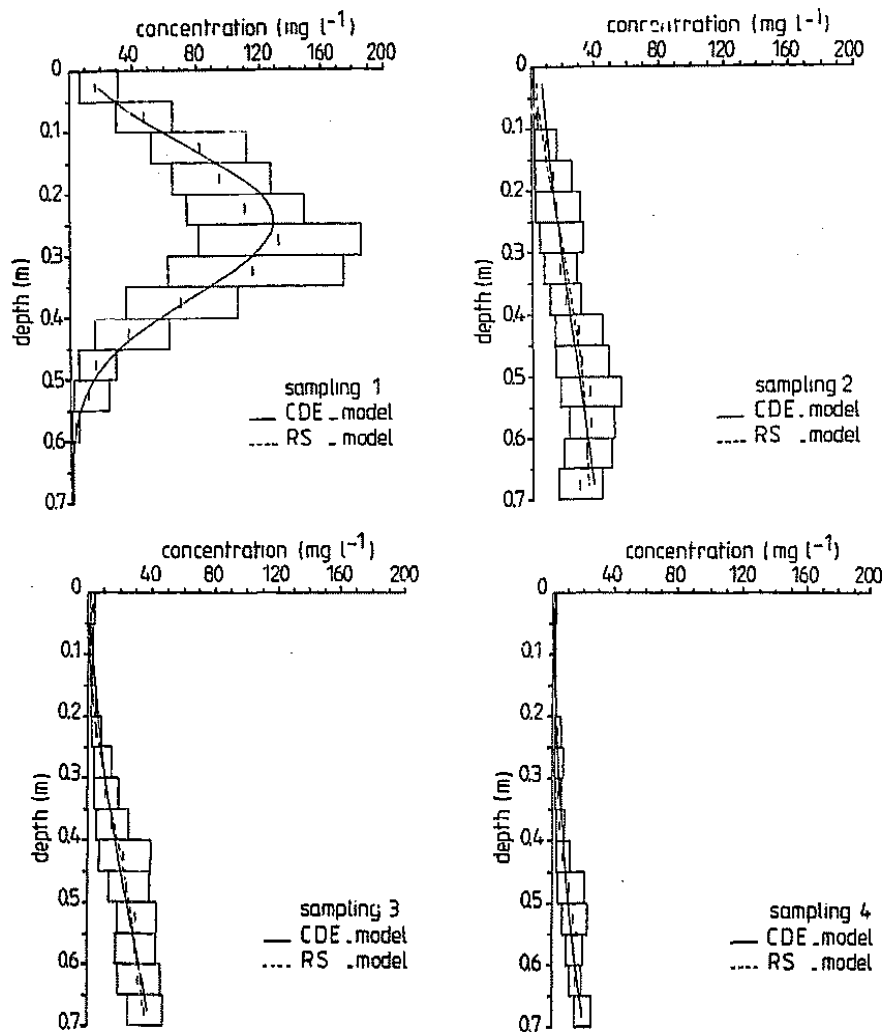
#### 4.2.1 Tracers

In the continuum approach, the soil system is considered to consist of one domain, with water flow and substance transport through the whole soil matrix. Differences in transport rate through the pore system are usually described by a dispersion coefficient in the convection-dispersion equation.

Undisturbed soil columns were taken from three depths in an agricultural humic-sandy soil: 0-30 cm, 30-60 cm and 60-90 cm (Beese and Wierenga, 1983). Pulses of chloride ion and tritiated water were applied in the constant water fluxes of 3 and 10 mm/day. The water flowing from the bottom of the columns was collected at a pressure of -100 hPa (unsaturated flow). The dispersion coefficients were calculated from the break-through curves of the tracers. The dispersion coefficient increased with depth of the layer, with the coefficient for the 60-90 cm layer being much higher than those for the layers above.

In field conditions with sandy soils under intermittent rainfall, the deviation from local equilibrium by lateral diffusion may not be extreme. In such cases, it can be attempted to describe the effect of gradual lateral diffusion by using enhanced values of the dispersion length in the convection-dispersion approach (Van Genuchten and Dalton, 1986).

Van Ommen et al. (1989) simulated the movement of bromide ion (applied in December) in the loamy-sand soil of an arable field (Hupsel, The Netherlands) using the convection-dispersion equation (CDE approach). Water flow was assumed to be steady-state at constant volume fraction of water, at a rate based on the tile-drain outflow. They estimated that a large fraction of the water phase in soil participated in water flow. A high value of the dispersion length had to be used to describe the wide spreading of the average concentration with depth in the soil profile (Figure 5). If they had simulated transient water flow (alternatively downward and upward), a lower dispersion length would have been applicable. The concentrations measured in the upper groundwater showed an erratic pattern (values not reported); they were not used in model testing.

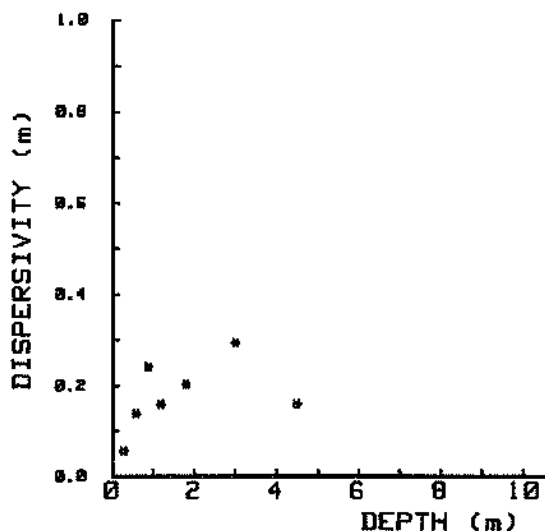


**Figure 5**

Concentration profiles of bromide ion (applied in December) in arable loamy-sand soil after 70, 167, 225 and 305 mm of drain discharge (Van Ommen et al., 1989; ©Elsevier, with permission). With confidence intervals of 90%. Solid lines: movement simulated with the convection-dispersion equation for steady-state water flow.

Attention is needed for the scale effects on the value of the dispersion length in the convection-dispersion equation. In parts of the vadose zone, a roughly linear increase of the dispersion length for anion tracer with depth in the soil was found (Butters and Jury, 1989; Khan and Jury, 1990). This may be related to the geogenetic build-up of the layers and to their structural condition. The increase is illustrated for the upper 5 m

of a vadose zone with loamy-sand soil (about 1 m thick) on a sequence of sandy and loamy layers (Figure 6). It should be noted that, in the PEARL model, the dispersion length in the convection-dispersion equation is introduced as a function of depth in the soil (Tiktak et al., 2000).



**Figure 6**

*Field-scale dispersion length (dispersivity) as a function of depth in the vadose zone (Butters and Jury, 1989).*

Beven et al. (1993) compiled dispersion-length values from transport experiments with tracers in undisturbed soil in cores and field. The range of dispersion lengths used to describe the measurements (for divergent soil types) was very wide. The dispersion tends to increase with increasing size of the experimental system. The authors indicated that other model-parameter combinations may describe a set of experimental data equally well (problem of parameter identifiability). They considered predictions of substance transport in other conditions, based on the fitted parameter values, to be rather uncertain.

Movement of bromide ions through the humic-sandy soil of the experimental field at Vredepeel (The Netherlands) was simulated by Van den Bosch and Boesten (1994) and Van den Bosch et al. (1999), using the SWACROP-PESTLA combination of models. They used a dispersion length of 3 cm. The movement of the main part of the distribution of bromide in soil (average concentrations) was described in a reasonable way, as compared to the measurements. Presumably, some bromide was lost during sampling, with the water flowing from the water-saturated lower end of the soil cores. In the later stages, part of the bromide distribution moved below the measuring depth, so comparison for the deeper soil layers (most relevant for preferential transport) was not possible. Presumably, the comparatively high measured concentrations in the top layer at later stages was caused by the release of bromide (taken up before) from senescent plant parts.

The movement of bromide ions in the humic-sandy soil of the Vredepeel (The Netherlands) experimental field was simulated also by Boesten and Gottesbüren (2000), using the SWACROP-PESTLA model. The simulation of water flow in the soil profile had to be calibrated, because water retention by the soil was over-estimated in the first runs. The dispersion length was set at the standard value of 5 cm. The distribution of the concentration of bromide ion with depth was described reasonably well by the model, as compared to the averages of the measured concentrations. However, part of the bromide distribution moved below the maximum measuring depth, which hampered comparison of computed and measured concentrations in the front part of the

distribution. Part of the measured distribution stayed behind in the top layer, as compared to the computed wave. Possible causes were bromide retention in finer pores (outside the flow pathways) and release of bromide (taken up earlier by the plants) from senescent crop parts (wheat and mustard).

Soil and water factors determining the type of transport in soils were discussed by Vanderborght et al. (2001) on the basis of the leaching of chloride tracer through divergent Belgian soils. At low and moderate rates of water flow, ample time is available for lateral equilibration of substance between the pores with faster and slower transport. As a result, transport can be described then by the convection-dispersion concept. Dispersion length tends to increase as water flow rate becomes higher. In soils without distinct preferential flow features, dispersion length was almost constant with depth in the soil. Layer transitions in the soil profile were expected to promote lateral mixing of the substance.

Vanderborght and Vereecken (2007) presented an overview of dispersion lengths derived from tracer leaching studies with undisturbed soils. The values were obtained by optimising the concentration profiles and breakthrough curves simulated with the convection-dispersion equation, as compared to the experimental results. The range of dispersion-length values obtained for all soils and water flow conditions was very wide. In sandy soils, dispersion length was roughly at the same level at different water-flow velocities. Dispersion length tended to increase with increasing vertical travel distance of the tracer in soil. This may be related to a certain degree of homogenisation of the top layer by the regular soil cultivations, as compared to geogenetic and pedogenetic impediments in the subsoil. The dispersion length in sandy soils tended to increase when the lateral scale of the experiment increased from column to field scale.

#### **4.2.2 Pesticides**

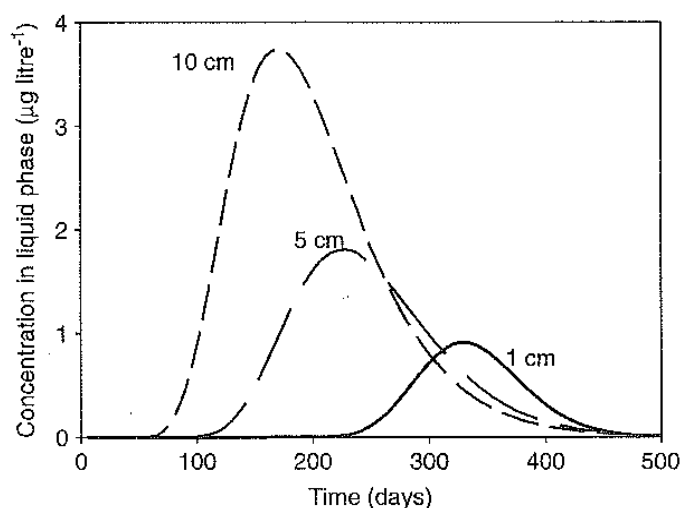
Bentazone behaviour in a soil profile with a sandy-loam top layer on a sand subsoil was simulated by Boesten (1994), using the PESTLA model. The input data were based on the lysimeter study of Bergström et al. (1994) with Mellby soil (Sweden). Laboratory-measured sorption and transformation data for the soil were used for deriving input data. The simulation of water flow in the lysimeter soil monoliths had to be calibrated. The dispersion length was set at the standard value of 5 cm. The model simulated no leaching of bentazone, which was in agreement with the absence of leaching in the lysimeter experiment.

Van den Bosch and Boesten (1994) simulated the movement of bentazone in the humic sandy soil of the Vredepeel (The Netherlands) experimental field, using the SWACROP-PESTLA combination of models. The dispersion length was taken to be 3 cm (as calibrated for bromide ion). A reasonable description of the movement of bentazone through the soil profile was obtained, as compared with the averages of the measurements. Presumably, some bentazone was lost during sampling, with the water flowing from the lower end of the water-saturated soil cores. At some comparison times bentazone had moved below the sampling depth, so comparison between computations and measurements was not possible at these depths. There was a tendency of over-estimation of the concentration in the top layer by the model at 241 and 278 days after application. The decrease in the intermediate soil layer (0.5 to 1.0 m deep) was computed to be slower than measured, presumably because of the rate of transformation in this layer in the field was under-estimated on the basis of the lab measurements (used as input). The more strongly adsorbed nematicide ethoprophos hardly moved below the top 0.2 m of the soil profile, according to both the computations and measurements.

