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Abstract

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Many agricultural areas with humic-sandy and loamy-sandy soils are used also for the extraction of water for drinking-water supply. Model concepts have been developed for the fast preferential transport of plant protection products (pesticides) in such soils, e.g. by fingered and funneled flow. An inventory is given of experiments that may be suitable for the testing of preferential transport models for cultivated sandy soils (without macropores). The pesticide concentrations per depth in soil are highly variable, due to local differences in transport, adsorption and transformation. Measurements in both the subsoil and in the upper groundwater are scarce, also due to sampling problems. Suggestions are given to improve the characterisation of soil profiles and weather conditions. Sampling methods for soil and soil solution can easily miss the preferential transport pathways. The methods of pesticide analysis in soils samples are often not sensitive enough to measure concentrations relevant for groundwater quality. The present study serves as the starting point for selecting the most suitable data sets for model testing and for the design of more complete and detailed data sets in the future.

Keywords: aquifer, chemical analysis, drinking water, leaching, plant protection products, soil columns, soil lysimeters, soil sampling, soil variability, subsoil, suction cups, transformation rate, tube drains.

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Summary

Much of the water used for drinking water supply is extracted from groundwater and water courses in areas with intensive agriculture (e.g. in the Netherlands), in which plant protection products (pesticides) are used. Environmental policy is focused on the prevention and reduction of the contamination of this water with pesticides. Usually it is supposed that water flow and pesticide transport in cultivated sandy soils (a major soil type in the extraction areas) proceed rather uniformly. However, it was shown that preferential water flow and pesticide transport can occur also in cultivated sandy soils. Such complicated transport leads to pesticide leaching to groundwater and water courses to be higher than expected from computer simulations with models assuming rather uniform transport (convection-dispersion approach).

Concepts for the modelling of preferential water flow and substance transport in sandy soils have been developed. In the present study, the question is whether there are data sets published/available to test models for preferential transport in sandy soils. In such testing it is especially interesting to have both, measurements in the soil profile and in the upper groundwater or tube-drain water for comparison. The present report discusses results of field experiments with tracers and pesticides in cultivated humic-sandy and loamy-sandy soils that may be suitable for testing preferential transport models.

In the Hupsel (NL) study for a field with loamy-sand soil, water flow and bromide-ion transport were studied. The upper part of the distributions of bromide ion in soil could be described reasonably well by the convection-dispersion approach. The front (deepest) parts of the distribution were missing for testing. The concentration pattern in shallow groundwater was too erratic for model testing.

The Vredepeel (NL) field experiment for bromide ion and bentazone in humic-sandy soil was carried out by our own research groups. The high variation of the concentration of bromide ion measured per depth in soil shows that water flow and substance transport were very heterogeneous. The high variation of the concentration of bentazone per depth in soil (composite of four samples) indicates that local differences in adsorption and transformation rate increased the variation. Because of problems with the sampling of wet subsoil, the earlier testing of convection-dispersion models was confined to the upper part of the unsaturated zone. The few measurements available to compare the concentrations in the subsoil with those in the upper groundwater indicate that complicated transport occurred.

In the literature, only few measurements are available on tracers and pesticides throughout the soil profile into the upper groundwater. Site-specific data on the adsorption and rate of transformation of the pesticides are often not available. In other cases there was a discrepancy in the transformation rates in the laboratory and in the field. The high variation in concentration measured per depth (which tends to increase with depth in the soil) is expected to hamper model testing. Concentration patterns in groundwater could not be reconstructed (too erratic). Only one experiment was reported which included chemical analysis of tube-drain water from a field with sandy soil.

In lysimeter and column studies with undisturbed sandy soil (relevant for the present study), only the leaching of a small fraction of the dosage was measured in a limited period after application of the substances. Measurements on the water and the concentrations within the soil are often not available (soil monolith considered as black box). Conclusions of the authors on preferential leaching from lysimeters/columns seem to be premature and they need further study. Lysimeter studies should be simulated in detail (as far as possible) with an appropriate model to check whether preferential transport actually occurred.

The concentration of inert tracers at a certain depth in soil shows a wide range of variation due to local differences in transport. Both the extent of adsorption and the rate of transformation of pesticides vary substantially in the soil of a field. These variations contribute to the variation of the concentration of pesticides at a certain depth in the soil. The leaching of pesticide residue from replicated columns/lysimeters taken from a field shows substantial differences. Variation in the transport of substances in soil can be related to features of soil formation, e.g. thickness of the soil horizons. The few observations on aquifer build-up in combined soil-groundwater studies indicate that they can be very heterogeneous.

Uncertainties in the accompanying processes in an experimental data set hamper its use in the testing of transport models. Spraying on plant and soil surfaces raises the question on the extent of the surface-dissipation processes and thus on the net load of the soil system. The uptake of some groups of substances by the crop roots is highly uncertain. Discrepancies in the rate of pesticide transformation in the lab and in the field also make transport-model testing problematic.

Many field studies suffer from imperfections in the characterisation of the soil and of the meteorological conditions; suggestions are given to improve this situation. Problems were encountered with the sampling of the (rather wet) soil deeper in the soil profile (water and soil flowing out of the sampling tube). In soil and soil solution sampling, preferential flow and transport pathways can be easily missed. In various cases the substance was measured earlier in samples taken near the groundwater table than in shallower samples (so part of the soil matrix was by-passed). Soil-core sampling and suction-cup sampling can give conflicting results. The question remains on how to sample a field with preferential water flow and substance transport in a representative way. The determination limit in the chemical analysis of pesticides in soil samples is usually much higher (less sensitive) than that in water samples. This low sensitivity hampers the comparison of the concentrations in (sub)soil with those in groundwater. Checks of the measurements by a second (independent) method of analysis is often highly desirable to prevent false-positive and too high values.

In conclusion, all field experiments have their (serious) imperfections. The very heterogeneous nature of sandy soils and of the processes in these soils lead to large variations in the concentrations. Technical problems, e.g. in sampling and chemical analysis, lead to incomplete and confusing data sets. In general, the experimental techniques have to be improved. Only a few data sets may be adequate for the testing of models for preferential water flow and substance transport in sandy soils. The present literature study can serve as the starting point for a) selection of the most suitable data sets for model testing and b) the design of more complete and detailed data sets.

1 Introduction

Much of the water used for drinking water supply is taken from groundwater and water courses in areas with intensive agriculture (e.g. in the Netherlands). In these areas, plant protection products (pesticides) are used, often in schemes of integrated crop protection. In measurement programs, residues of the pesticides are commonly found in groundwater and water courses in these areas. This contamination necessitates expensive purification of the water in the preparation of drinking water. Residues in water courses may have toxic effects on aquatic organisms. Environmental policy is focused on the prevention and reduction of these contaminations.

Usually it is supposed that water flow and pesticide transport in cultivated sandy soils proceed rather uniformly. This in contrast to the flow and transport in soils with macropores (shrinkage cracks, inter-aggregate voids, earthworm burrows, root channels), which were quite intensively studied in the last two decades. However, it was shown that preferential water flow and substance transport can also occur in cultivated sandy soils (Leistra and Boesten, 2010). Such complicated transport leads to pesticide leaching to groundwater and water courses to be higher than expected from computer simulations with models assuming rather uniform transport.

Concepts for the modelling of preferential water flow and pesticide transport in sandy soils were discussed by Leistra and Boesten (2011). The concepts seemed to be suitable for incorporation into the SWAP-PEARL combination of models (Tiktak et al., 2000; Leistra et al., 2001). The concepts have to be comparatively simple to allow determination/estimation of the input parameters.

In the present study, the question is whether there are suitable data sets published/available to test the sub-models for preferential pesticide transport in sandy soils. Field experiments are time-consuming and expensive, so results from the past have to be fully utilised. Information on the transport of water tracers can also be usable. Detailed measurements of substances in the upper groundwater, in addition to measurements throughout the soil profile, are especially useful to establish whether there was preferential transport.

A literature review of tests of four simulation models for pesticides in the soil-plant system was presented by Van den Bosch and Boesten (1995). Frequently-occurring shortcomings in the experimental data sets used for the tests were:

- Poor characterisation of soil profile and composition of the layers.
- Weather conditions not quantified (rainfall/irrigation pattern).
- No information on crop growth during the experiment (soil cover/leaf area index, root development).
- Few soil-sampling times, low number of samples and too shallow soil sampling (only the top layer).
- Duration of the experiment was too short to study deeper movement.
- No check of the water-flow part of the model.
- Too low sensitivity of the concentration measurements in soil (high determination limit).
- No site-specific measurements on adsorption and rate of transformation in soil as model input (e.g. data taken from handbooks and data bases).
- Pesticide uptake by the plant roots set to zero (because of lack of data).

The test quantities in the study of Van den Bosch and Boesten (1995) were the depth and height of the peak of the pesticide distribution with depth in soil (not the possible fast transport of the front part of the distribution).

A usual sequence in the testing of computation models for transport in soil is (Boesten and Gottesbüren, 2000):

1. testing and calibration of the sub-model for water flow;
2. testing and calibration of the sub-model for transport of an inert tracer;
3. testing of the model against the behaviour of the pesticide, using laboratory data on adsorption and rate of transformation.

In the testing of models for preferential substance transport, it is especially interesting to have both, measurements throughout the soil profile and in the upper groundwater or tube-drain water (Vanderborght, 1997). If the resident concentration measured in the lower part of the soil profile differs distinctly from the concentration leached from the profile (flux concentration), this is a clear indication of preferential transport. Especially in the initial stages of leaching, the concentration in the leachate could be distinctly higher than that averaged over the water phase in the lower part of the soil profile.

The present study discusses results of field experiments with tracers and pesticides in cultivated humic-sandy and loamy-sandy soils, which may be suitable for the testing of preferential-transport sub-models. The modelling work that already was done with (part of) the data, often using the convection-dispersion approach, is briefly discussed. Most attention is paid to two field experiments in the Netherlands (Chapter 2): those of Hupsel and Vredepeel. A survey of field experiments with sandy soils from all over the world is given in Chapter 3. Besides experiments with soil and groundwater sampling, those with sampling and analysis of tube-drain water are interesting. Chapter 4 deals with lysimeter and soil-column studies using undisturbed soil. The high variation in the concentrations measured per depth in soil and groundwater triggered the collection of more data on this variation and on possible causes (Chapter 5). Limitations in the experimental procedures are discussed (Chapter 6): a) soil characterisation and meteo data, b) sampling procedures and c) analytical methods. Such limitations can be expected to hamper the use of data sets for model testing. General aspects of transport-model testing are discussed in Chapter 7. The general discussion and conclusions are presented in Chapter 8.

2 Field experiments in the Netherlands

2.1 Hupsel

The first field experiment in the Netherlands that may be suitable for further model testing deals with the Hupsel study. A solution of bromide ion was sprayed on a loamy-sand soil in the Hupsel catchment area in December (Van Ommen and Dijksma, 1988; Van Ommen et al., 1989a). The field strip, used for arable farming, was tube-drained at about 1 m depth and at a distance of 11 m. Rainfall was 480 mm and drain discharge was 370 mm in the study period of 190 days. At four time intervals, the soil was sampled by coring to 0.7 m depth (ten cores per time). Samples from the shallow groundwater above a low-permeable clay layer (starting between 1.5 and 2.5 m depth) were taken via tubes with filters. The depth of the water table and the depths of the filters were not reported. The tube-drain water was sampled frequently. Bromide concentrations in the soil profile, groundwater and tube-drain water were measured by ion chromatography. In the computations, water flow was assumed to be steady-state, with the flux based on the drain discharge.

The concentration profiles of bromide ion (to 0.7 m depth) could be simulated reasonably well by the convection - dispersion approach (Figure 2.1). The volume fraction of mobile water was estimated from the average transport distance to be about 0.25, which was about 0.8 times the measured volume fraction of water. The concentrations measured in groundwater showed a highly irregular pattern (values not given by the authors). Possible explanations are: 1) highly irregular breakthrough from the soil profile, and 2) large variation in permeability, and thus water flow, in the shallow aquifer.

Bromide transport in the groundwater zone to the drain tubes was simulated with a stirred-reservoir model. Breakthrough of bromide ion via the tube-drain water could be explained only by assuming fractions of mobile and immobile water. A fraction of mobile water of 0.6 (of the total volume fraction of water) was assigned to the lower part of the water-unsaturated zone; it was assumed to be caused by fingered flow. However, the early arrival of bromide in tube-drain water can partly have been the result of non uniform transport in the aquifer.

A iodide solution was sprinkler-irrigated on bare soil plots in ten gifts of 10 mm each, in a period of two days (Van Ommen et al., 1989b). Horizontal cross sections were excavated at various depths and coloured by spraying chloride and starch, which gives a blue colour of the iodine-starch combination. Movement of iodide in the cultivated top layer was quite uniform. Clear non-uniform transport started below this top layer.

<u>Concluding remarks</u> (Hupsel)

- reasonable description of the bromide distributions with depth in the soil profile (at least the upper part) by the convection-dispersion approach, assuming the fraction of mobile water to be about 0.8;
- rather uniform substance movement in the cultivated top layer can be followed by more heterogeneous transport in the layers below (fingering/funneling);
- as no measurements are available for depths greater than 0.7 m in soil, computations for the front part of the distribution below this depth cannot be tested.
- the authors considered the variation in the concentration in the shallow groundwater (values were not given) to be too high for model testing;
- the assumption of complete substance mixing in the aquifer was not substantiated (and is not likely).

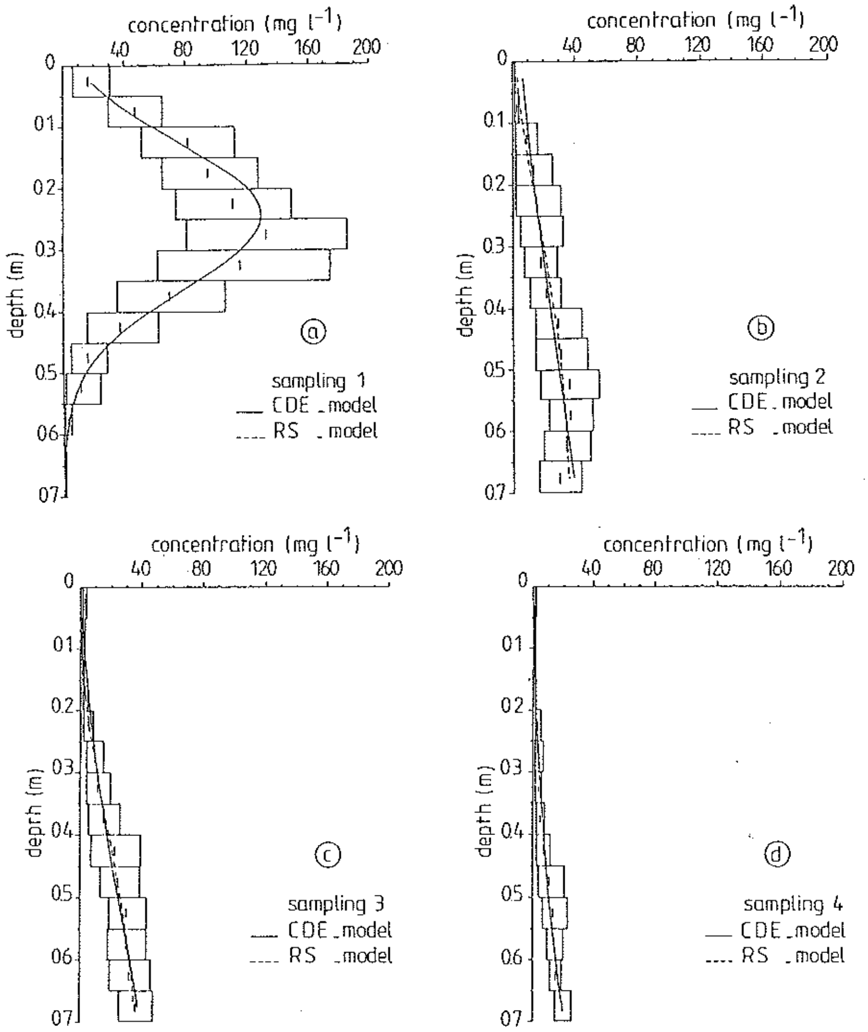

Figure 2.1

Measured and calculated concentration profiles of bromide ion in the Hupsel loamy-sand soil profile (Van Ommen et al., 1989a; ©Elsevier, with permission). Measurements indicated by the 90% confidence intervals. CDE = calculated with convection-dispersion model.

2.2 Vredepeel

2.2.1 Experimental data

The second field experiment in the Netherlands that may be suitable for further model testing deals with the Vredepeel study for a humic-sandy soil (gley podzol) (Hamminga et al., 1994; Boesten and Van der Pas, 1999, 2000). Organic carbon content in the humic-sandy top layer (on average 0.32 m thick) was 2.3% and below that it decreased to around 0.1% in the sand subsoil below 0.5 m. The hydraulic characteristics of the soil were determined in the laboratory. The groundwater table fluctuated around 1.2 m depth, with the shallowest depths in winter due to the rainfall surplus. The field was used for arable farming and it was sown with winter wheat at the start of the experiment in November. Shortly after sowing, the field was sprayed with the tracer bromide ion and the herbicide bentazone. Some meteorological conditions were measured in detail at the site: air temperature, soil temperature and rainfall. Other meteo data were obtained from nearby weather stations.

For the samplings, the field was divided into four Sections, which were each divided further into four plots. At seven times after application (up to 474 days), the soil profile was sampled by taking cores (16 per time; four per Section), which were separated into layers. Groundwater samples were taken regularly via filter tubes. Contents and concentrations of the substances in the soil and water samples were measured by extraction and chromatographic analysis. Adsorption and transformation rate of bentazone in soil material taken from different layers were measured in the laboratory.

The results of the measurements of bromide ion and bentazone in soil and groundwater of the Vredepeel field were reported in detail by Van der Pas (1993) and Hamminga et al. (1994). Subsequently, some results were published in figures, in the form of the average concentrations at the measuring depths in soil (Boesten and Van der Pas, 1999, 2000). Up to now, little attention has been paid to the spreading in the measurements in soil. Further, the results of the measurements in groundwater have not been included in the evaluations yet.

2.2.2 Computer simulations

The first computations for the Vredepeel data set were carried out by Van den Bosch and Boesten (1994) and Van den Bosch et al. (1999), using the SWACROP-PESTLA combination of models. The simulation of water flow in the soil with the Richards equation had to be calibrated. The use of the soil moisture retention curves measured for some layers in the laboratory led to over-estimation of moisture retention in the field. The hydraulic conductivity curve of the 30 to 60 cm layer had to be increased to improve the simulation of water redistribution after rainfall. The movement of the wave of bromide ion in the soil profile (average concentrations per depth) was simulated in a reasonable way by the convection-dispersion approach, using a dispersion length of 0.03 m. After an initial period, the front part of the distribution in soil was below the depth of measurement, so the computation for this part could not be compared. The uncertainty in the uptake of bromide by the crop roots hampered the comparison of computed and measured transport.