Movement of bentazone in the field with humic-sandy soil at Vredepeel (The Netherlands) was also simulated with the PESTLA model by Boesten and Gottesbüren (2000). First of all the water flow had to be calibrated, until a reasonable description of the soil moisture profiles (lower retention in the field) was obtained. Compared with the averages of the concentrations measured at days 103 and 278, bentazone movement was simulated reasonably well. Because some bentazone moved below the maximum measuring depth, comparison of

computed and measured concentrations in the front part of the distribution was not possible. Later on (comparison at day 474) a bentazone peak was computed to be present around 1 m depth, whereas the herbicide could not be measured anymore. Deviation between the rate of transformation of bentazone in the lab (used as input; comparatively slow) and that in the field was considered to be a main cause. The more strongly adsorbed nematicide ethoprophos was measured to remain in the top 0.2 m of the soil profile. After accounting for the onset of accelerated transformation of ethoprophos at about 200 days after application, the low extent of downward movement of ethoprophos in soil was simulated reasonably well.

In convection-dispersion transport models, greater heterogeneity in transport can be described using a higher value of the dispersion length. The concentration distribution in soil and the breakthrough curve (at 1 m depth) for a hypothetical pesticide in a simplified soil system was calculated by Boesten (2004). Breakthrough of the pesticide was earlier and in higher concentrations as the value of the dispersion length was increased from 1 to 10 cm (Figure 7). According to this approach, pesticide distribution in soil and its breakthrough curve were wave-shaped. The much higher leaching concentration at 10 cm dispersion length is caused by the comparatively short residence time (and thus the lower extent of transformation) of the pesticide in the front part of the distribution.



**Figure 7**

*Effect of dispersion length on the concentration of a hypothetical pesticide in the water flowing from the soil profile at 1 m depth, as a function of time (Boesten, 2004; © John Wiley & Sons, with permission). Dispersion lengths of 1, 5 and 10 cm.*

#### **4.2.3 Concluding remarks**

A fast way to account for heterogeneous transport is to take comparatively high values of the dispersion length (dispersivity) in models based on the convection-dispersion equation. Then there is no need to adapt the models themselves. In various studies, the dispersion length was derived from the concentration distribution in the soil profile. Reasonable correspondence was obtained with the distribution of the average of the measured concentrations per depth. This implies that, in those cases, much of the substance was transported via the bulk of the soil matrix. However, the wide ranges in the concentration measured per depth indicate that transport was heterogeneous.

It should be realised that the dispersion length is a lumped parameter for different processes. It can represent different water-flow rates in the pore system, the time needed for transversal exchange (convection, diffusion) and sorption kinetics at the sorbing surfaces. For soils in the field, it is usually not possible to distinguish the contributions of each of these processes to the spreading in the distribution. Dispersion lengths for non-sorbed tracers and weakly-sorbed pesticides could be at the same level, but they can be expected to be distinctly higher for moderately and strongly sorbed pesticides. The rate of transversal diffusion is comparatively low and the amount to be transported for transversal equilibration is comparatively high for sorbed pesticides.

There are indications that the dispersion length in sandy soils can increase with depth. The dispersion length could be comparatively low in the cultivated top layer, with a certain degree of homogenisation. Differences in texture (e.g. sedimentation pattern), structure (e.g. compacted layers) and soil-formation features (e.g. enrichment horizons) below the top layer could lead to comparatively high dispersion lengths.

Preferential transport can take place through a small part of the soil, so it can be easily missed by soil coring and soil solution sampling. More attention is needed for the concentrations flowing from the soil profile to groundwater and tube-drains. The few experiments with concentration measurements in groundwater and tube-drained water of sandy soils fields need to be investigated further. Possibly, more experiments are needed on the relation between the concentration distribution in the sandy-soil profiles (especially in the lower part) and the concentration in groundwater and tube-drain water.

## **4.3 Mobile-stagnant domains**

### **4.3.1 Introduction**

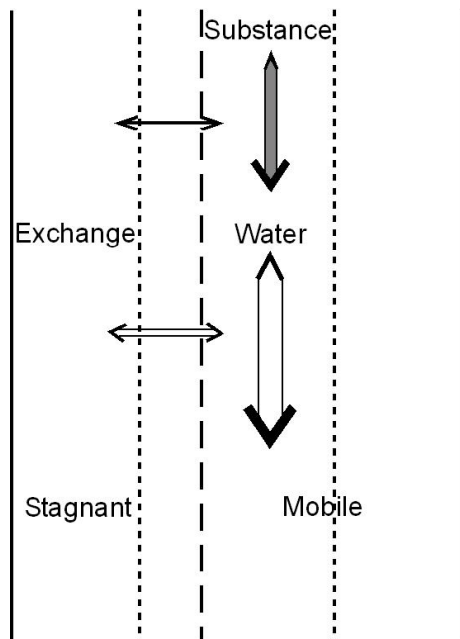
In the mobile-stagnant models, two soil domains are distinguished (Figure 8):

- 1) a mobile domain in which the water flows vertically. The substance is transported vertically by convection (accompanied by dispersion) and by diffusion;
- 2) a stagnant domain in which the water is 'immobile' (no vertical flow). The substance is transported by horizontal exchange between the mobile and stagnant domains.

The mobile domain is assumed to contain the comparatively large and more continuous pores. The pores in the stagnant domain are considered to be comparatively small and less continuous. The horizontal exchange of substance between the mobile and stagnant domains can be described in different ways. An example is the use of the first-order rate equation on the basis of the difference in concentration in the water phases of the two domains. This equation mimics the diffusion of substance between the water phases in the domains.

Often, the substance is considered to be uniformly distributed in the water phase of a domain at each depth. In both the mobile and stagnant domains, adsorption and transformation of a pesticide have to be considered. The concept of distinguishing soil domains with mobile and stagnant water has been used already for several decades (Van Genuchten and Cleary, 1982); the use in soil studies from the 1970s on is discussed here.





**Figure 8**

*Outline of the mobile-stagnant concept for heterogeneous water flow and substance transport in soil. Variable soil moisture condition. Dashed line = wetter condition; dotted lines = drier condition.*

#### 4.3.2 Studies in the 1970s

The water phase in soil was divided into a mobile fraction and a stagnant fraction (Van Genuchten and Wierenga, 1976). Downward water flow (steady state) and substance transport (convection + dispersion) occurred in the mobile phase. Substance transfer between the mobile and the stagnant water was described by the first-order rate equation (based on concentration difference), which represents diffusion between the phases. In a dynamic soil region (fraction  $f$ ), sorption was assumed to be in equilibrium with the concentration in the mobile water phase. The stagnant soil region (fraction  $1-f$ ) was in sorption-equilibrium with the stagnant water phase.

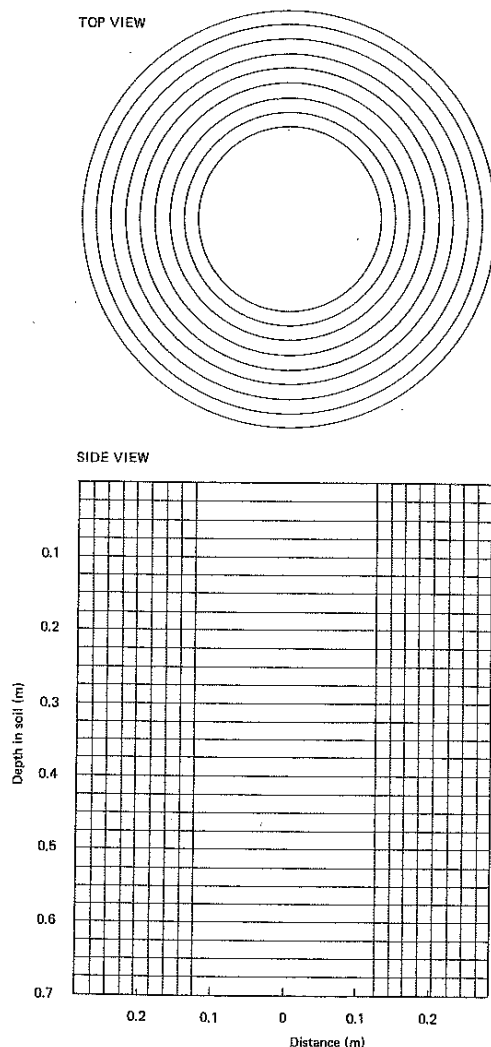
Gaudet et al. (1977) distinguished soil regions with mobile and stagnant water, respectively, in unsaturated packed-sand columns. Chloride-ion transport with steady-state water flow in the mobile region was described by the convection-dispersion equation. The lateral exchange of substance between the two regions was described by the first-order rate equation, which imitated lateral diffusion. The position of the front part of the breakthrough curve was mainly determined by the fraction of mobile water. The dispersion coefficient determined the slope of the front part of this curve. The tailing in the breakthrough curve was mainly determined by the lateral exchange coefficient.

#### 4.3.3 Studies in the 1980s

Water flow was assumed to occur only in the mobile region, e.g. through larger cracks, channels and inter-aggregate voids (Van Genuchten and Cleary, 1982). The rate of exchange of substance between the mobile and stagnant domains was taken to be proportional to the difference in concentration in the domains. The sorption sites in soil were divided into two fractions, corresponding to the mobile and stagnant regions, respectively. Calculations demonstrated that the concentration in the stagnant domain lagged behind that in

the mobile domain (as can be expected). The difference between the concentration in the two domains was calculated to be more pronounced for an adsorbed (hypothetical) substance than for a non-adsorbed substance.

Preferential water flow and pesticide transport in greenhouse soil were simulated by Leistra (1985). The soil systems were divided into mobile regions with vertical water flow through the profile and stagnant regions with horizontal flow to the plant-root systems. The exchange of pesticide between the regions occurred by convection with the flow to the root systems, accompanied by dispersion and diffusion. The computations were carried out for two geometries: vertical soil slabs and vertical soil cylinders (Figure 9). The stagnant region was divided into eight vertical sub-slabs or sub-shells, respectively, for the numerical solution of the transport equations. The whole system was assumed to be in steady-state flow at rather high volume fractions of water (representing regular sprinkler irrigation in greenhouses). The non-uniform water flow led to a highly increased computed leaching of the pesticides from the root zone. The differences between the effluent curves computed for the slab and cylinder geometries were small.



**Figure 9**

*Division of the soil system into core (mobile water), sub-shells (stagnant water) and compartments for the computations on preferential water flow and pesticide transport in greenhouse soils (Leistra, 1985).*

#### 4.3.4 Studies in the 1990s

When modelling preferential water flow and substance transport in water-repellent and wettable sandy soils, Van Dam et al. (1990; 1996) divided the soil system in two domains:

- 1) a first domain in which water flow and substance transport occurs;
- 2) a second domain without any flow and transport.

The mobile fraction  $F$  represents the volume fraction of soil occupied by the domain with water flow and substance transport. The stagnant domain (fraction  $1-F$ ) is left out of consideration in the model (no processes). The mobile fraction  $F$  increased with depth in the soil profile, while it was assumed to be constant in time (Van Dam et al., 1990). The authors proposed to estimate the factor  $F$  from observations on wetting patterns and dye-coloured patterns. The movement of bromide ions in a wettable topsoil was simulated with a mobile fraction of  $F = 0.85$  and that in a water-repellent topsoil with  $F = 0.70$  (Van Dam et al., 1990). A possible extension of the concept is to introduce a relationship between mobile fraction  $F$  and the pressure head of the water in soil (Van Dam et al., 1996). The mobile fraction would increase with increasing pressure head (less negative; wetter soil).

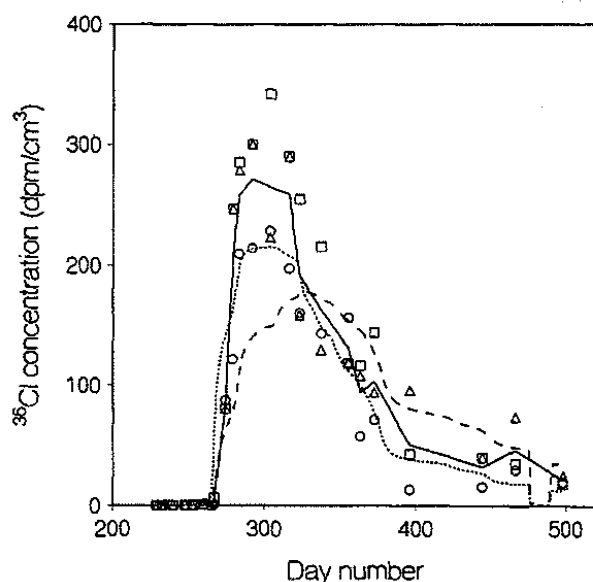
The concept of mobile and stagnant water domains was used in a model for field conditions with transient water contents (Tillman et al., 1991). Downward solute transport in the mobile domain was described by the convection-dispersion equation. Horizontal transport of solute occurred by both convective transport and first-order exchange based on the concentration difference (mimicking diffusion in the water phase). When bromide ions were applied by sprinkling in 5 mm water on a comparatively dry soil, the ions could be transported by the water flowing to the finest pores (capillary suction). The water from heavy sprinkling shortly after application (50 mm) by-passed much of this bromide. Downward transport of bromide sprinkled on a pre-wetted soil was comparatively fast, because less water penetrated into the water-unsaturated domain of the top layer by capillary suction. The model could explain the measured difference in bromide transport in the initially drier and the pre-wetted soils.