The movement of much of the weakly-adsorbed herbicide bentazone (average concentrations per depth) was also simulated reasonably well by the SWACROP-PESTLA model combination (Van den Bosch and Boesten, 1994). However, measurements of the front (deeper) part of the distribution in soil were missing for comparison of the computations (Figure 2.2). For bentazone too, the uncertainty in uptake by the crop roots was high. The rate of transformation of bentazone in the 0.5 to 1.0 m layer in the field was distinctly higher than expected from the incubation study for this layer in the laboratory.

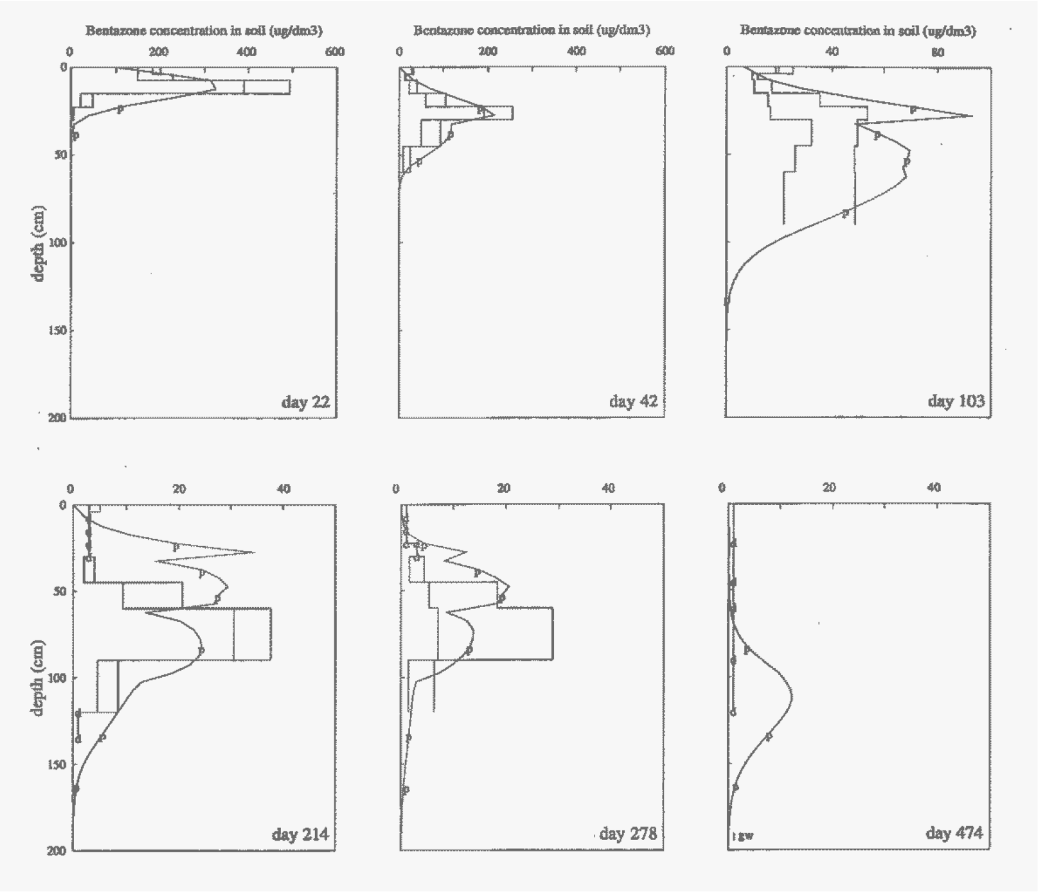

Figure 2.2

Comparison of computed and measured concentration profiles of bentazone in soil at six times after application (Van den Bosch and Boesten, 1994). Step lines: averages of measurements plus and minus one standard deviation. Smooth lines: computed.

Tiktak et al. (1998) tested the PESTRAS model (PESticide TRansport ASsessment) against the measurements for the Vredepeel experimental field. The simulation of water flow in soil with the Richards equation, using the hydraulic relationships from the laboratory, had to be calibrated. A large part of the bromide-ion distributions in soil could be described reasonably well. However, the front (deepest) part of the distributions were not available for testing. Similarly, a large part of the movement of the herbicide bentazone in soil could be described in a reasonable way, but the front parts of the distribution were not available for testing. For both compounds (anion and weak acid, respectively), the uncertainty in the uptake by the wheat crop hampered the testing of the transport part of the model. Further, the rate of transformation of bentazone in the 0.5 to 1.0 m layer in the field was presumably faster than the very low rate measured in the laboratory. This deviation in transformation rate also hampered the test of the transport part of the model.

Computations for the Vredepeel data set were continued by Boesten and Gottesbüren (2000), also using the SWACROP-PESTLA combination of models. Using the soil moisture retention curves measured in the laboratory (starting from water-saturated samples) resulted in over-estimation of the moisture retention in the field. So the retention curves had to be calibrated to a lower level. The exponential function for groundwater discharge, which described the course of the groundwater level with time, also had to calibrated. Using the convection-dispersion equation, taking the dispersion length to be 0.05 m, a reasonable description of the bromide distributions in soil was obtained. The uncertainty in uptake of bromide by the crop roots and its release later on hampered the test of the transport description for the upper part for the soil profile. At the later times, the front part of the bromide distribution had moved below the depth of measurement in soil. The movement of the main (upper) part of the distribution of bentazone in soil was described reasonably well. However, the rate of transformation of bentazone in the intermediate soil layer in the field was faster than expected on the basis of the incubation study in the laboratory. This diverging transformation rate interfered with the test of the transport part of the model.

2.2.3 Further evaluation: bromide ion

The concentrations of bromide ion measured in the soil of the Vredepeel field at 42 days after application (3 January) were presented graphically (scatter plot) by Hamminga et al. (1994). They expressed the concentrations in mg dm^{-3} soil system. For the present study, these concentrations were converted to concentrations in the water phase, using the average values of the volume fraction of water per depth (Hamminga et al., 1994). In this way, the concentrations measured in soil and groundwater are expressed both on water-phase basis and can be compared directly.

The concentrations of bromide ion measured in groundwater at 42 days after application were given in Table form by Hamminga et al. (1994). The sampling depths for groundwater were 1.1 and 1.5 m. The four sub samples per depth in each of the four field sections were combined into one sample, so four measurements (one per Section) are available per depth for the whole field.

The results of the measurements of bromide ion in soil and groundwater at 42 days after application are presented together in Figure 2.3. The groundwater level was at 0.7 m depth at this time. At most of the sampling depths the concentration in the water phase showed a wide range of variation. This indicates that bromide transport in soil was rather heterogeneous. Nevertheless, the distribution of the averages of the concentrations per depth was roughly wave-shaped. The measurements down to about 1 m depth were obtained by soil sampling, while the measurements at 1.1 and 1.5 m depth deal with groundwater samples. With the condensed concentration scale in Figure 2.3 (and used in the figure of Hamminga et al., 1994) it is difficult to distinguish visually the low levels of bromide ion at the various depths in subsoil and groundwater.

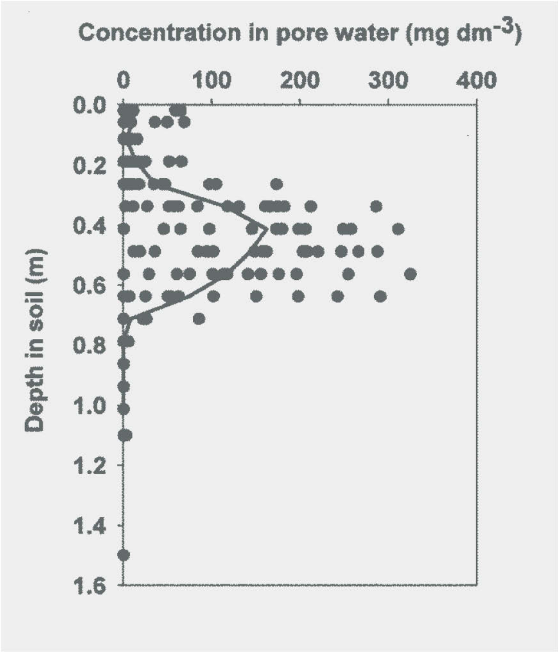

Figure 2.3
Concentrations of bromide ion in the water phase of the Vredepeel soil profile at 42 days after application. Soil samples taken down to about 1 m depth; groundwater samples taken at 1.1 and 1.5 m depth (basic data from Hamminga et al., 1994). Line = averages of the concentrations per depth.

For a correct interpretation of the measuring results, the details of the methods of analysis of bromide ion should be considered. In the HPLC analyses of the soil-sample extracts, nitrate ion interfered severely with the analysis of bromide ion (Hamminga et al., 1994; page 27). They seemed to handle a determination limit of 0.7 mg dm^{-3} soil system, which corresponds to about 2 mg dm^{-3} water phase. However, this limit of determination seems to hold for cases of minimal interference by nitrate ion. They indicated that in several cases the determination limit was much increased by the interference, up to the order of tens of mg dm^{-3} water phase. The conclusion is that the comparatively low concentrations of bromide ion reported for the subsoil samples are uncertain.

The concentrations of bromide ion in groundwater at 42 days after application were measured by an external laboratory, using a strongly improved HPLC method in which the interference by nitrate ion was much reduced. The results of these measurements are given in Table 2.1.

Table 2.1
Concentrations of bromide ion in groundwater of the four field Sections at 42 days after application, measured by a strongly improved HPLC method (Hamminga et al., 1994).

Depth (m)	Concentration (mg dm^{-3}) in			
	Section 1	Section 2	Section 3	Section 4
1.1	< 1	2.9	1.5	2.0
1.5	< 1	< 1	< 1	< 1

Due to the analytical problems with the soil samples, comparison of the concentrations measured in the subsoil with those in the upper groundwater (Table 2.1) is not possible for 42 days after application. The analyses of bromide ion in the soil samples taken at the later times after application suffer from the same interference by nitrate ion, so they are also unreliable. Further, there was a considerable distance between the deepest soil samples (e.g. around 1.3 m deep) and the upper groundwater samples (mostly taken at 2.2 m depth). So there may have been a distinct effect of lateral groundwater flow and bromide transport on the deeper concentrations. The general conclusion is that the data set of Hamminga et al. (1994) for bromide ion is not suitable for the investigation whether preferential transport occurred in the sandy-soil profile.