The movement of chloride ion and tritiated water through undisturbed columns of a coarse-sand soil (2.3% organic matter in the top layer) was studied by Jacobsen et al. (1992). The water (applied via syringe needles) flowed (steady state) at a rate of 9 to 16 mm/day. Suction was applied to the bottom of the columns to maintain water-unsaturated conditions. Some columns showed rather symmetrical breakthrough curves, while others showed distinct tailing. Physical non-equilibrium was simulated with a mobile-stagnant model. The mobile water phase was calibrated to range from 0.73 to 0.94 (average of 0.86) times the total volume fraction of water.

Vanclooster et al. (1992) simulated the behaviour of nitrogen compounds in an arable loamy soil grown with maize. They distinguished a mobile and a stagnant water phase. Soil regions were assigned to these phases in proportion to their volume fraction. Downward water flow in the mobile region was simulated with the Richards equation. Transport (vertical) of the substances in the mobile region was described by the convection-dispersion equation. Horizontal exchange of substances between the regions was described by the first-order rate equation based on the difference in concentration in the phases, thus mimicking diffusion. Transformation of the compounds in soil and uptake by crop roots were included in the computations. Only two additional parameters were needed for this model: the fraction of mobile water in the total water phase and the rate coefficient for the exchange of substance between the mobile and stagnant phases. However, the values of these parameters under field conditions required further investigation.

Water flow and chloride transport in an undisturbed sandy soil in lysimeters were simulated by Saxena et al. (1994) and they compared the computed results with measurements. Water flow was described by Richards' equation and chloride transport by the convection-dispersion equation. Simulation of a single micropore

domain for the whole soil system resulted in the computed breakthrough curve to appear later than the measured curve (Figure 10). Therefore it was assumed that a factor  $F = 0.8$  of the soil system participated in flow and transport (approach of Van Dam et al., 1990). The earlier chloride breakthrough computed with  $F = 0.8$  improved the correspondence to the measured breakthrough curve, as compared to that with  $F = 1.0$  (Saxena et al., 1994).



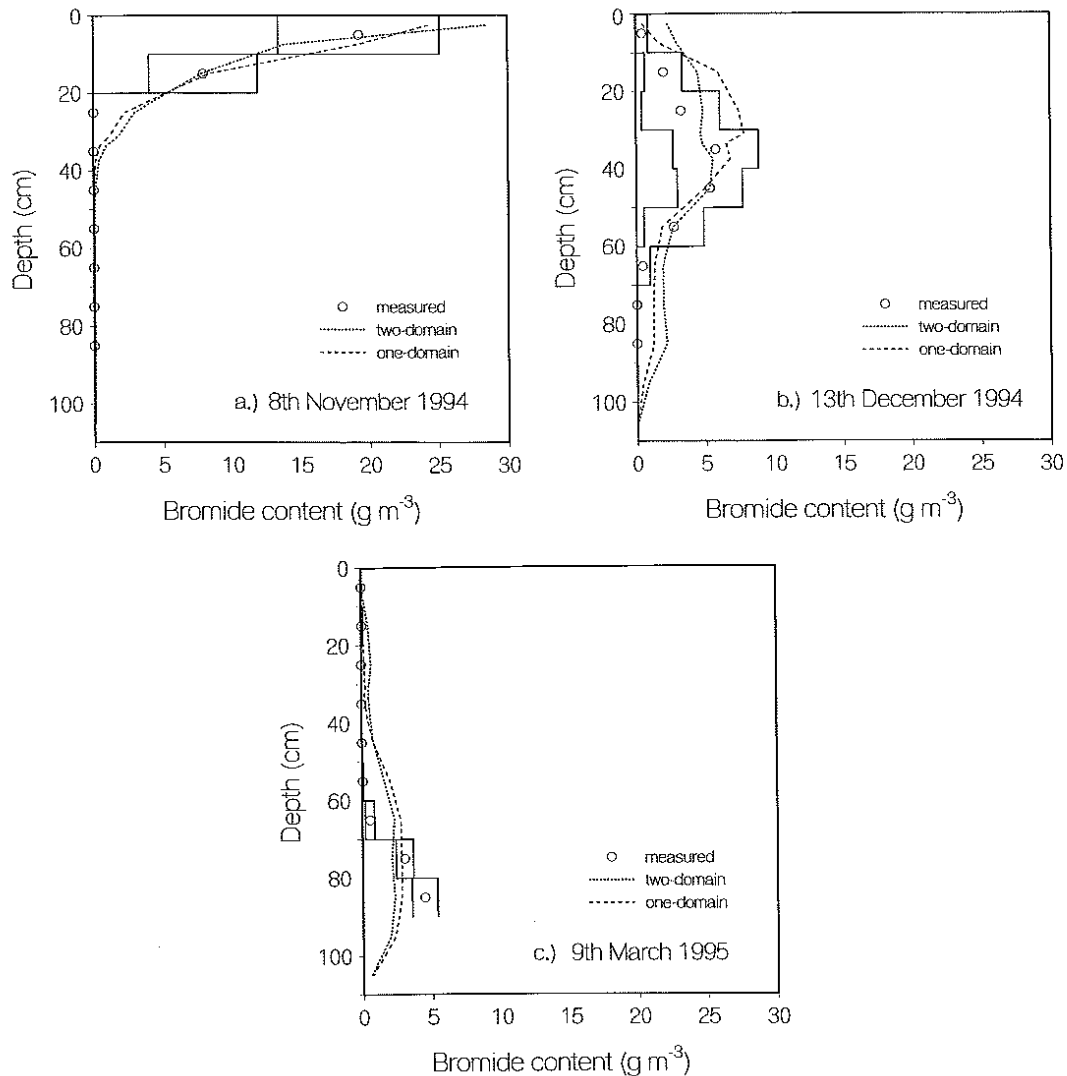
**Figure 10**

*Measured and computed breakthrough of chloride ion from sandy soil lysimeters (Saxena et al., 1994; ©Elsevier, with permission). Symbols: measurements for individual lysimeters. Solid line: average of the measurements.  $F$  = fraction of the soil system participating in flow. Dashed line: computed for  $F = 1.0$ . Dotted line: computed for  $F = 0.8$ .*

Conditions in which the mobile-stagnant model could be preferred above the convection-dispersion model were described by Vanderborght et al. (1997). The mobile-stagnant concept is considered to hold especially for soils with macropores subjected to high rates of water supply. The shape of the concentration-depth distribution or the breakthrough curve should deviate clearly from that obtained by the convection-dispersion approach. Only then it is possible to obtain reliable values of the mobile-stagnant parameters by inverse-modelling optimisation, provided the variation in the measuring points is not too high. Under field conditions, with intermittent rainfall, the mobile-stagnant pattern tends to reduce to the convection-dispersion pattern. Then there is often ample time between the showers for transverse (horizontal) equilibration of the substance between the regions.

Water flow and bromide transport in a field with loamy-sand soil were described by the mobile-stagnant concept (Larsson et al., 1999). Water flow in the mobile domain was described by using Richards' equation. The fraction of the soil volume containing mobile water (unsaturated at different volume fractions) was taken to range from 0.7 in the top layer to 1.0 below 0.8 m. The volume fraction of water as a function of depth in soil was described reasonably well. On the contrary, the one-region model (all water mobile) over-estimated the volume fraction of water. Vertical transport of bromide in the mobile domain was described by the convection-dispersion equation, with some horizontal convection to/from the stagnant domain. The two-domain model described the position of the bromide peak in the soil profile in winter somewhat better than the one-domain model (Figure 11). However, both models tended to over-estimate the movement of the leading edge of the

bromide distribution deep in the profile. The earlier breakthrough of bromide with the tile-drain effluent computed with the two-domain model corresponded somewhat better with the measured breakthrough than breakthrough computed with the one-domain model.



**Figure 11**

*Calculated and measured distributions of bromide ion in a field with loamy-sand soil (Larsson et al., 1999; ©Elsevier, with permission). Calculations with one- and two-domain models*

#### 4.3.5 Studies 2000 to 2010

Ritsema et al. (2001) incorporated preferential water flow and substance transport in the SWAP model (Soil Water Atmosphere Plant model). The model describes water flow with Richards' equation and substance transport with the convection-dispersion equation. They dealt with the case of preferential water flow caused by water repellency in a sand soil. Above the critical volume fraction of water (no water repellency), the flow was simulated to be comparatively uniform. Below this critical value (water repellency), the model switched to the description of preferential water flow. At each rainfall event, the preferential flow pathways recurred in

the same places in the grass-grown sand soil. When preferential flow was included, bromide ion was computed to arrive much earlier in the groundwater at 1.05 m depth than with more uniform flow.

The classical type of mobile-stagnant model deals with steady-state water flow at constant volume fractions of water in soil. The concept was extended with the description of transient water flow, including water exchange between the mobile and stagnant regions (Köhne et al., 2004a). Two options were used for the driving force of horizontal water transfer:

- a) the difference in pressure head in the regions;
- b) the difference in effective water saturation in the regions.

As a consequence there was a contribution of transverse convection to the exchange of substance between the regions, besides the transverse diffusion. The sub-models were implemented in the HYDRUS-1D simulation model. Various parameter values had to be estimated by optimisation of the computations against the results of soil column leaching experiments.

In their subsequent studies, Köhne and Gerke (2005) and Köhne et al. (2006a) also described water flow in the mobile region by the Richards equation, extended with a term for lateral water flow between the mobile and stagnant regions. The first-order rate equation for water exchange was driven by the difference in effective water saturation in the two regions. The convection-dispersion equation for longitudinal substance transport in the mobile region was extended with a term for lateral transport by convection and diffusion. The concept, incorporated in the HYDRUS-1D and HYDRUS-2D models, was applied to water discharge and bromide leaching to tube drains.

The concept of mobile-stagnant regions, as incorporated in the HYDRUS-1D software, was described by Šimůnek and Van Genuchten (2008) and Šimůnek et al., 2008. In a first option, there is no water transfer to/from the stagnant domain (with constant volume fraction of water). Solutes are exchanged (horizontally) between the mobile and stagnant domains by mimicked molecular diffusion. In an extension of the concept, the volume fraction of water in the stagnant domain is variable. The exchange of water with the mobile domain is described as a first-order-rate process. In that case, solutes are exchanged between the domains by both convection (with the exchanging water) and molecular diffusion. The physical non-equilibrium simulation can be combined with that for chemical non-equilibrium (Appendix C). In the mobile domain, sites with instantaneous sorption equilibration and sites with first-order kinetics equilibration were distinguished.

#### **4.3.6 Concluding remarks**

The concept of mobile and stagnant domains is capable to explain preferential transport behaviour of substances in soils: fast transport of the front part of the distribution and (long) tailing of the back part. An important advantage is that the concept is comparatively simple and that it requires only a few additional parameters.

In the simplest case of this concept, parameter values have to be assigned to:

- 1) the volume fractions of water in the mobile and stagnant water phases;
- 2) the volume fractions of the soil domains connected to the mobile and stagnant water phases;
- 3) the first-order rate coefficient for exchange of substance between the two domains.

Usually, the fraction of the soil in contact with the mobile phase (e.g. adsorption) is set equal to the fraction of mobile water phase (Ma and Selim, 1997), in the absence of a better estimation. Then only two parameters remain to be estimated. An objection is that the rate coefficient for substance exchange in its simplest form is purely empirical, even without consistence of the dimensions in the equation.

The fraction of mobile water and the exchange-rate coefficient for the substance have usually been obtained by calibration of computations against measurements: distributions in soil or breakthrough curves. Tension-infiltration methods have been developed and used to obtain these parameters in a more direct way (see Appendix A).

The concept of mobile-stagnant domains has often been used for situations with regular or even steady-state water supply at rather high rates. Then the volume fractions of the domains can be considered to be almost constant. However, soil moisture condition in field conditions often varies strongly, which makes this concept in its simplest form less suitable for the field.

The first-order rate equation gives a rather empirical description of the horizontal exchange of substance between the mobile and stagnant regions. This equation mimics substance diffusion between the regions. This diffusional transport can be expected to depend on the diffusion coefficient and on the adsorption of the substance. It is a problem to account for these factors via an empirical rate coefficient.

The mobile-stagnant concept with variable volume fractions of the water phases and water exchange between the soil regions is a step forward in its usability for field conditions. This at the cost of a more extensive model and the need for more assumptions and input parameters. Transverse water flow between the domains, with the accompanied convection, can be expected to enhance the rate of exchange of substances substantially. The description of water and substance uptake by the crop roots also requires the simulation of variable volume fractions of water. Uptake of water by the roots has to be simulated dependent on the soil moisture status in each of the domains.

A question is to what extent the applicability of the concept of mobile-stagnant water phases can be distinguished from that of the concept of convection-dispersion under field conditions. The assumption of mobile-stagnant water phases has to be based on distinct deviation (fast front, long tailing) from the convection-dispersion behaviour (wave shape). When the spreading in the measuring results for the field is substantial, the distinction between the validity of the concepts becomes difficult.