2.2.4 Further evaluation: bentazone

The results of the measurements of bentazone in the soil and in the upper groundwater of the Vredepeel field were given in detail by Van der Pas et al. (1993) in table form. The course of the concentration in groundwater with time differs strongly for field Section 1 on the one hand and field Sections 2, 3 and 4 on the other hand (Table 2.2). In field Section 1, bentazone started to appear in groundwater at 103 days after application and the concentration increased to comparatively high values after 474 days. On the contrary, in the groundwater of the Sections 2, 3 and 4 bentazone started to appear in distinct concentrations at 474 days after application, at the end of the experimental period. In view of this large difference, bentazone transport in Section 1 on the one hand and that in the Sections 2, 3 and 4 on the other hand have to be investigated separately.

Table 2.2
Concentrations of bentazone in groundwater measured by HPLC (Van der Pas et al., 1993). < = below the determination limit of 0.25 µg dm^{-3}. - = not measured.

Time after application (days)	Depth (m)	Concentration (µg dm^{-3}) in				
		Field Section 1		Field Section 2	Field Section 3	Field Section 4
		Plot A	Plots B, C and D (combined)			
22	1.1	<	<	<	<	<
42	1.1	<	<	0.3	<	<
	1.5	<	<	<	<	<
103	1.5	0.25	0.25	<	<	<
	2.2	0.8	3.9	<	<	<
214	2.2	1.8	2.3	<	<	<
278	2.2	0.6	3.0	<	<	<
474	1.5	205	127	-	-	-
	2.2	8.2	3.4	6.0	0.7	<

The concentrations of bentazone measured in soil were converted to their concentrations in the water phase. In this way the concentrations measured in soil and in groundwater can be compared directly. The concentration of bentazone in the water phase was calculated by:

$$C_w = \frac{C_s}{\Theta + \rho_b K_{oc}\ oc} \qquad \text{(Equation 1)}$$

where:
C_w = concentration in the water phase (mg dm^{-3})
C_s = concentration in soil (mg dm^{-3})
Θ = volume fraction of water (dm^3 dm^{-3})
ρ_b = soil bulk density (kg dm^{-3})
K_{oc} = coefficient of adsorption to soil organic carbon (dm^3 kg^{-1})
oc = organic carbon content (kg kg^{-1}) of soil

The concentrations of bentazone in the soil of each of the four field Sections were given in table form by Van der Pas et al. (1993). The soil bulk densities and volume fractions of water per depth were reported by Hamminga et al. (1994). The percentage of organic carbon at various depths in soil was given by Boesten and Van der Pas (2000); it ranged from 2.29% in the top 0.25 m layer to around 0.11% in the sand subsoil below 0.5 m. A K_{oc} value of 4.59 dm^3 kg^{-1} was derived from measurements of the adsorption of bentazone to Vredepeel topsoil material in the laboratory (Boesten and Van der Pas, 2000).

The concentrations of bentazone in soil and groundwater of field Section 1 at day 103, expressed as concentrations in the water phase, are represented in Figure 2.4 (left). The groundwater level was at 1.0 m depth at this time. Relatively high concentrations were present in the soil profile. At this compressed concentration scale, the concentrations deeper in the soil and in groundwater cannot be compared. In Figure 2.4 (right), the concentration scale is extended. The two concentrations of 0.00025 mg dm^{-3} measured at 1.5 m depth in the groundwater are just above the limit of determination. The concentrations measured in the groundwater at 2.2 m depth were distinctly higher than those at 1.5 m depth. This indicates that bentazone transport was rather heterogeneous.

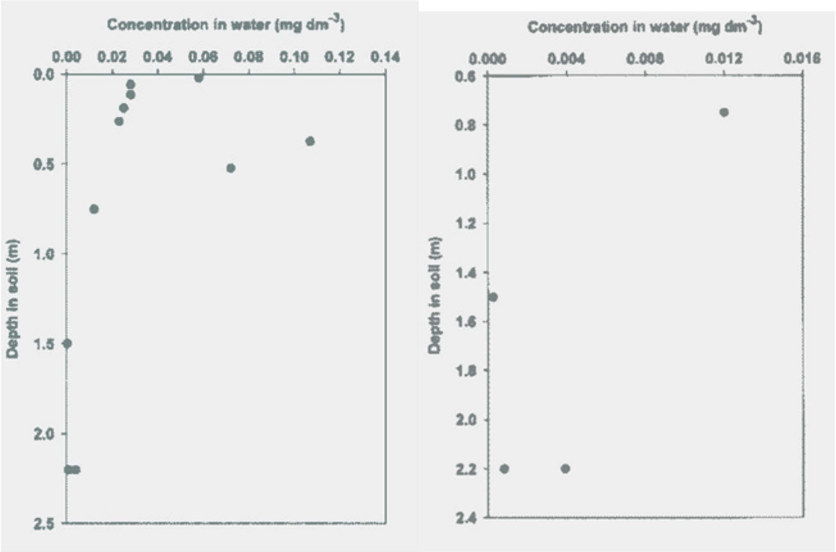

Figure 2.4
Concentrations of bentazone in the water phase of Vredepeel soil and groundwater (field Section 1) at 103 days after application. Left: entire profile. Right: extended concentration scale for the lower part of the profile. Duplicate measurements at both 1.5 and 2.2 m depth.

The concentrations of bentazone in soil and groundwater of Section 1, measured at 214 days after application, are represented in Figure 2.5 (left). At this time the groundwater level was at 1.5 m depth. Comparatively high concentrations were still present in the soil profile. For a better comparison of the concentrations deeper in soil and in groundwater, the concentration scale was extended in Figure 2.5 (right). The two concentrations measured at 2.2 m depth in the groundwater were higher than the single concentration below the limit of determination at 1.25 m depth (as was the case after 103 days). This is an indication for heterogeneous transport of bentazone.

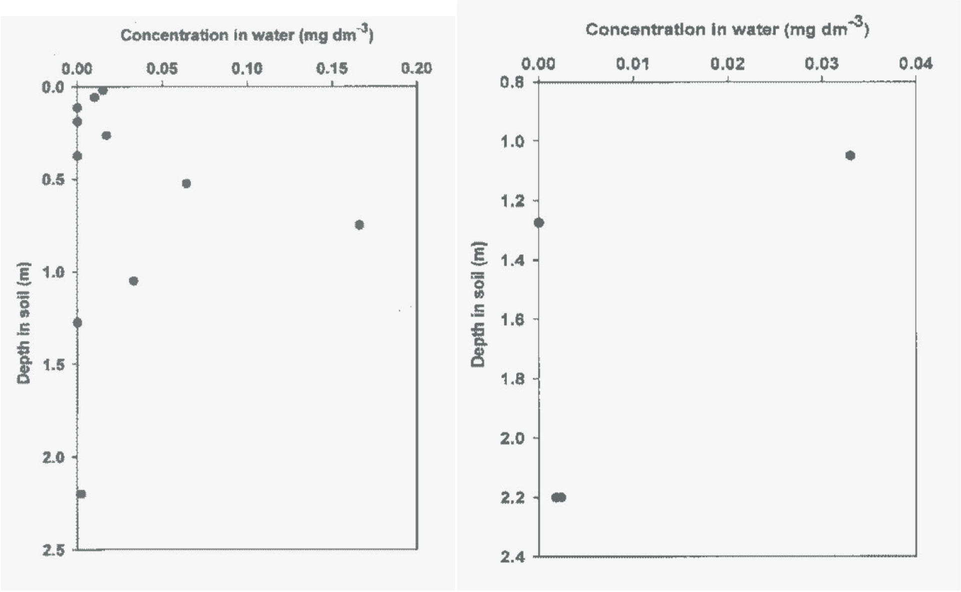

Figure 2.5

Concentrations of bentazone in the water phase of Vredepeel soil and groundwater (Section 1) at 214 days after application. Left: entire profile. Right: extended concentration scale for the lower part of the profile.

The distribution of bentazone with depth in the soil at 278 days after application is represented in Figure 2.6 (left). The groundwater level was at 1.7 m depth at this time. The concentrations in the top of the soil profile (to about 0.3 m depth) had become very low. The highest concentration was found at 0.75 m depth in soil. The much lower concentrations in subsoil and groundwater are given on an extended concentration scale in Figure 2.6 (right). The concentrations in groundwater at 2.2 m depth were much lower than that in the subsoil at 1.05 m depth. The distance between these measuring depths is quite large. The data do not give an indication on the type of transport.

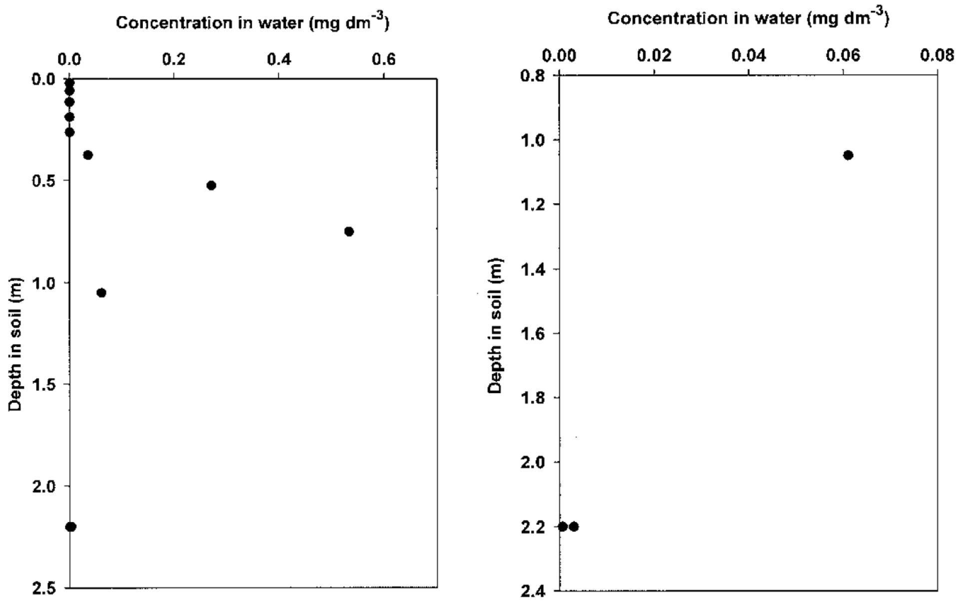

Figure 2.6
Concentrations of bentazone in the water phase of Vredepeel soil and groundwater (Section 1) at 278 days after application. Left: entire profile. Right: extended concentration scale for the lower part of the profile.

At 474 days after application no concentrations of bentazone could be measured in the soil profile of Section 1 anymore. Rather high concentration were present in the groundwater at that time (Table 2.2). The concentrations at 1.5 m depth were much higher than those at 2.2 m depth. No indication on the type of transport in the soil profile can be obtained from these data.

In the field Sections 2, 3 and 4, no bentazone could be measured in the groundwater up to and including 278 days after application, except for one detection of 0.3 µg dm^{-3} at 1.1 m depth on 42 days after application (Table 2.2). At 474 days after application, concentrations of 6.0 µg dm^{-3} (Section 2), 0.7 µg dm^{-3} (Section 3) and zero (Section 4) were measured at 2.2 m depth (Table 2.2). At that time no concentrations of bentazone could be measured in the soil profile anymore, so the concentrations in soil and groundwater cannot be compared. Information on the type of transport of bentazone in the soil profile cannot be derived directly from these data.

2.2.5 Concluding remarks (Vredepeel)

- Moisture retention in field soil is lower than expected from laboratory measurements for thoroughly wetted soil samples. This indicates that soil wetting in the field is irregular.
- The high variation of the concentration of bromide ion in soil shows that water flow and substance transport were very heterogeneous.
- The high variation of the concentration of bentazone per depth in soil (composite of four samples) indicates that local differences in adsorption and transformation increased the variation.
- Because of the problem with sampling the wet subsoil (soil flowed from the auger), the front (deepest) parts of the distributions are not available for model testing.
- Earlier testing of convection-dispersion models gave reasonable results, but was confined to the upper part of the unsaturated soil zone.

- Uncertainty in the extent of uptake of the substances by the crop roots interfered with the testing of transport modelling, especially in the topsoil.
- Interference in the chemical analysis of low bromide-ion concentrations in soil and groundwater prevent the use of the front parts of the distributions in model testing.
- Testing of models for bentazone transport, especially in the subsoil, was hampered by deviation between the rate of its transformation in the field (faster) and that in the laboratory. The question rises whether there are more examples of such deviations (see Chapters 3 and 4).
- In field Section 1 on the one hand and field Sections 2, 3 and 4 on the other hand the leaching behaviour of bentazone was highly different, which necessitates separate evaluation.
- The analyses for bentazone in the groundwater of field Section 1 indicate that transport was heterogeneous, but the number of measurements for the testing of preferential transport models is low.
- The question rises whether there are reports/publications on field experiments with sandy soils that are more suitable for testing preferential transport models (see Chapter 3).
- The question rises how variable the concentration measurements are in other field experiments with sandy soil (see Chapters 3 and 5).
- The question rises whether there are more examples of differences in leaching behaviour of a pesticide in different field sections (see Chapters 3, 4 and 5).
- The question rises whether process studies have been carried which can explain the high variation in pesticide concentration within a field (see Chapter 5).

3 Field experiments from all over the world

3.1 Fields without tube drains

The two data sets on substance movement in sandy soils obtained in the Netherlands (Chapter 2) have limitations with respect to their usability for testing preferential transport models. This holds for both the Hupsel and the Vredepeel data sets. The question is now whether more suitable data sets on field experiments have been reported in the international literature. In this Chapter, a survey is given of field experiments on the movement of tracers and pesticides in cultivated sandy soils, whose results can possibly be used for model testing. Studies with measurements only in the top of the soil profile are not included. A short description of each experiment is followed by an evaluation of its suitability for use in testing preferential-transport models. Experiments for tube-drained fields are discussed in Section 3.2.

The herbicide napropamide was sprayed on a field (California) with loamy-sand soil (bare) containing on average 0.6% organic carbon (Jury et al., 1986). The field was sprinkler-irrigated at 5 mm h^{-1} (no ponding): 30 mm shortly after spraying and 280 mm water in the next two weeks (daily gifts). Evaporation was estimated to be 50 mm in this period. The soil was sampled by coring at 19 places to 3 m depth. The highest concentration of napropamide remained in the top 0.1 m of the soil profile. At some depths in the soil (e.g. near 0.8 m) substantial concentrations were measured with a high variation per depth, down to 1.8 m. This deep movement could not be explained from convective-dispersive movement of this quite strongly adsorbed herbicide.
Evaluation.
Uncertainties in this study are: 1) incomplete description of the composition of the soil in layers, 2) no information on preceding soil cultivation, 3) only one type of sampling (soil coring), 4) results for only five cores (of the 19 cores taken) and the averages were given (graphically) and 5) no independent measurement of the rate of transformation in soil.

Jury et al. (1988) studied the movement of bromide ion in the loamy-sand soil (bare) of a field (California) which was sprinkler-irrigated frequently. The variation in the concentration measured per depth was high. In the computer simulation of the movement with a convection-dispersion model, high values of the dispersion length had to be used to describe the spreading of the distribution with depth. Further, the value of the calibrated dispersion length increased with depth in the soil profile (roughly linearly to a few metres depth). This could be related to the occurrence of more textural transitions deeper in the soil.

The herbicides bromacil, napropamide and prometryn were sprayed on the surface of field plots (California) of low-humic loamy-sand soil (Jury et al., 1988). In daily gifts, total amounts of 100 and 180 mm, respectively, of sprinkler irrigation water were given (no specification of distribution in time). Soil samples were taken by coring to 2 m depth. Only the mean concentrations per depth were presented. Bromacil was the most mobile herbicide; it moved in a kind of wave, faster than expected from a computation. The greatest part of the more strongly adsorbed napropamide and prometryn remained in the top 0.4 m of the soil after 180 mm of sprinkling. Besides, substantial concentrations were measured at some depths in the subsoil, e.g. around 1 m depth (double peak pattern). For the details, the authors refer to an unpublished MSc thesis.
Evaluation.
Uncertainties in this study deal with: 1) incomplete description of the soil profile and the composition of the soil in layers, 2) times of the irrigations (only total amounts given), 3) one way of sampling (soil coring), 4)

spreading in the concentrations not given and 5) no independent measurement of the rate of transformation in soil.

Smith et al. (1990) studied the movement of bromide ion and atrazine in low-humic sandy soil (Georgia) to groundwater. The soil solution was sampled by suction samplers (three depths down to 1.8 m) and the groundwater (table around 3 m depth) was sampled via tubes. The voids around the access tubes were filled with soil and sealed with bentonite clay, to prevent short-circuit flow of water. They applied a lot of irrigation water (amounts and times not given) to keep the soil profile wet enough for solution sampling in the vadose zone. Highly different breakthrough curves of bromide ion were measured by the six soil-solution samplers per depth. Soil sampling showed that measurable concentrations of atrazine moved to 1.8 m depth in the first 40 days. The concentrations of bromide ion in groundwater showed an erratic pattern; the flow pattern could not be reconstructed. Atrazine was measured in groundwater at concentrations of e.g. around 20 µg dm^{-3}. Down-slope movement of atrazine in the groundwater could be followed by the measurements. It was estimated that 5% of the dosage of atrazine had leached to groundwater, at half a year after application in the autumn. For the details, the authors referred to an unpublished PhD thesis.
<u>Evaluation</u>.
Shortcomings in this study are: 1) incomplete description of the soil in layers, 2) amounts and times of rainfall and irrigation were not given, 3) no comparison between the concentrations measured in soil and groundwater and 4) no site-specific measurements on adsorption and rate of transformation of atrazine.

Bromide ion and aldicarb were applied to a large field with sandy loam and loamy sand soils (Georgia) after planting of peanuts (Smith and Parrish, 1993). Granular aldicarb was applied in bands along each seed row. At various times after application, soil samples were taken by coring on tens of sites in the field. The variation in the concentrations measured at the various depths, indicated by the standard deviation of the mean concentration, was substantial. The concentrations of bromide ion measured via suction sampling were much lower than those measured via soil sampling at the same depths. Residues of aldicarb (total toxic carbamates) were measured to penetrate to depths around 1 m (maximum sampling depth). In the graphs, carbamate concentrations were shown down to the level of 0.01 kg ha^{-1} per 0.15 m thick soil layer. The authors concluded that transport was minimal. This amount in the layers can be translated to a concentration in the water phase of 29 µg dm^{-3} (Appendix A). This is very high as compared to the EU limit value for drinking water.
Evaluation.
The shortcomings in this study deal with: 1) poor characterisation of the soil horizons, 2) rainfall/irrigation was not given, 3) different results of soil coring and solution sampling, 4) chemical analysis was not sensitive enough and 5) unusual/inaccurate presentation of concentrations.