In the case of cultivated sandy soils, the convection-dispersion approach gives a reasonable description of the movement of a great part of the substance distribution in the soil profile (see previous subchapter). Besides, there is the possibility of fast transport of a smaller fraction of the substance in soil. For that reason, a concept with a completely stagnant water fraction seems to be not applicable. Then the dual-velocity concept seems to be more appropriate (see next subchapter).

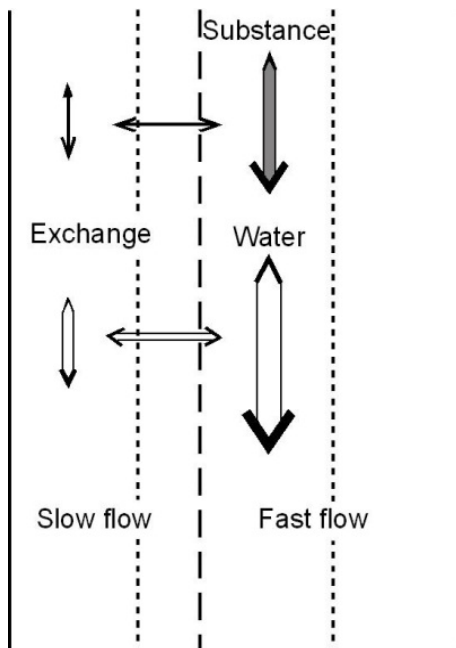
## **4.4 Dual-velocity domains**

### **4.4.1 Introduction**

In the dual-velocity concept, the soil system is divided into the following two domains (Figure 12):

- 1) a domain with comparatively fast water flow and substance transport;
- 2) a domain with comparatively slow water flow and substance transport.

In both domains, the substance is transported downwards by convection (accompanied by dispersion) and by diffusion. Exchange of substance between the two domains can be described e.g. by the first-order rate equation on the basis of the difference in the concentrations in the water phase in the two domains. This equation mimics exchange by diffusion. When the rate of exchange is high, the model approximates the convection-dispersion description for the whole soil system (Section 4.2). When the exchange rate is very low, the model approximates the soil columns description (no interaction between the columns; Section 4.6).



**Figure 12**

*Outline of the dual-velocity concept for heterogeneous water flow and substance transport in soil. Variable soil moisture condition. Dashed line = wetter condition; dotted lines = drier condition.*

#### **4.4.2 Studies in the 1990s**

Two domains in the soil system were distinguished: one with a comparatively high water flow rate and one with a lower flow rate (Gerke and Van Genuchten, 1993; Van Genuchten and Gerke, 1993). Transient water flow in both domains was described by the Richards equation. Solute transport in both domains was simulated using the convection-dispersion equation. Water transfer between the domains was described by the first-order rate equation, on the basis of the difference in pressure head. Lateral substance transfer occurred by convection (accompanied by dispersion) and diffusion. The highly non-linear and transient nature of the water-flow process posed difficulties to the numerical solution procedure (improvement was needed).

Ray et al. (1997) also developed a computation model based on the dual-velocity approach. They found the concept to be flexible with respect to the simulation of preferential flow and transport in variably-saturated soils. Other essential processes could be incorporated in the model: sorption kinetics, transformation and uptake by plant roots. Some numerical problems had to be solved, e.g. caused by high values of the coefficient for water transfer between the regions. The authors realised that the use of such a model as a regulatory tool requires various parameter values and quantitative relationships as input.

#### **4.4.3 Studies 2000 to 2010**

Horizontal water flow and substance transport between the two flow-velocity domains is usually described in a combination of physical and empirical ways. According to Šimůnek et al. (2003), the most frequently used possibilities to describe exchange of water are first-order rate equations based on:

- difference in pressure head;
- difference in effective water saturation.



Horizontal transfer of substance between the two domains can be calculated as the sum of convective and diffusive fluxes.

The numerical solution for the exchange of water between the two variably-saturated flow domains tends to be unstable. Therefore, Köhne et al. (2004b) developed the following two-step calculation. In the first step, the hydraulic conductivity was evaluated as a weighted average function of the pressure heads in the two adjacent domains. In the second step, pseudo-hysteresis due to the change in the direction of water transfer between the regions was prevented by resetting an initial pressure head. Implemented in the HYDRUS-1D dual-velocity sub-model, the two-step computation improved the accuracy of preferential water flow simulation, as compared to the earlier one-step computation.

The flexibility of the dual-velocity approach was further demonstrated by Ray et al. (2004). Their S\_1D\_DUAL model allowed variation of the preferential flow domain with depth. Herbicide sorption was a function of depth in the soil and sorption kinetics could be described. The rate of transformation decreased with depth in the soil and it could be taken different in the two domains. Unfortunately, field measurements to test these illustrative computer simulations for atrazine and trifluralin in a silt loam soil were not available.

Köhne et al. (2006b) used three submodels for physical non-equilibrium flow and transport in soil:

- 1) a mobile-stagnant submodel;
- 2) a dual-velocity submodel;
- 3) a submodel with fast-flow, slow-flow and stagnant regions.

In all cases, transient water flow in soil could be simulated. First-order rate equations were used for the exchange of water between the domains. The exchange of substance between the domains was described by the combination of a diffusion term and a convection term. The descriptions of physical non-equilibrium could be combined with a description of chemical non-equilibrium (sorption kinetics; Appendix C). The three submodels were implemented in the HYDRUS-1D model. As the complexity of the model increases, the problem of obtaining parameter values becomes more and more problematic.

A dual-velocity model (incorporated in HYDRUS-1D) was used in the evaluation of the transport of bromide ion and isoproturon in soil columns at steady-state water flow (Dousset et al., 2007). Vertical transport in both regions was described by the convection-dispersion equation and the horizontal exchange between the regions was described by the first-order rate equation. By using bromide ion as a tracer, they assumed to be able to isolate the effect of physical non-equilibrium (dual velocity) in the breakthrough curve for the silty clay loam soil. In case of isoproturon, the description of sorption at two sites (equilibrium and first-order kinetics, respectively) was added for both regions to the model.

Gerke et al. (2007) used the dual-velocity approach to simulate the leaching of bromide ions from a field plot to tube drains. The fast-flow and slow-flow pore domains had their own sets of hydraulic relationships. Water flow was described by two coupled Richards' equations. A first-order rate equation based on the difference in pressure heads was used for horizontal water transfer between the domains. Solute transport in the two domains was described by two coupled convection-dispersion equations. The equation for the transfer of solute between the two domains consisted of a convection term (by water transfer) and a diffusion term.

The concept of dual-velocity regions, as incorporated in the HYDRUS-1D model, was described by Šimůnek and Van Genuchten (2008) and Šimůnek et al. (2008). Water and solute moved vertically in two domains: a domain with fast flow/transport and a domain with slow flow/transport. Water and solute are exchanged (horizontally) between the domains. There is convection-dispersion transfer of substance between the two domains. An option is to distinguish a stagnant domain besides the slow-flow domain. Simulation of physical non-equilibrium can be combined with that for chemical non-equilibrium in both domains (Appendix C). Then, sites with instantaneous sorption equilibration and sites with first-order kinetics for sorption equilibration are

distinguished. Physical and chemical non-equilibrium models tend to yield similar breakthrough curves, so it is not possible to discriminate between the processes in a simple way.

#### **4.4.4 Concluding remarks**

In the case of cultivated sandy soils, the dual-velocity type of model seems to be preferable above the mobile-stagnant concept. In computations with the convection-dispersion approach (Section 4.2), the movement of the bulk of the substance in sandy soils in the field can often be explained reasonably well. Then there is no indication that much of weakly-sorbed substances is captured for longer times in soil regions with stagnant water, e.g. near the soil surface. The dual-velocity concept allows description of substantial soil-matrix transport plus fast transport through preferential pathways under certain conditions. The volume fractions of water in both domains can be simulated to be highly variable, which corresponds to field conditions with wetter and drier periods. The detailed simulation of water exchange between the flow regions tends to lead to unstable numerical solutions. The development of especially-adapted ways of modelling has started

The dual-velocity concept is based for the greater part on physical process descriptions. This approach corresponds to that in the mechanistic/deterministic SWAP-PEARL combination of models. The flexibility of SWAP-PEARL in describing a range of soil, weather, crop, pesticide and management processes can be retained.

A series of input parameters and relationships is needed for computations with the dual-velocity concept. Examples are:

- division of the soil system in slow-flow and fast-flow regions;
- moisture retention curves for the regions;
- hydraulic conductivity curves for the regions;
- transport parameters for vertical transport;
- transport parameters for horizontal exchange between the regions.

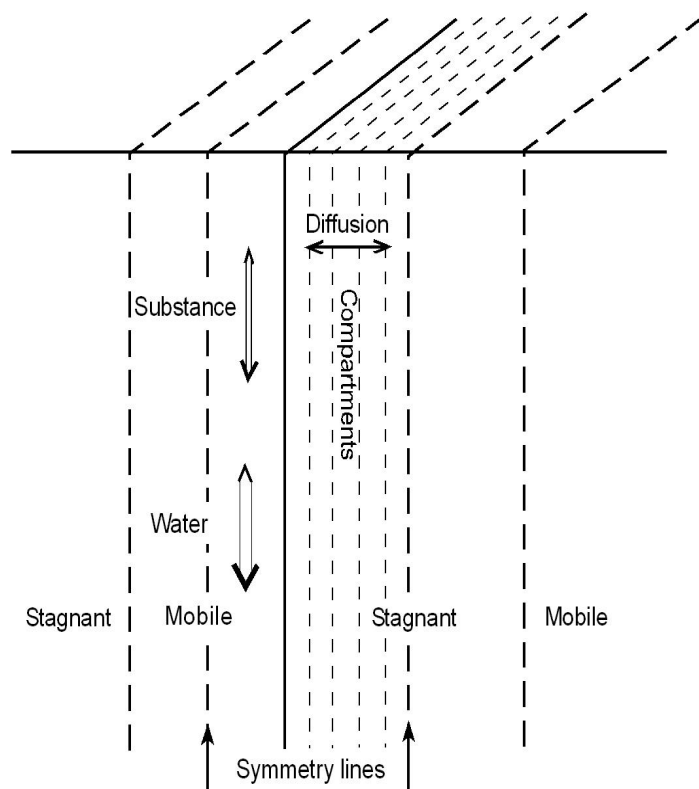
Little guidance is available on how to obtain the input data and relationships (Šimůnek et al., 2003). For the pesticide-soil adsorption and transformation interactions the question rises whether they are different for the two regions. Further the boundary conditions can be complicated, e.g. with respect to water and pesticide supply to the domains at the soil surface.

Ideally input data and relationships for the dual-velocity concept can be determined beforehand, independent from the transport experiments themselves. In this area much further research is needed. In many cases, input data have to be obtained by calibration of computations against the results of transport experiments. Sufficiently-detailed transport experiments under field conditions for testing/calibration/validation are scarce (Šimůnek et al., 2003). The optimisation of the parameters becomes highly problematic when more than a few quantities have to be calibrated. In principle, it is possible to extend the number of soil regions with different water-flow rates (Appendix B). However, the problem of obtaining representative input data and relationships becomes even more severe then.

Besides physical non-equilibrium, chemical non-equilibrium (sorption kinetics) is an important phenomenon in soils (Appendix C). Physical and chemical non-equilibrium sub-models tend to have similar effects on the shape of the concentration distributions and breakthrough curves (early arrival and long tailing). This makes it difficult to discriminate the contribution of each of the concepts to preferential transport. Physical equilibration (mainly by diffusion) for a sorbed pesticide can be expected to be slower than that of a non-sorbed tracer.

## 4.5 Transverse diffusion mobile-stagnant

A soil system was divided into vertical slabs, consisting of regions with mobile and stagnant water phase, respectively (Leistra, 1977). Downward water flow in the mobile-phase region occurred at constant volume fraction of water. Sorption equilibrium was established instantaneously within the mobile region (Figure 13). A weakly-adsorbed pesticide was computed to move by diffusion in the regions with stagnant water phase. A period of 2 days was computed to be too short for lateral sorption equilibration by diffusion over distances more than a few mm. With a rainfall pattern distributed over 20 days, diffusion allowed a great deal of sorption equilibration over 1 cm distance. However, equilibration over lateral distances of 4 cm was far from complete then.