Trapp et al. (1995) installed a plate with 25 suction cells (total area of 0.64 m^2) underneath an undisturbed block of sandy-loam soil (Germany), at 1.1 m depth. Bromide ion, isoproturon and terbuthylazine were sprayed on the soil surface (crumb structure). Rainfall was simulated with a spray bar: 153 mm in 25 days. The average drainage collected by the suction cells (pressure of - 20 hPa) was 48 mm of water, with high differences in the volumes between the cells. Only a small front part of the substances was collected with this drainage. Arrival of bromide ion in the various cells was highly variable, which indicates that preferential transport paths were present. The herbicides were detected in the early outflow collected in seven (out of the 25) cells, simultaneously with bromide ion. In the course of time, the effluent concentrations of the herbicides seemed to be increasingly reduced by adsorption and transformation in the soil.
Evaluation.
The limitations of this study are: 1) soil organic matter contents were not given, 2) only the arrival of the first small part of the distributions was measured, 3) no site-specific data on adsorption and rate of transformation, 4) in general highly incomplete reporting (for only a few cells) of the results.

Bromide ion, atrazine and metolachlor were applied to the soil surface of a cultivated field plot (Virginia) with sandy-loam soil (Heatwole et al., 1997). The composition of the soil profile was defined well. At 40 hours after the application in spring, 37 mm of water was applied in one hour using a rainfall simulator. After that, the plot received much natural rainfall: 704 mm in five months. At six times in the growing season of the corn crop, the soil was sampled by coring to 1.5 m depth at 20 random locations. The water table was at 8 to 10 m depth (not sampled). The variation in bromide-ion concentration per depth was high, with several zero values. Comparison between computer simulations and measurements indicated that there was preferential transport of bromide ion. The measurements for the herbicides also indicated that preferential transport to 0.9 - 1.2 m depth occurred as a result of the high amount of rainfall/irrigation soon after application. The coefficients of variation of the herbicide concentration at the various depths were much higher than those for bromide ion. Further, the variation coefficient increased with depth in the soil (Figure 3.1). This indicated that local differences in adsorption and rate of transformation contributed to the variation in herbicide concentration per depth. The authors considered the contents of around 0.01 mg kg^{-1} measured for atrazine in the 1.2 to 1.5 m layer to be an indication of little leaching. However, the corresponding concentration in the water phase can be estimated by calculation to be 30 µg dm^{-3} (Appendix A), which is high in view of the EU drinking water limit.
Evaluation.
Comments on this study are: 1) the soil is heavier than the main target group of soils in the present study, 2) soil moisture profiles were not measured, 3) recovery percentages of the chemical analyses were low, 4) incorrect conclusion of low leaching arising from the high determination limit for soil (low sensitivity) and 5) no site-specific measurements on adsorption and rate of transformation.

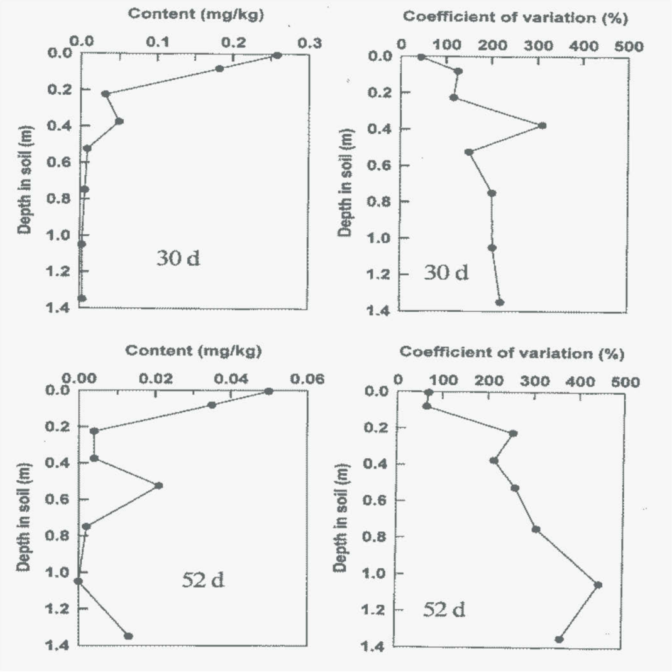

Figure 3.1

Average contents of atrazine in a sandy-loam soil at 30 and 52 days after application, with the coefficient of variation per depth (from data of Heatwole et al., 1997).

Bromide ion was applied to the surface of two field plots with sandy-loam soil (Germany) in November (Jene, 1998, Chapter 6; Jene et al., 1998). The soil was sampled by coring to about 1.3 m depth, at about three, six and ten months after application. Each time six to 15 cores were taken from each of the plots and separated into layers, which were combined in different ways. The range of bromide-ion concentrations at each depth was very wide, as indicated by the standard deviations. The concentration distributions of bromide ion with depth were presented, but in most cases the front of the distributions had moved below the sampling depth. Measurements for the herbicide benazolin were only made for the top 0.3 m of the soil.

Evaluation.

Comments with respect to this study are: 1) the soil was heavier than the main target soils in the present study, 2) in most cases the front part of the bromide-ion distribution is missing.

Zander et al. (1999) applied bromide ion and chlorotoluron to an arable field with loamy-sand soil (Germany) on 21 October. In the past, the forest soil was brought into cultivation by ploughing to 0.5 m depth. After 103 mm rainfall in 32 days, the soil was sampled by augering at 26 locations in the field down to 1 m depth. The measured contents of bromide ion in soil were converted to the concentrations in the water phase. The peak of the field-averaged concentration distribution of bromide ion was at about 0.42 m depth. However, the spreading in the concentration per depth was very high (Figure 3.2). The herbicide chlorotoluron seemed to remain in the top 0.3 m layer (no deeper sampling) in a winter period of 4.5 months.

Evaluation.

The duration of the experiment was short and no measurements were made in the shallow groundwater zone. Nevertheless, the measurements for bromide ion can be considered to be used for the testing of transport models against the concentrations in the soil profile.

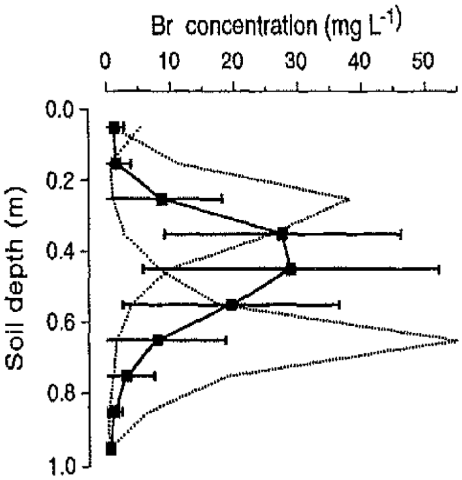

Figure 3.2

Concentrations of bromide ion in the soil solution of a loamy-sand soil at 32 days after application (Zander et al., 1999; ©American Society of Agronomy, with permission). Points: average concentrations per depth. Bars: standard deviation. Dotted lines: local concentration profiles with extreme peak positions.

Water flow and transport of substances in a field plot with loamy-sand soil (Sweden) was studied in detail by Öhrström et al. (2004). The soil was levelled and did not have an apparent structure. Short ponded irrigations of 11.9 mm d^{-1} were given for three days. The irrigation water contained dye and bromide ion. The dye-colouring pattern on vertical cross sections of the soil profile showed that fingered water flow occurred. The soil parts that were wettest increased most in volume fraction of water upon a new irrigation gift (main flow paths). Bromide ion distribution in soil, as measured by TDR, was very heterogeneous. The soil parts with the highest differences in volume fraction of water contained the highest bromide ion concentrations. These parts were most active in water and solute transport.

Evaluation.

The bromide-ion results were represented as a (heterogeneous) pattern of relative concentrations on a vertical transect of only 0.5 m depth. Such presentation hampers the use of the results for model testing.

In their review, Sarmah et al. (2004) described comparisons between computer simulations using various models and the results of field experiments in New Zealand. Often, there were no site-specific measurements of adsorption isotherms and transformation rates in soil. First estimates of these input data were obtained from handbooks and data bases. The high variability in the concentration measured per depth in soil was considered to be an obstacle in model testing. They considered the predictive capability of model uses to be low. They advised to perform more comprehensive/detailed experiments and modelling in combined efforts.

3.2 Tube-drained fields

In principle, field studies with measurements of pesticides in tube-drain water can be suitable for the assessment of preferential transport in soil. The Hupsel (NL) field experiment for a sandy soil (Section 2.1) dealt with a tube-drained field, with samples of drainwater taken for chemical analysis. The question rises whether there are more experiments for tube-drained fields of sandy soils published in the literature. This Section gives a survey of such experiments and discusses their usability and limitations with respect to the testing of preferential-transport models.

Bromide ion was sprayed in a dosage of 32.4 kg ha^{-1} on an arable field with loamy-sand soil (Mellby, Sweden) in October (Larsson et al., 1999). The field was tube-drained at 0.9 m depth and at 6.75 m distance. There was a clay layer deeper than 1 m in soil, but its characteristics were not known. Soil cores (in layers) and tube-drain water (flow-proportional sampling) were analysed for bromide ion in a winter period of five months. The tube-drain discharge was higher than precipitation on the plot, which showed that water flowed from the surroundings and/or from deeper groundwater into the plot. In the beginning of March, bromide ion concentrations at 0.9 m depth in soil were around 5 mg dm^{-3} (soil). At the saturated volume fraction of water at this depth (about one-third) this corresponds to 15 mg dm^{-3} (water) in groundwater. The concentrations measured in the tube-drain water at this time were around 3.5 mg dm^{-3}. The concentration of bromide in tube-drain water was never above 6 mg dm^{-3} in the 5-month period. It seems that the inflow of groundwater into the plot resulted in a substantial dilution of bromide ion.
Evaluation.
Some results on the concentration of bromide ion within the soil profile were presented, which can be used for the testing of transport models. The complicated (unknown) groundwater flow precludes close comparison of the concentrations in subsoil and drainwater, and thus hampers drawing a conclusion on the type of transport in soil.

The review of Brown and Van Beinum (2009) shows that almost all measurements of pesticides in tube-drain water in Europe were carried out for loamy and clayey soils (outside the scope of this study). Ideally, simultaneous measurements in the soil profile and in the tube-drain water should be available for the assessment. However, such a combination of measurements seems to be extremely scarce. In cases in which only concentrations in tube-drain water are available, it can be attempted to describe the processes in soil with models. However, without measurements, the soil profile is a black box; the uncertainties are of the same type as those in lysimeter/column studies with only leached concentrations (Chapter 4). The uncertainties in the water balance (upward/downward seepage, horizontal flow) and thus in the substance balance may be even greater for tube-drained fields than for lysimeters.

3.3 Concluding remarks (field experiments)

- The description of the soil system may be poor, e.g. with respect to the layers in the profile, soil composition, soil cultivation, soil use, soil structure, etc.
- Remarkably high is the number of studies in which the rainfall/irrigation pattern is poorly defined.
- Only few measurements are available on tracers and pesticides throughout the soil profile into the upper groundwater.
- In various computer simulations of field experiments, no input data were available on adsorption and/or transformation rate in the soil at the site.
- Measurements by soil coring and by suction sampling of soil solution showed large deviation.
- Chemical analyses for pesticides in soil samples were not sensitive enough to measure relevant low concentrations, which leads to under-estimation of leaching.
- High variation in the concentrations measured per depth, even for inert tracers, is expected to hamper model testing.
- Local variation in the leaching of pesticides is increased by differences in adsorption and rate of transformation in the transport pathways.
- Concentration patterns in groundwater could not be reconstructed.
- Characterisation of the geology and hydrology of the water-saturated zone is poor.
- Drain discharge from a field section can be higher than precipitation, as a result of groundwater flowing from its surroundings or from deeper layers.
- Results of tube-drain measurements for sandy soils usable for testing preferential-transport models could not be found.

4 Lysimeter and column studies

Many experiments were carried out on the transport of pesticides in lysimeters and soil columns. In the present study on the type of transport in soils, the experiments with 'undisturbed' soil monoliths or soil columns are relevant. Further, the water fluxes should be representative for field conditions. In this Chapter a survey is given of lysimeter and column studies with sandy soils that might be usable for the testing of preferential transport models. Again, a short description of the experiment is followed by an evaluation of its usability for the testing of preferential transport models.

Advantages of using large lysimeters with undisturbed soil in outdoor lysimeter stations were summarised by Jene (1998; his Chapter 1):
- Many field properties are combined and part of the field variability is reflected.
- The soil surface is large enough to mimic agricultural practices like tillage, cropping and pesticide application.
- The lysimeter is exposed to natural climatic conditions.
- All substances that pass the bottom of the lysimeter are completely sampled.
- It is possible to use radiolabelled pesticides for a more complete material balance.

Main differences between lysimeter systems and field conditions were noticed to be:
- Even when attempting to collect an undisturbed monolith, soil structure may be disturbed.
- Water-saturated condition and a capillary fringe build up before water can flow from the lysimeter bottom.
- The lysimeter wall prevents lateral (horizontal) water flow and solute transport over somewhat larger distances in the soil profile.

The difference in water condition at the bottom end can be accompanied by differences in biochemical condition affecting pesticide transformations.

Undisturbed columns (inner diam. 0.12 m; length 0.8 m) were taken from a humic-sandy soil (Vortum Mullem, NL) and placed in the soil outdoors, near a weather station (Smelt et al., 1983). The nematicide aldicarb was incorporated into the top 0.095 m of the soil in mid-May, after which grass was sown on the columns. Over a year, the effluent from the columns was collected via a sand filter. Some leaching (0.03, 0.04 and 0.21% of the dosage) of the weakly-adsorbed and toxic oxidation products (sulfoxide and sulfone) occurred from three of the six soil columns in June, with 107 mm of rainfall. The highest residues (up to 6.4 µg L^{-1}) leached in winter. More leaching occurred from fallow humic-sandy soil columns (0.6 m long) in summer. Residue distributions in three soil columns were measured at the end of October and at the beginning of April.
Evaluation.
The soil is characterised well. Only monthly amounts of rainfall seem to be available.

Six undisturbed soil columns (0.3 m diam.; 1.0 m long) were taken from a field with loamy-sand-on-sand soil (Nåntuna, Sweden) and placed in a lysimeter station (Bergström, 1992; Bergström et al., 1994). The soil was cultivated and sown with spring barley, which was followed by sowing winter wheat in the autumn. Bentazone was sprayed on the columns with young plants in the beginning of June, at usual dosage (three columns) and at double dosage (the other three columns). Weather was rather dry in summer/autumn 1989, but with the supplemental irrigation (145 mm) total water supply was 69 mm above the average (in 10.7 months). The highest concentrations of bentazone in the leachate (around 4 µg dm^{-3}) appeared at the end of September, after a few mm of drainage. From November on, the leached concentration had decreased to values between nil and 0.4 µg dm^{-3} (normal dosage) and between 0.3 and 1.1 µg dm^{-3} (double dosage) throughout the experimental period. Total leaching of bentazone corresponded to 0.12% of the usual dosage and 0.15% of

the double dosage. The variation in herbicide leaching from the columns was greater than the variation in water outflow.
Evaluation.
The authors suggested that preferential transport of bentazone occurred. However, model simulations seem to be needed to check whether this was actually the case. Information on water flow and on the water balance in the lysimeter is essential for that.

The leaching of the herbicide bentazone in two undisturbed loamy-sand-on-sand soil columns (Nåntuna, Sweden) was simulated with the MACRO model in the option of convection-dispersion in one flow domain (Jarvis et al., 1994). There was uncertainty on the dissipation processes in the crop canopy and at the soil surface, and thus on the net load of the soil with the herbicide. The rate of transformation of bentazone in soil in the laboratory was introduced into the computation. Following application of the herbicide in spring, the herbicide appeared in the first drainage water in the autumn. Breakthrough of bentazone from the two sandy-soil monoliths was simulated by the model to be much later than measured. The authors concluded that preferential transport of the herbicide occurred. When the computations were continued, most leaching was computed to occur in the second winter period after application (extrapolation; no measurements).
Evaluation.
Leaching of bromide ion with the first drainage water can also be explained if the soil moisture profiles were distinctly lower than expected (little displacement of 'clean' soil solution). However, measurements on the soil-moisture profiles were not presented. The uncertainty in the net load of the soil with herbicide hampers the use for testing transport models.

Four undisturbed soil columns (0.3 m diam.; 1.0 m long) were taken from a field with sandy-loam-on-sand soil (Mellby, Sweden) and placed in a lysimeter station (Bergström and Jarvis, 1993; Bergström et al., 1994). The soil was cultivated and sown with spring barley. Dichlorprop was sprayed on the columns with young plants in the beginning of June, at the usual dosage (1.6 kg ha^{-1}). Weather was rather dry in summer/autumn of 1989, but with the supplemental irrigation total water supply was 57 mm above the average precipitation (in 10.7 months). Concentrations of dichlorprop (2.3 μg dm^{-3}) appeared at the end of September at the start of the drainage and leaching continued (<0.5 to 4.4 μg dm^{-3}) during winter. Leaching was unexpected because the rate of transformation in topsoil and subsoil in the laboratory was very fast. The average total leaching of dichlorprop corresponded to 0.03% of the dosage, with substantial differences between the columns. Under high precipitation on four other columns, average leaching of dichlorprop was 0.06% of the dosage.
Evaluation.
The authors suggested that preferential transport of dichlorprop occurred. The discrepancy in rate of transformation in the lab and in the field makes it difficult to check this by computations. Only the leaching of a first small percentage of the dosage was measured in a limited period.

The leaching of the herbicide dichlorprop in an undisturbed sandy-loam-on-sand soil column (Mellby, Sweden) was simulated with the MACRO model in the option of one-flow domain (Jarvis et al., 1994). The (very high) rate of transformation of dichlorprop in the soil in the laboratory (half-life of a few days) was introduced into the computation. Leaching computed with the model was nil, whereas distinct leaching from the monolith was measured to occur over a substantial period. The conclusion was that the rate of transformation of dichlorprop in the field soil was much slower than that in the soil in the laboratory.
Evaluation. The discrepancy in rate of transformation in the lab and in the field precluded testing of the computation model.
In the experiment of Bergström and Jarvis (1993) the leaching of chloride ion from an undisturbed sandy-loam-on-sand soil profile (Mellby, Sweden) in columns (0.3 m diam.; 1.0 m long) was studied (besides that of dichlorprop; see above). The columns were grown with spring barley and chloride ions were sprayed on the columns with young plants in the beginning of June. Under high-rainfall condition (by supplemental irrigation)

chloride ion appeared after about 40 mm of water outflow. Under average rainfall condition (adjusted by irrigation), chloride ion appeared in the first effluent after the summer period.
Evaluation. The authors ascribed the difference in leaching to more preferential transport of chloride ions in the drier soil columns. However, such leaching with the first outflow water can also be expected when the soil dries out by water uptake in the growing season (no displacement of 'clean' water). Differences in leaching from drier and wetter soil columns (on the basis of outflow) can possibly be elucidated by simulations with a computation model.