**Figure 13**

*Outline of geometry and processes in the concept of transverse diffusion mobile-stagnant.*

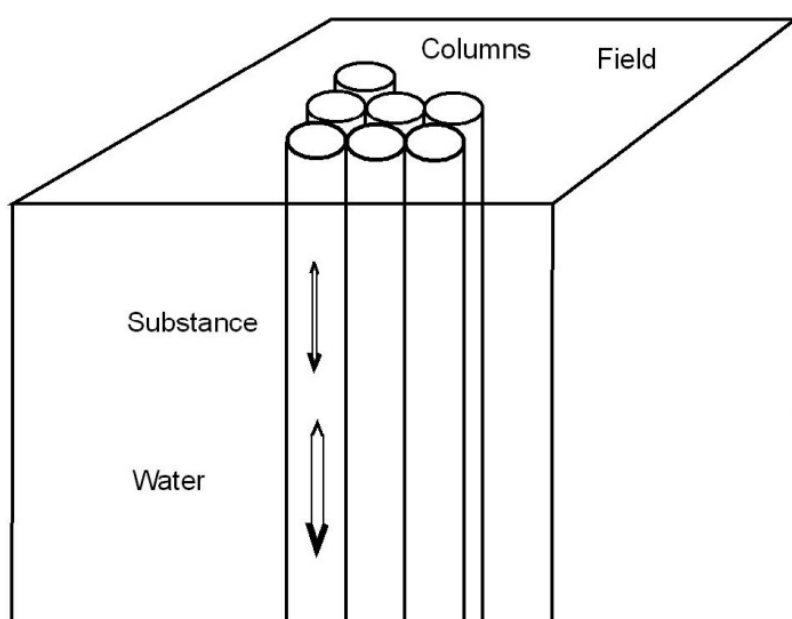
Sandy soils usually do not have structure elements with a distinct geometrical shape and size. Therefore, models dealing with intra-aggregate diffusion from the mobile region over specific distance in the stagnant region (Van Genuchten and Dalton, 1986) cannot easily be used. This implies that in the case of sandy soils, parameter values for the two regions can only be obtained by calibration of the computations against results of transport experiments. A system of parallel slabs of alternative regions with mobile and stagnant water was taken as concept (Van Genuchten and Sudicky, 1999). Lateral exchange between the regions can be described by diffusion from the mobile region in the stagnant region.

Summarising, transverse diffusion in cultivated sandy soils may be simulated explicitly in systems with vertical slabs with e.g. mobile and stagnant regions. This because of lack of a clear geometry (size, shape) of structural elements in sandy soils. Up to now, steady-state water flow in rather wet soils has been simulated in this way. As changes in water condition are not considered, the concept is not suitable for field conditions with

drier periods. The concept has some value for theoretical studies on the nature and size of the effect of transverse diffusion of substances on their transport in soils.

## 4.6 Soil-column approaches

A field was considered to consist of independent vertical soil columns (Van Genuchten and Jury, 1987). Each column has its own flow and transport properties (Figure 14). The columns can be subjected to specific local boundary conditions (if known). Transport within the columns can be described by e.g. the convection-dispersion equation. Lateral (horizontal) transport between the columns is not considered.



**Figure 14**

*Outline of geometry and processes in the soil-column approach.*

Often the soil columns are distinguished on the basis of the variation in hydraulic conductivity in a field, which leads to different rates of water infiltration. It is assumed that there is no horizontal transfer between the soil columns (Van Genuchten and Šimůnek, 1996). Flow and transport within the soil columns can be described in different ways, e.g. in a soil continuum (Section 4.2) or in regions with different water-flow rates (Sections 4.3 and 4.4). When the field is flood-irrigated, the same pressure head holds on top of the soil columns. Under rainfall and sprinkler-irrigation, the water-infiltration rate can be rather uniform or it is affected by horizontal redistribution of water in the crop canopy and at the soil surface.

Jensen and Refsgaard (1991) also considered agricultural fields to be composed of an ensemble of non-interacting soil columns. Each column represented a studied soil profile. They paid particular attention to the variation in hydraulic properties in the soil profile of a field. Water flow in each of the columns was described by the Richards equation. The transport of the anion tracer was described by the convection-dispersion equation.

The field was viewed as a series of independent vertical soil columns, without horizontal exchange of water and solute between them (Toride and Leij, 1996). Substance transport within each column was described by

the convection-dispersion equation. The variability in pore water velocity between the stream columns was considered to dominate the field-scale substance spreading with depth.

When considering a field to consist of an ensemble of soil columns, an option is to describe water flow in each of the columns by the Richards equation (Jacques et al., 1997). The convection-dispersion equation can be used for substance transport in each soil column. The stream tubes are considered to be independent: there is no horizontal exchange of water and solute between the tubes. The effective dispersion coefficient for solute movement in the whole field can be expected to be greater than the local dispersion coefficient (per plot/column). In their study for chloride tracer in loamy soils, however, Jacques et al. (1997) measured the scale effect on dispersion only for soils with macro-pores.

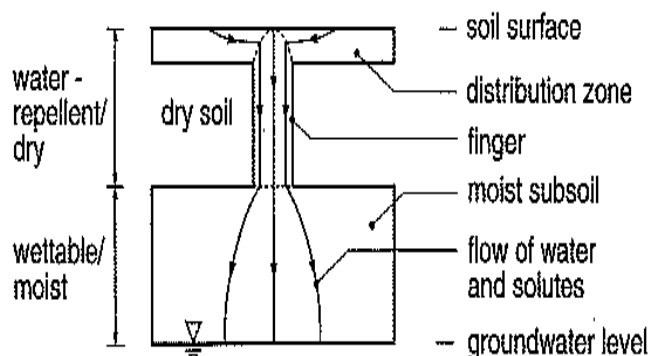
In summary, soil-column systems are often considered to represent soil plots with different hydraulic properties. The concept is generally used in studies on the variability in transport on field scale. Besides the hydraulic properties, a series of parameters and relationships can be assumed to be different for the columns. There is no need to modify one-dimensional computation models for this concept. The results for the whole field can be obtained by combination of the results computed for each of the soil columns. Selection of the boundary conditions, e.g. those at the soil surface, may present problems.

## 4.7 Flow fingers in a water-repellent layer

Water flow through a soil with water-repellent parts was described in three zones (De Rooij, 1995; De Rooij and De Vries, 1996):

- 1) a zone with mainly lateral (horizontal) flow in which the water converges to the top of an underlying finger;
- 2) a zone with vertical flow through a water-conducting finger in a layer with otherwise water-repellent dry soil;
- 3) a zone with wettable sand in which water flow diverges from the lower end of the finger (disc source) due to capillary forces.

Thus the steady-state water flow was described in an axi-symmetrical system (Figure 15). Solute leaching from the soil profile was highly dependent on the thickness of the layer with wettable sand above the groundwater table (at the cost of the finger length). The model concept could also be applied to more wettable soils, containing a thicker distribution layer (e.g. cultivated layer) and an intermediate zone with a limited number of preferential flow paths (De Rooij and Cho, 1999).



**Figure 15**

*Outline of the steady-state three-region model for fingered water flow and substance transport (De Rooij, 2000; ©Elsevier, with permission).*

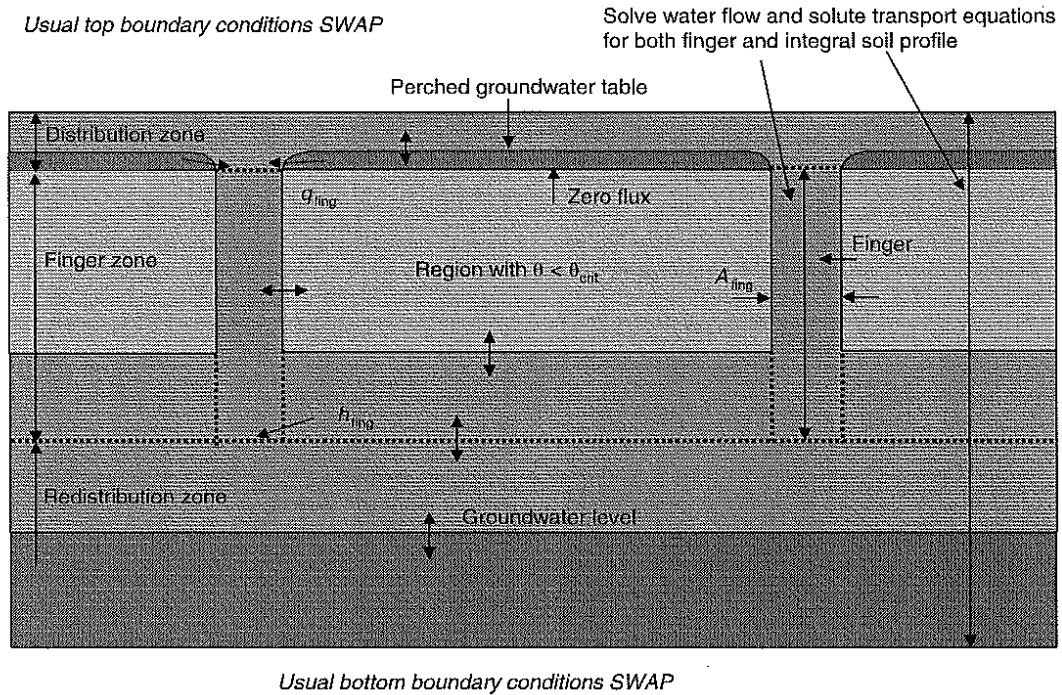
De Rooij (2000) again described the model concept of flow fingers derived from experiments for sandy soils with a water-repellent intermediate layer. Soil was wetted well in a comparatively thin distribution zone on top of the profile (Figure R00). Water flowed through fingers in the water-repellent intermediate layer. The third zone (wetable) extended down to the groundwater zone. The computations were set up for steady-state water flow in an axisymmetrical soil system. Water flow (saturated) in the distribution zone converged to the top of the fingers and diverged below the fingers, in the wettable subsoil. The three-region model can explain the early arrival of chloride ion leached from a lysimeter with undisturbed soil.

Steenhuis et al. (2001) distinguished a distribution zone near the soil surface and a zone with fingered water flow below that. The distribution zone was treated as a mixed reservoir of water and solute. Water flows through fingers of fixed geometry, without horizontal exchange with the surrounding soil. Transport of the tracer (chloride) in the fingers was described by the convection-dispersion equation. The concept applies to soil conditions with the volume fraction of water above field capacity.

The model SWAP was extended to describe preferential water flow and bromide transport in water-repellent sand soil grown with permanent grass (Ritsema et al., 2005). When the volume fraction of water was above the critical value for water repellency, water flow through the soil layers was described by Richards' equation and substance transport by the convection-dispersion equation. Below the critical volume fraction of water, three zones were distinguished in the soil profile:

- 1) a wettable distribution zone on top,
- 2) a zone with water-repellent soil parts and wettable fingers and
- 3) a wettable redistribution zone below (Figure 16; Van Dam et al., 2004; Kramers et al., 2005).

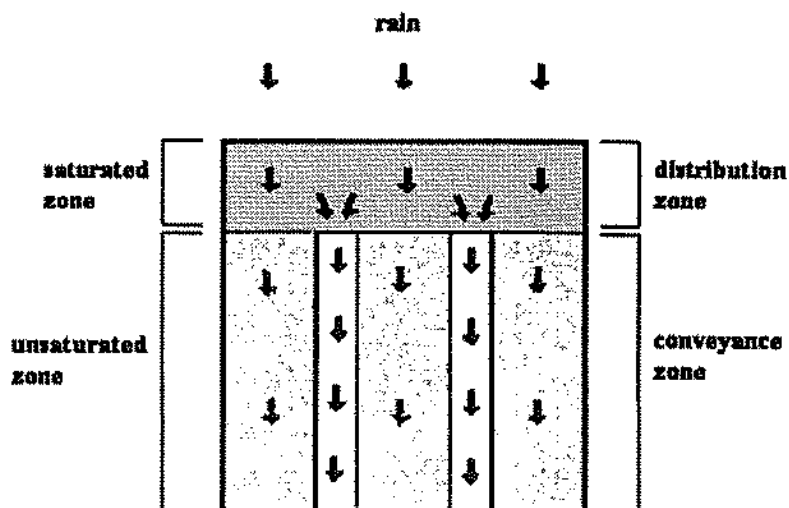
Water flows vertically through the wettable distribution zone on top. This is followed by lateral (almost horizontal) flow over the water-repellent soil parts to the fingers with downward flow. Below the finger zone, the water spreads out in the wettable redistribution zone above the groundwater table. The fingers appear as soon as the water content in the intermediate layer falls below the critical level for water repellency (Van Dam et al., 2004). The fingers disappear from below when groundwater level and capillary zone rise. The fingers disappear from above at large water fluxes in the distribution layer on top, due to substantial precipitation. The computation described the upper part of the distribution of bromide ion with depth in the sand soil (which could be sampled) in a reasonable way (Ritsema et al., 2005). Bromide breakthrough at 1.05 m depth was simulated to be much faster in the case of fingered preferential transport than in the case of convection-dispersion transport through the whole soil matrix (chromatographic transport).



**Figure 16**

Conceptual diagram of the incorporation of preferential water flow and bromide transport in the SWAP model for a potentially water repellent sand soil grown with permanent grass (Van Dam et al., 2004; Kramers et al., 2005; ©CSIRO, with permission).

In the preferential flow and transport model of Kim et al. (2005), the soil system is divided into a distribution zone near the soil surface and a conveyance zone below (Figure 17). The thickness of the distribution zone depends on land use and tillage practices (e.g. depth of the cultivated layer). A set of flow paths was assumed to be present in the conveyance layer (can be extended to the combination of preferential flow and matrix flow). The solute is assumed to be completely mixed in the distribution zone. Transport in the flow paths of the conveyance zone occurs by convection-dispersion, with water flow at steady-state. The model can be extended by considering both fast flow in paths and slower between the paths in the conveyance zone. Note that the presence of the water-saturated distribution zone on top is the difference with the mobile-stagnant (Section 4.3) and dual-velocity (Section 4.4) approaches. The model was tested for the transport of chloride ion in loamy-soil and sand columns under simulated rainfall.



**Figure 17**

*Schematic diagram of the flow process in the soil with distribution zone on top and conveyance zone with preferential flow paths (Kim et al., 2005; ©SSSAJ, with permission). The stagnant regions in the conveyance zone can be replaced by slow-flow regions.*

In summary, the concept of flow fingers in water-repellent soils seems to represent rather extreme situations. It was derived from experiments for non-cultivated sand soil with permanent grass cover. In the first versions of the concept, the water-repellent soil parts in the intermediate layer were excluded completely from water flow and solute transport. In later versions, the possibility of wetting of the intermediate layer from above and below was considered. This concept was already incorporated in the SWAP hydrological model. The concept may be too extreme for cultivated sandy soils. However, the simulation of (slower) water flow and substance transport in the soil between the fast-flow paths in the intermediate layer can enhance the usability of the concept.



## 5 Useful experiences with macropore models

There is quite a lot of experience with preferential flow and transport in soils with macropores, both with respect to measurement and modelling. Although outside the scope of the present study, various general experiences seem to be applicable to preferential flow and transport in cultivated sandy soils. Therefore, general experiences discussed in a series of review articles are presented below, as far as they seem representative for the present study.

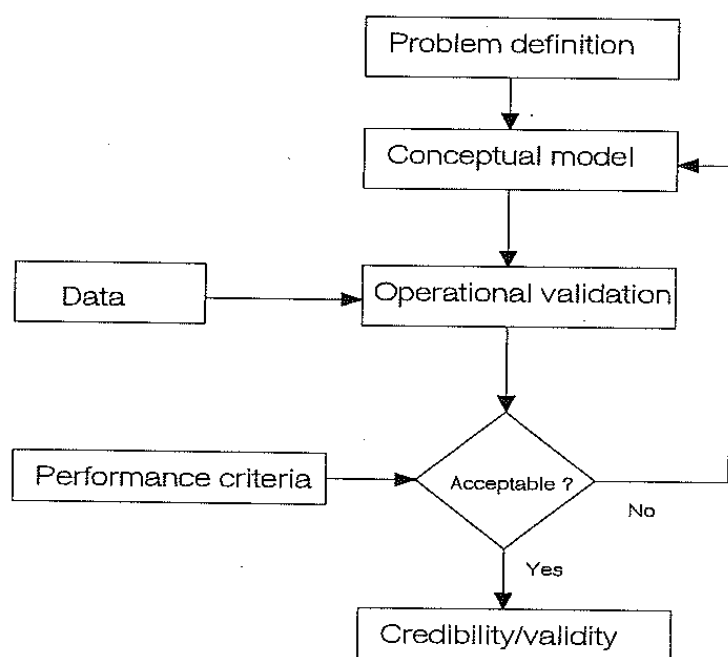
The size and connectiveness of the soil pores determine the water flow characteristics. Water flow and substance transport in the wider and more connective pores can proceed comparatively fast. In the narrower and less connective pores, downward water and substance movement will be slower. It is not possible to fully describe the pore size arrangement and the associated water flow geometry (Ma and Selim, 1997). The complexity of the pore systems exceeds that considered in the model concepts. The field situation is often much more variable than simulated by the models, usually derived from (steady-state) column studies in the laboratory. Selection of the boundary conditions for field situations presents additional problems. Therefore the present physical non-equilibrium models are conceptual rather than mechanical or deterministic (Ma and Selim, 1997). Although they may explain certain experimental results (by calibration), the prediction capability of the models for other situations is low. Independent methods of measuring/estimating input data are often lacking.

The parameters in preferential transport models have to be obtained by calibration of computer simulations against measured results: e.g. concentration distributions with depth or breakthrough curves. Estimation of parameters for preferential flow and transport is most feasible when the measured transport behaviour of a substance deviates substantially from that described by the convection-dispersion equation. Parameters of dual-region models were difficult to obtain from breakthrough curves when using steady-state water flow at rates representative for field conditions (Vanderborght, 1997). With intermittent rainfall in the field, there is ample time for horizontal substance exchange between the flow regions. Attempts can be made to make independent estimates of transport parameters, but this may be not easy. Effluent concentrations can be expected to give a better picture of preferential transport than the residual concentrations measured in the lower part of the soil profile.

It can be expected that the degree of heterogeneity in soil increases with increasing scale of the system (Brusseau, 1999). Heterogeneity then increases in the sequence soil column, lysimeter monolith, field plot and whole field. It is desirable to distinguish the processes causing preferential transport of substances in soil. However, the factors responsible for the measured preferential transport in soil, and their relative importance, often cannot be fully elucidated. Calibration of more complex models with several unknown parameters against field data is a problem. Various parameters cannot be obtained beforehand, in an independent way.

A general problem in the predictive use of preferential-transport models for field soils is that the transport parameters cannot be measured independently (Van Genuchten et al., 1999). They have to be derived from comparisons between the results computed by a model and the results measured in the transport experiment.

A sub-model for preferential transport of pesticides in soils should be based as much as possible on physical description of the processes. This increases the chance that a sub-model can be applied to divergent field conditions (Jarvis, 1999). The sub-model should be relatively simple to allow estimation of the input parameters and relationships (hopefully only a few). The sub-model should be suitable to be incorporated in numerical simulation models for soil-plant systems containing many other processes. A combination of sub-model and set of parameters can gain credibility by repeated testing in the field (Figure 18). Dependent on the results of the testing and on the amendments, the sub-model can become increasingly more acceptable for its intended use.



**Figure 18**

*Scheme of the procedure of increasing model credibility (Jarvis, 1999; ©WAP, with permission).*

Preferential flow and transport models with different domains require a substantial amount of input data and relationships (Šimůnek et al., 2003). They deal with both the domains and with the exchange of water and substance between the domains. Only some of the input data can be obtained in way independent of the transport experiment. Transport experiments rarely provide enough information to allow independent calibration of the model parameters. It can be possible to simulate the results of an experiment by different preferential flow and transport models. There will usually not be enough details to distinguish between the correctness of various model concepts. Finally there is an urgent need for testing the models under field conditions.

In principle, water flow and substance transport in soils should be described in three-dimensional systems, by corresponding models. In three dimensions the possibilities to account for preferential flow and transport are increased. The same holds for heterogeneous conditions at the soil surface. In the coupling of unsaturated transport in soil (mainly vertical) and saturated transport in groundwater (mainly horizontal), the use of models three dimensions is desirable. Van Dam et al. (2004) summarized some difficulties with respect to three-dimensional model systems:

- a larger amount of input data is needed (often not available);
- the boundary conditions become more complex;
- computer times are much longer, which is especially a problem with many runs in optimisations and regional applications;
- interpretation of the results is laborious.

When lines of symmetry are present, it may be possible to describe flow and transport in two dimensions. Examples are fields with ridges and furrows, and tube-drained fields. In some cases, a cylindrical model system can be used.

A selection can be made from different model concepts for the description of preferential water flow and substance transport in cultivated sandy soils. It is difficult to evaluate the correctness of each of the concepts in an objective way (Vanclooster et al., 2004). Parameters for the corresponding models were usually obtained by calibration, using one or a few specific experiments. The calibration can be hampered by deficits in the measuring data, like large variation and incompleteness. The predictive value of the parameters for other conditions is usually not known. Model tests against a series of high-quality data sets are needed to make progress in the testing of the predictive capabilities of the combination of model and parameters.

Preferential flow and transport models can substantially improve the description of substance leaching from soils to tube drains (Gerke et al., 2007). However, independent estimation of the input parameters for the geometry of flow domains and rates of the processes in the system is a serious problem. Similarly, specific initial and boundary conditions are needed for preferential flow and transport models, e.g. at the soil surface. Detailed observations on the spatial and temporal changes in soil and at the soil surface may be helpful in the estimations.

The results of various transport experiments can be explained by different model concepts (Šimůnek and Van Genuchten, 2008). The mathematical description of physical and chemical non-equilibrium tends to be identical. Thus it is not possible to simply discriminate between the processes, e.g. on the basis of breakthrough curves. In principle, transport experiments with different substances (non-sorbed tracers, sorbed substances) can be helpful in the estimation of the contribution of different processes to the preferential transport.

Convective-dispersive transport of a non-sorbed tracer indicates that much transverse equilibration between the flow domains has taken place. The question rises what can be expected for the equilibration of a sorbed pesticide. First of all, the diffusion coefficient of the usually greater molecule in water is lower. Because of the sorption of the substance in the domains with slowly flowing water, much more transport has to take place before a substantial degree of equilibration is reached. It can be assumed that the deviation from the convective-dispersive transport is greater for sorbed organic substances than for a non-sorbed tracer like bromide ion.

Models have been developed for multiple-velocity domains. They are discussed in Appendix B. It is difficult to obtain the values of the many parameters in such more complex models.

In various studies, a description of physical non-equilibrium was combined with a description of chemical non-equilibrium (adsorption-desorption kinetics). Those studies are described in Appendix C. The mathematical description of physical and chemical non-equilibrium tends to be equivalent, so the contribution of the two types of non-equilibrium cannot be easily distinguished.

### Main lines in the experiences

- The sub-models for preferential water flow and pesticide transport in soil should be comparatively simple. Only then it is feasible to estimate the input parameters.
- Different concepts can be selected for the description of preferential water flow and pesticide transport in cultivated sandy soils. Specific experimental results can often be described by different concepts.
- The mathematical description of physical and chemical non-equilibrium tends to be equivalent, so the contribution of the two types of non-equilibrium cannot be easily distinguished.
- Essential model parameters for physical non-equilibrium often have to be obtained by comparison of computations with results measured in transport experiments, so by calibration. Options to measure/estimate parameter values in an independent way should be explored further.
- The derivation of parameter values for non-equilibrium during substance transport in soils is most feasible when measured transport deviates substantially from convective-dispersive transport. Further, the spreading in the measuring data should be relatively small.
- In the case of preferential flow and transport, special attention is needed for the initial and boundary conditions of the simulated system. E.g. the amount of precipitation water and the pesticide dosage have to be divided among the regions with fast and slow flowing water.
- Attention is needed for the differences in transverse equilibration for tracers and adsorbed pesticides. The lower diffusion coefficient, the retardation of diffusion by adsorption and the greater amount to be transported for the pesticides can be expected to have substantial effect.
- There is a lack of testing of sub-models for preferential flow and transport in cultivated sandy soils in the field. A series of tests and amendments can gradually result in reasonable estimates of preferential transport parameters.
- Comparison of the concentrations in groundwater with those in the water phase of the lower part of the soil profile is helpful in the assessment of preferential transport.
- Regions of lateral flow and transport (with horizontal component) can occur in soils, e.g. at textural and structural interfaces. Then preferential flow and transport have to be described in two- and three-dimensional systems.

## 6 Models in the evaluation of leaching risk

Various requirements for (sub)models to be used for emission/exposure estimation in registration procedures were described by Donigian and Carsel (1992). Scenarios representative of field conditions have to be specified for the computations. It should be possible to run the model with a limited number of input data. Detailed guidance on the selection/derivation of such input data are needed. In principle, it is desirable to account for the variations in the processes and parameters with position and time. However, the amount of work should fit in the registration procedure. Tests/calibrations/validations of the (sub)model for representative field conditions must be available to gain confidence in their results.

Requirements for models to be used in the registration procedures of pesticides were described also by Russell and Layton (1992) and Russell et al. (1994). The models should reflect the current scientific understanding of the physical, chemical and biological processes in soil. Testing of a model on the basis of some well-defined and detailed field experiments is needed. Specific representative scenarios have to be selected in the framework of the registration procedure. Guidance on the derivation of input system-parameters is needed and default values should be given for quantities, where possible. Connection to data bases is suggested, e.g. for soils and weather conditions. The use of models has to be combined with the use of laboratory data and results of field experiments in tiered assessment schemes, to obtain an integrated picture of the leaching risk of a pesticide.

New model concepts for water flow and pesticide transport in soil have to be tested under various soil and climatic conditions. Some of the parameters in the models have to be obtained by calibration. Especially in the case of preferential transport, the computations should be calibrated also against the concentrations measured to leached from the soil profile (Jarvis et al., 1995). An option is to use the combination of field experiment and calibrated model parameter values as scenario for the evaluation of leaching risk of pesticides. The reason is that predictions with the new sub-models for non-studied field situations are likely to be highly uncertain.

A general problem is the selection of input data for models describing preferential flow and transport in soils (Brown et al., 1999). This holds for both, soils with macropores and cultivated sandy soils. Usually, model parameters are obtained by calibration of the model computations against experimental results. Thus the simulations mainly have descriptive value, rather than predictive value. This is an obstacle for the use of preferential flow and transport models in regulatory procedures.

Various steps have to be taken before a new sub-model is suitable for the estimation of the risk of preferential leaching of pesticides (Jarvis, 1999). The sub-model should be tested using the results of some well-defined and representative field experiments. Measurements of pesticide concentrations leaching from the soil profile should be included in the test set (not only measurements in the soil profile). Input parameters which cannot be obtained otherwise have to be obtained by calibration. Leaching-risk evaluation scenarios have to be defined, which are usually derived from the field experiments for which the parameters were calibrated.

The risk of preferential transport of pesticide residues (also in sandy soils) to groundwater did not play an explicit role in the registration procedures (Flühler et al., 2001). The reason was that preferential flow and transport could not be predicted by models.

The uncertainties in model concept and parameters values are serious obstacles in the use of preferential flow and transport models for the evaluation of leaching risks for pesticides (Vanclooster et al., 2004). There is a tendency to use a certain combination of model approach, experimental data set and calibrated parameters in the evaluation. As the description of preferential transport becomes more detailed, the number of unknown parameters values increases which makes calibration increasingly difficult (risk of non-unique values in the optimisation). Various parameters cannot be obtained in a way independent of a specific transport experiment. There is a clear need to increase the predictive value of the models by further testing for field conditions.

The procedures in the European Union for the evaluation of the risk of leaching of pesticides to groundwater have been described recently by FOCUS (2009). There is scientific consensus that preferential transport occurs under field conditions. It is recognised that there can be e.g. finger flow in sandy soils. However, there is a lack of the combination of appropriate models and parameters. The FOCUS Work Group realised that it is difficult to carry out preferential leaching experiments for registration purposes, due to the spatial heterogeneity of soils, etc. A few EU member states account for the risk of preferential pesticide leaching via macropores, so at the national evaluation level. Other types of preferential leaching are not considered in an explicit way nowadays.

**Main aspects** of the future use of preferential transport models in the evaluation of pesticide leaching risks are:

- The uncertainty in the predictions is an obstacle for the use of preferential transport sub-models in registration procedures. Confidence should be increased by continued testing against the results of detailed field experiments, followed by amendments.
- There is need for comparatively simple sub-models for which derivation of the limited number of input data is feasible.
- Well-defined scenarios are needed in the evaluation, that are expected to be derived from representative and detailed field experiments.
- Guidance should be given on the derivation of input data and relationships for the models. Default values and relationships should be given where possible.
- The combination of model and input data must have been tested under various field conditions. Testing against concentrations leached from the soil profile (in groundwater and via drain tubes) should be included.
- Estimates of various transport parameters have to be obtained by calibration of the computations against the results of detailed field experiments. Where possible, methods for independent estimation of the parameter values should be developed.

## 7 General discussion, conclusions and recommendations

Humic-sandy and loamy-sandy soils are used on a large scale for agriculture in catchment areas for ground-water and surface water intended to be used for drinking water. There is ample experimental evidence that complications in water flow and pesticide transport can occur in such soils. This can lead to the pesticide concentrations in groundwater and water courses to be higher than expected on the basis of computations with conventional models for the evaluation of leaching risks. Sub-models are needed that simulate the complications in pesticide transport in soil in the computation models.

The heterogeneity of water flow and substance transport in cultivated sandy soils is illustrated by discussing the results of some field experiments. The ranges in volume fraction of water and in concentration of substances measured per depth at the sampling times are very wide. Therefore it can be difficult to select the most appropriate model concept to describe the data. Further, gaps and uncertainties in the data can hamper their use in the testing of preferential transport models.

Experiences with the simulation of water flow in sandy soils with the Richards equation, using laboratory-measured hydraulic relationships, are described. Wetting of the soil in the field was found to be irregular and less complete than expected from the moisture retention of completely-wetted soil samples in the lab (based on the water-withdrawal curve).

We made an inventory of model concepts that may be suitable for simulating preferential water flow and pesticide transport in cultivated sandy soils. It should be possible to incorporate the concepts in a mechanistic/deterministic model like the SWAP-PEARL combination. The flexibility of SWAP-PEARL in dealing with the many processes in the field (soil, hydrology, crop, pesticide, management, etc.) should be retained. Comparatively simple concepts are preferred, which require only a few additional parameters that can hopefully be measured.

The concept of enhanced dispersion in a single soil domain for each layer (convection-dispersion approach) does not require modification of the model. Only the input value for the dispersion length needs to be increased to account for preferential transport. The concept corresponds to wave-shaped distributions in soil and breakthrough curves. The dispersion length can be taken to be different for the soil layers (so considering each of them as one soil domain).

The concept of mobile-stagnant water phases is comparatively simple and only requires a few additional parameters. It can explain fast transport of the front part of the concentration distribution and long tailing of the back part. A substantial stagnant water phase for prolonged periods does not seem to be representative for cultivated sandy soils, as movement of weakly-sorbed substances from the top layer is common. The incorporation of variable volume fractions of water in both domains improves the usability of the concept for field soils (drier end wetter periods).

An attractive concept for cultivated sandy soils is the dual-velocity concept with slow-flow and fast-flow water phases, respectively. It allows for a substantial contribution of matrix transport, with an additional contribution of preferential transport. The volume fractions of water in both domains can be simulated to be highly variable, which corresponds to field conditions. However, various parameters and relationships are needed which may be difficult to determine.

The concept of transversal (horizontal) diffusion in a stagnant domain in sandy soils from a mobile domain (vertical transport) has mainly been used as a research tool. It does not allow for the highly variable soil moisture conditions in the field.

The soil columns approach (without transversal interaction) is mainly used for the simulation of plots in the field, e.g. with different hydraulic properties. Leaching from the whole field is calculated from the leaching contributions for each of the soil columns, computed with the one-dimensional model (no model modification needed).

The concept of finger flow in a water-repellent intermediate layer (no horizontal interaction) was derived from experiments for a sand soil with permanent grass cover. Water flow and substance transport in the wettable layers above (top layer) and below (subsoil) the intermediate layer are assumed to be rather uniform. This concept seems to be too extreme for cultivated sandy soils, which are less water-repellent. Consideration of two flow domains in the intermediate layer (fingers and between-fingers) may increase the usability of the concept.

We made an inventory of experiences with the modelling of preferential flow and transport in soils with macropores, as far as they seem relevant for cultivated sandy soil. In the calibration of two-domain computations against measurements, the estimation of parameters is most feasible if the transport behaviour deviates substantially from convection-dispersion behaviour (wave shape). Calibration is facilitated if the variation in measuring results is comparatively small. The difference in transverse equilibration between non-sorbed tracers and sorbed pesticides by diffusion needs further investigation.

Various requirements for sub-models dealing with preferential flow and transport, to be used in the evaluation of leaching risks, are discussed. Well-defined scenarios are needed, that are often derived from specific detailed field experiments. The combination of sub-model and input data must have been tested under various representative field conditions, to gain confidence in the results.



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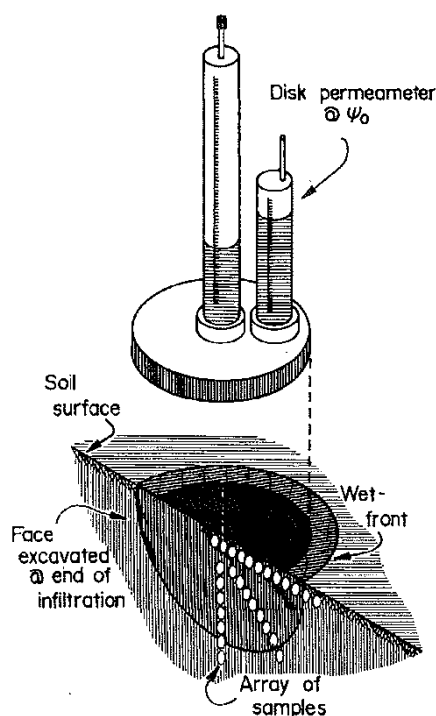
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# Appendix A Measurement of the fraction mobile water by tension infiltrometer

Often, transport parameters can be obtained only by calibration of computations against the results of transport experiments. It is desirable to have also independent ways of obtaining the transport parameters. An example is the measurement of the fraction of mobile water phase in soil, as discussed in Section 4.3, using tension infiltrometers. Such independent measurements could give the computations more predictive value, rather than only descriptive value.

A solution of bromide ion in a tension infiltrometer (at slight negative pressure) was infiltrated into the surface of a pre-wetted sandy-loam soil (Clothier et al., 1992, 1995). The concentration of bromide ion in the top layer of the soil was measured, well behind the calculated bromide-penetration front (Figure 19). The fraction of mobile water was calculated from the ratio between the concentration in the soil water phase and the concentration supplied. Under various water conditions, they found the fraction of mobile water to be mostly around 0.49 (Clothier et al., 1992) and 0.65 (Clothier et al., 1995) times the total volume fraction of water. Attempts to estimate the rate coefficient for the exchange of bromide ion between the flow domains did not give consistent values.



**Figure 19**

*Experimental set up for the measurement of the fraction mobile water by tension infiltrometer (Clothier et al., 1992; ©SSSAJ, with permission).*

Jaynes et al. (1995) also divided the soil into domains with mobile and a stagnant water. Substance transport in the mobile domain was described by the convection-dispersion equation. The first-order rate equation based on the difference in concentration was used to describe the exchange of substance between the mobile and stagnant domains. The parameters were obtained from field measurements using steady-state infiltration of aqueous solutions of different anionic tracers from tension infiltrometers (head -3 cm). The experiments started with one tracer and at time intervals another tracer was added to the previous ones. Both the mobile water fraction and the exchange-rate coefficient showed a wide range of values for the loam and clay loam soils studied.

A tension infiltrometer method was used by Casey et al. (1997) to measure the fraction of mobile water and the rate of exchange of substances between mobile and stagnant water regions. Water was infiltrated on a series of field sites with loam soil, at a pressure head of -3 cm. Chloride ion and four fluorobenzoate tracers were added in succession to the infiltration water. The infiltration started with one tracer and at time intervals another tracer was added, so that at the end all tracers were infiltrated. After measuring the concentrations in the soil underneath the infiltrometer (fronts had passed), the fraction of mobile water and the exchange-rate coefficient for the weakly-sorbed substances could be calculated.

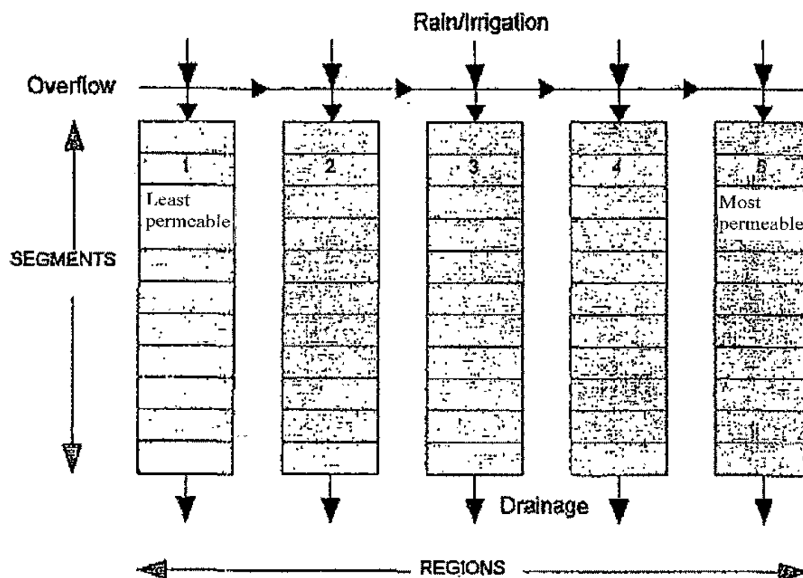
Casey et al. (1998) continued the measurement of transport parameters in the mobile-stagnant model with a tension infiltrometer in the field. Again, they used the sequential tracer application technique using chloride ion and a series of fluorobenzoate tracers. Now the measurements were carried out at water-saturation and at different negative pressure heads in the range down to -15 cm. The fraction of stagnant water differed somewhat for the pressure heads, but there was no clear trend. The rate coefficient for mass-exchange of the substances decreased as the pressure head became more negative (less wet soil).

## Appendix B Multiple-velocity approaches

A number of proposals was made to describe preferential flow and transport by distinguishing a larger number of transport regions in soil than the two regions in Sections 4.3 and 4.4. An example is the Preferential Flow Model described by Steenhuis et al. (1990). The model describes vertical steady-state water flow (gravity flow) through a soil system with five pore regions having different hydraulic conductivities. Solute exchange between the pore regions was described by mimicking diffusion. Even for this highly simplified system, several parameter values were needed without a method for measurement or estimation. This problem becomes even worse for the simulation of more realistic transient-flow systems in the field using several pore regions.

Gwo et al. (1995) distinguished three soil regions containing macropores, mesopores and micropores, respectively. Such models contain a comparatively high number of parameters whose values are difficult to obtain. The boundary conditions (e.g. at the soil surface) even become more complicated than with two-region models. Further, distinguishing a region with macropores is not expected to be relevant for cultivated sandy soils.

Hutson and Wagenet (1995) distinguished multiple vertical segments (e.g. five) in their hypothetical soil system (Figure 20). The segments are interrupted at certain depths and then rejoined at random. Assumptions have to be made on the sizes of the segments and on their hydraulic characteristics. Besides vertical transport in the segments, horizontal movement of water and solute between the segments occurs. All water flows are described by Darcy's law and all substance transport by the convection-dispersion equation. The simulated system is flexible with respect to the incorporation of other types of heterogeneity. Such more complicated models require a lot of input-parameter values, which are highly uncertain.



**Figure 20**

*Division of the soil profile into regions (vertical) and segments (horizontal). Patterns of overflow and infiltration at the soil surface (Hutson and Wagenet, 1995; ©SSSAJ, with permission).*

Another concept of a multi-domain model for water flow and solute transport was described by Durner and Flühler (1996). In their example, five vertical soil regions were distinguished, each connected to a pore-size class. The volume fractions of water and the hydraulic conductivities of the pore-size classes were derived from the hydraulic relationships of the soil. Vertical solute transport in the domains occurred by convection. The horizontal solute flux between the pore domains involved convection, dispersion and diffusion. The latter two were simulated by using an empirical 'pore-domain interaction coefficient' times the concentration gradient. The model was considered to be a research tool rather than a tool for practical use in field. The estimation of the many parameter values for such multi-domain models is a major problem.

In summary, more complex sub-models can be developed than described in the main text (Chapter 4) of the present report. However, such sub-models require a series of input data and relationships which are very difficult to obtain.

## Appendix C Physical versus chemical non-equilibrium

Concepts of preferential flow and transport (physical non-equilibrium) are the main topic of the present report. Besides there is often chemical non-equilibrium, also indicated by adsorption - desorption kinetics, at the soil surfaces. In various reported studies, both types of non-equilibrium were considered. The question rises to what extent the contributions of the two types of non-equilibrium to pesticide transport in soils can be distinguished.

The results of leaching experiments for atrazine and 2,4-D using columns of three soils (water-saturated, steady-state flow) were simulated with two models (Rao et al., 1979). In the first model, two types of sorption site were distinguished, showing instantaneous and kinetic adsorption-desorption, respectively. In the second model, soil regions with mobile and stagnant water phases were distinguished, with the first-order rate equation for substance exchange. Both models could describe the breakthrough curves of the herbicides, by calibrating some of their parameters (curve fitting). By simulating the breakthrough curves of tritiated water, the authors inferred that the stagnant water phase played a minor role in these experiments (which may not hold for sorbed substances).

The non-equilibrium transport of ions in soil (steady-state saturated water flow) was described by Nkedi-Kizza et al. (1984) in two ways:

- 1) by distinguishing mobile and stagnant water phases, with the first-order rate equation for the exchange of substance between the phases;
- 2) by distinguishing sites with instantaneous and kinetic sorption equilibration, respectively.

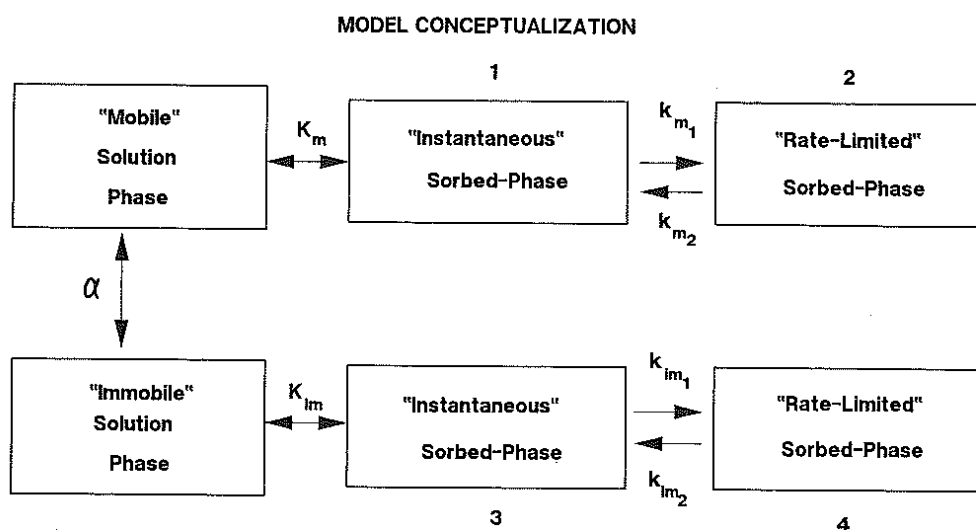
The equations for the mechanisms could be converted to the same dimensionless transport equation.

Consequently, the two models are equivalent with respect to the description of the type of breakthrough curve. So the mechanism of non-equilibrium of sorbed substances cannot be derived from the shape of the breakthrough curve. Measurement of the breakthrough curve of a non-sorbed (conservative) tracer for the same soil system may be helpful in distinguishing the effect of physical non-equilibrium.

An operational definition for the distinction between physical and chemical non-equilibrium was presented by Boesten (1986). Chemical equilibration of a pesticide can be measured in a continuously-mixed soil-water suspension. Physical equilibration deals with the lateral transport between water phases with different flow velocities or even stagnant water.

When distinguishing soil phases, soil regions and sorption sites, the problem arises of assigning transformation rate coefficients to the pesticide in each of these compartments. Van Genuchten and Wagenet (1989) combined the mobile-stagnant concept with two-site sorption equilibration (instantaneous and kinetic). They considered the possibility to distinguish transformation in the water phase from transformation on whole-soil basis. The question was raised also by Gärdeninger et al. (1990), but could not be solved in their study on transport and transformation of atrazine and 2,4,5-T in silt loam soil columns. They had to assign the same transformation rate coefficient to the herbicide in all soil compartments.

A dual non-equilibrium approach, including physical non-equilibrium and sorption-related non-equilibrium, was discussed also by Brusseau et al. (1989) and Brusseau and Rao (1990). Physical non-equilibrium was described in a system of mobile and stagnant water phases. Rate-limited equilibration between the two phases occurred by transversal diffusion through the water phase, mimicked by the first-order rate equation. The mobile and stagnant water phases were each connected to an instantaneous and a rate-limited sorption phase (Figure 21). Sorption-related non-equilibrium included terms for intra-sorbent diffusion and for rate-limited sorption at the surfaces. However, diffusion in the sorbing matrix can also be assigned to physical non-equilibrium. A more consequent distinction between physical non-equilibrium (transport processes) and chemical non-equilibrium (processes at the sorbing surfaces) is desirable.



**Figure 21**

*Scheme of the combined concepts of physical and chemical non-equilibrium (Brusseau et al, 1989).*

Ball et al. (1991) accentuated the distinction between physical and chemical non-equilibrium. Physical non-equilibrium should involve the transport processes in pores of all sizes, so also those in the sorbing matrix. Chemical non-equilibrium deals with the processes at the sorbing surfaces. The authors expect physical equilibration by diffusion to be slower for sorbed substances than for non-sorbed tracers. First of all, the diffusion coefficients of the compounds in water are different. Further, diffusion of the sorbed substance is slower and the capacity of the matrix for the sorbed substance is higher, as compared to non-sorbed tracers. Thus physical equilibration can be expected to proceed slower for sorbed substances than for non-sorbed tracers.

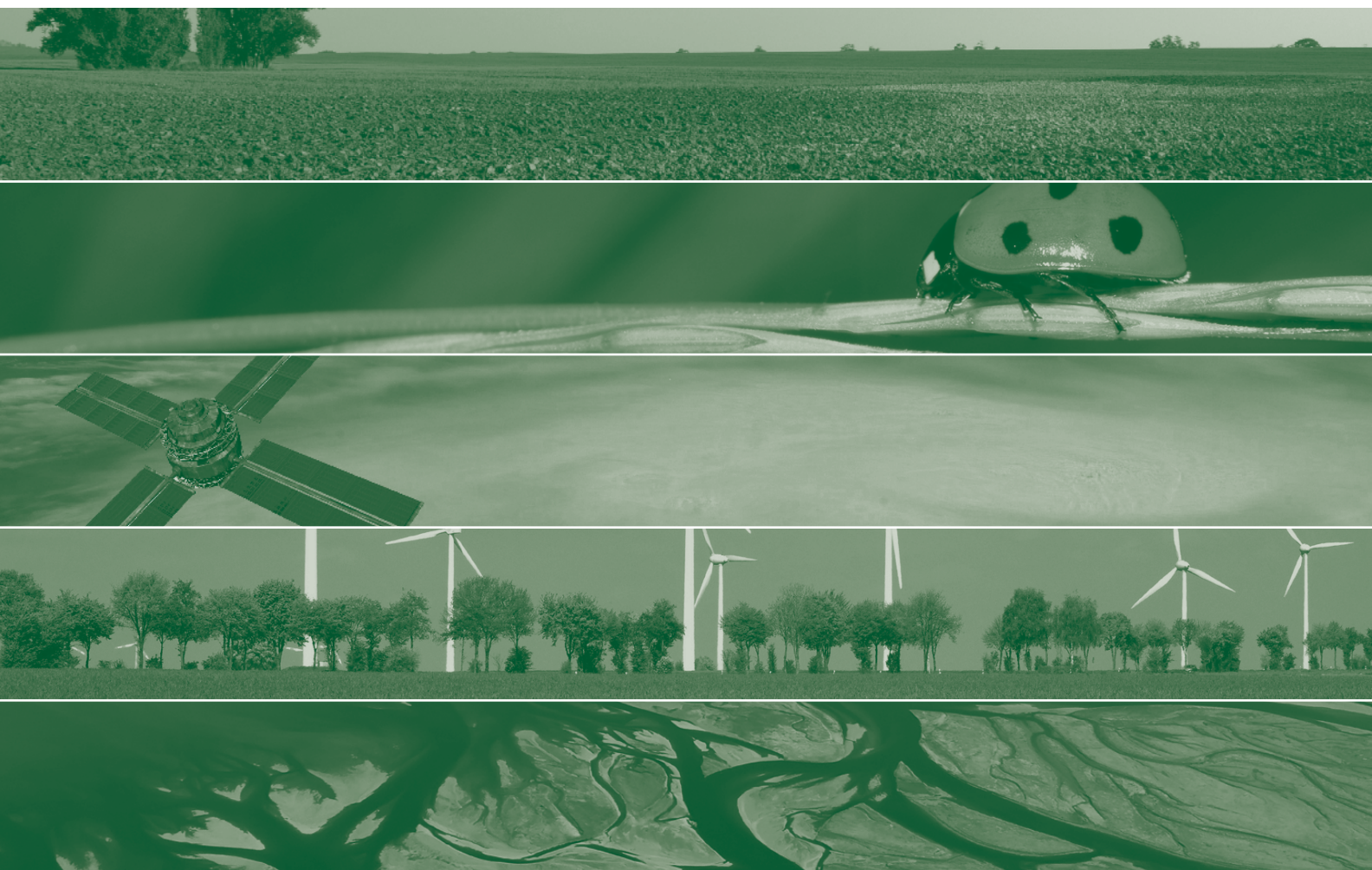
Gaber et al. (1995) used concepts of both physical and chemical non-equilibrium in attempts to explain the transport of tritiated water and atrazine in undisturbed silty clay loam soil columns. At comparatively high pore water velocities, equilibrium of tritiated water between the mobile and stagnant regions was far from complete (early breakthrough and tailing). However, at comparatively slow water flow, there was adequate time for equilibration between the regions (symmetrical breakthrough curves). In the case of atrazine there was non-equilibrium at all pore water velocities, possibly because sorption kinetics contributed to the non-equilibrium. However, the authors met the problem of quantitative distinction between physical and chemical non-equilibrium processes.



The relationship between physical and chemical equilibration of substances in soils has been the subject of several reviews (a.o. Boesten, 1986; Van Genuchten and Jury, 1987; Van Genuchten and Šimůnek, 1996; Ma and Selim, 1997; Van Genuchten and Sudicky, 1999; Brusseau, 1999). Common traits in these reviews are:

- in field conditions, physical and chemical non-equilibrium can occur at the same time (except for non-sorbed substances);
- the mathematical description of physical and chemical non-equilibrium tends to be equivalent, which makes it difficult to estimate the contribution of each of them, e.g. from breakthrough curves;
- it is a challenge to design experiments in such a way that the contribution of the two types of non-equilibrium can be distinguished;
- the transport behaviour of non-sorbed tracers is sometimes used to show physical equilibrium, but this may not hold for sorbed substances;
- models accounting for both physical and chemical non-equilibrium tend to have several unknown parameters, which makes estimation by calibration problematic;
- making predictions of preferential transport for non-studied situations is still difficult.

In summary, physical and chemical non-equilibrium have the same type of effect on pesticide transport in soil: early arrival of the front part and long tailing of the back part of the distribution. The mathematical description of the two phenomena tends to be similar. It is questionable whether physical equilibrium of a non-sorbed tracer implies the same for a sorbed pesticide. Distinction between the two types of non-equilibrium in the field seems to require much further research.



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