Parsons et al. (1995) measured the leaching of compounds and radioactivity after application of six organic substances to sets of two lysimeters with undisturbed sandy soil (0.8 m diam.; 1 m deep; England). The volumes of water flowing from the duplicate lysimeters (cropped) were almost the same. In three out of six cases, the amounts of radioactivity and of substances/metabolites were highly different between the duplicates. At the end of the study, the soil monoliths were inspected by excavation from the casings in 10 cm layers. There was a tendency of more leaching from monoliths with a higher number of earthworm burrows in the lower part of the soil profile.
Evaluation.
This paper contains hardly any input data for computer simulations.

A two-region model with mobile and stagnant water phases was found to be a suitable tool for analysing solute breakthrough curves in soil-column studies (Griffioen et al., 1998). They analysed a large set of published data on partially saturated and aggregated/saturated soil columns in the laboratory. Early breakthrough and distinct tailing in the effluent curves could be described by the model. Relationships were derived for the fraction of mobile water and the coefficient of mass transfer between the mobile and stagnant regions. However, the derivation of relationships for the parameters in cases of undisturbed soil columns taken in the field was not successful.

Bromide ion and the herbicide benazolin-ethyl (^{14}C-labelled) were applied to undisturbed monoliths of sandy-loam soil in triplicate lysimeters (1 m diam., 1.3 m high) installed outdoors (Jene, 1998; Jene et al., 1998). The substances were applied to the tilled soil surface in November. The climatic conditions were measured in detail and evapotranspiration was estimated. By supplemental slow irrigation (no ponding) a total of at least 800 mm precipitation per year was attained. The soil was cropped with summer rape from April on. Free water outflow and breakthrough curves of bromide-ion and of benazolin with some transformation products are presented (Figure 4.1). Independent measurements of adsorption and rate of transformation are available.
Evaluation.
The soil is somewhat heavier than the main target group of soils in the present study. Otherwise this data set seems to be suitable for the testing of transport models.

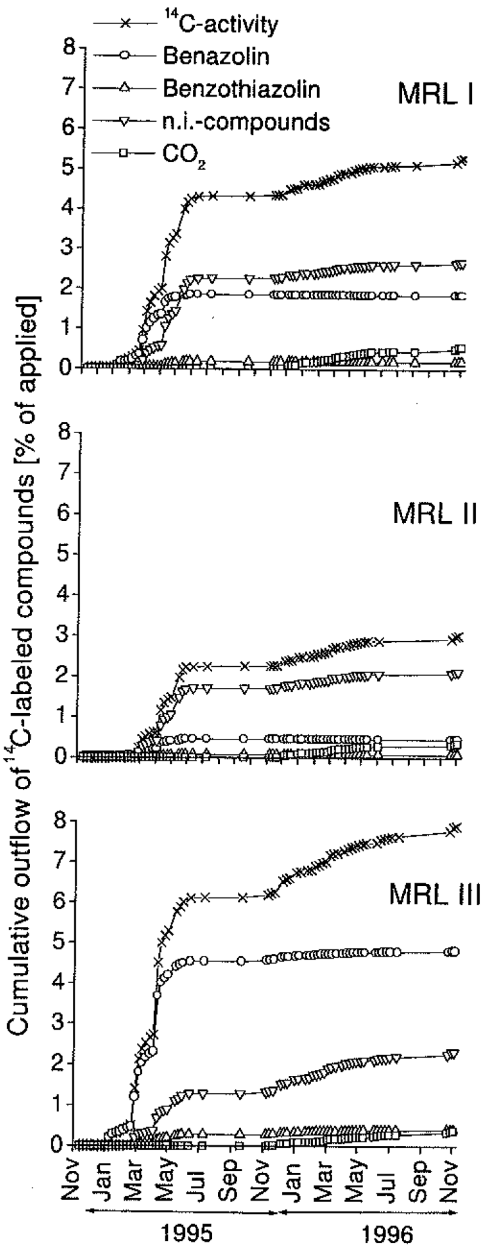

Figure 4.1
Cumulative leaching of ^{14}C activity and the contribution of ^{14}C labeled compounds after application of ^{14}C-benazolin-ethyl to lysimeters with sandy-loam soil in November (Jene, 1998; ©B. Jene, with permission).

A lysimeter experiment with a series of soils of different texture was carried out by Brown et al. (2000). The undisturbed soil monoliths (diam. 0.8 m; length 1.0 m) were placed in a lysimeter station (same weather conditions; England), tilled and sown with winter wheat. Bromide ion and isoproturon were applied to the soil surface in the autumn of two successive years. The leaching of bromide ion and isoproturon from the sandy soil over a 2-year period showed substantially less preferential transport than that from the loamy/clayey soils. The maximum concentration of isoproturon leached from the sandy soil was 4-5 µg dm^{-3} in the first leaching season and 1-2 µg dm^{-3} in the second season.

Evaluation. Shortcomings in this study are: 1) no rainfall data for most of the time and 2) data on the adsorption and rate of transformation of isoproturon were taken from a compilation in the literature.

The water tracer 2,6-difluorobenzoic acid was applied to 23 monoliths of loamy-sand soil in lysimeters (0.8 m^2 surface area; 2.3 m deep; Germany) (Fent, 2000). In a winter period of 6.75 months following the application (27 September) to the bare soil surface, total rainfall plus irrigation was 449 mm. Fast preferential transport of the tracer was measured to occur in about a quarter of the lysimeters. The fast transport was estimated to corresponded to 0.7 to 7.4% of the total tracer leaching of about 80% of the dosage.
Evaluation. Limitations in this study are: 1) incomplete description of the soil in layers, 2) previous cultivation in the field was not described and 3) highly variable leaching patterns.
Water flows from a zero-tension lysimeter only when the soil at the bottom is water-saturated, with an almost saturated capillary zone above. Such water flow is different from that in the same soil profile in the field with a deeper groundwater table. Within the bottom part of the lysimeter the water may be mixed somewhat by lateral flow, which can be expected to diminish the expression of preferential transport. Further, the residence time of water in lysimeter soil can be longer than that in the same soil profile in the field (Boesten, 2007), which increases the time for pesticide transformation.

In international guidelines on lysimeter studies it is not prescribed to measure the adsorption and rate of transformation of the pesticide in the soil. Further, there are usually no measurements on the pesticide concentration in the lysimeter soil in the course of time. The dispersion length for the soil/water-flow combination is often not known. Consequently, the lysimeter soil monolith can be considered to be a 'black box' then (Boesten, 2007).

Concluding remarks (lysimeters and columns).
- Spraying in the presence of a crop (interception, dissipation at the surfaces) leads to uncertainty on the net load of the soil.
- Measurements on the volume fraction of water at the various depths in soil and in the course of time are usually not available.
- The walls of lysimeters/columns restrict the extent of lateral flow and transport.
- Water flows only from lysimeter/columns when the bottom part has become water-saturated, which may lead to some extent of lateral mixing.
- Measurements on the concentrations of the substance in the soil are often not available (lysimeter/column soil as black box).
- In most cases the leaching of the first small fraction of the dosage is measured in a limited period after application to the lysimeter/column.
- The difference in pesticide leaching from replicate lysimeters/columns from the same field/plot can be great, so replicates are needed in experiments.
- Local differences in adsorption and rate of transformation seem to enhance the differences in leaching.
- Site-specific input data on adsorption and rate of transformation of the pesticide (as a function of depth in soil, etc.) are often not available.
- In other cases, these is a distinct deviation between the rates of transformation in the laboratory and in the field.
- Lysimeter/column studies should be simulated in detail with an appropriate model to check whether preferential transport occurred.
- Very few lysimeter/column studies with undisturbed sandy soil are available for the testing of preferential transport models.

5 Variability at field scale

In measurements of tracers and pesticides in soil, large variations in the concentration per depth were found (Chapters 2 and 3). The question rises whether there is more information on the variability of the concentration of substances in soil. Possibly, research has been carried out on the factors and processes causing such variation. This Chapter gives a survey of studies on the occurrence and causes of the spatial variation in substance concentration in soils in the field, with the emphasis on sandy soils.

The variability of the transformation rate of two herbicides with position in the field (England) was studied by Walker and Brown (1983). At ten locations distributed over a field with sandy-loam soil (80 x 80 m) they collected soil samples from the top 0.10 m. Metribuzin and simazine were incubated in the soil samples at 25 °C, while soil moisture was maintained at 12.5%. The course of the transformation approximated first-order kinetics. The range of half-lives of metribuzin was 25.0 to 48.3 days (average 36.6 days; coefficient of variation 21.1%). For simazine the range of half-lives was 24.7 to 29.8 days (average 27.7 days; coefficient of variation 6.9%).

The herbicides cyanazine and metribuzin were sprayed in spring, on a loamy-sand soil (the Netherlands) exposed to natural rainfall conditions (Boesten, 1986). The contents of the herbicides in soil were measured by coring and division into layers, at various time intervals in 120 days after application. The herbicides were measured to remain in the cultivated top layer in this period. The coefficients of variation of the areic mass of the herbicides in soil were found to increase from mostly 10-20% shortly after application to around 50% after 120 days (his page 52). This increase was ascribed to local variations in the rate of transformation of the herbicides in soil.

A review was given by Smith et al. (1987) on the variation of soil characteristics in experimental fields. The highest coefficient of variation was found for saturated hydraulic conductivity. The coefficient of variation of the bromide-ion and chloride-ion concentrations at a certain depth in soil was often high: it ranged from 19 to 127%. This variation may represent transport variability in soil. The coefficient of variation in pesticide concentration at a certain depth in a field (3.9 ha) with loamy-sand and sandy-loam soils was even higher (Figure 5.1): for three pesticides it ranged from 34 to 450 %. In most cases, the variation in concentration increased with time after application and with depth in the soil profile. This comparatively high variation (as compared to tracers) may be caused by local differences in extent of sorption and rate of transformation. Estimation of the mean concentration per depth at the leading edge of a distribution requires a comparatively high number of measurements of the often low concentrations.

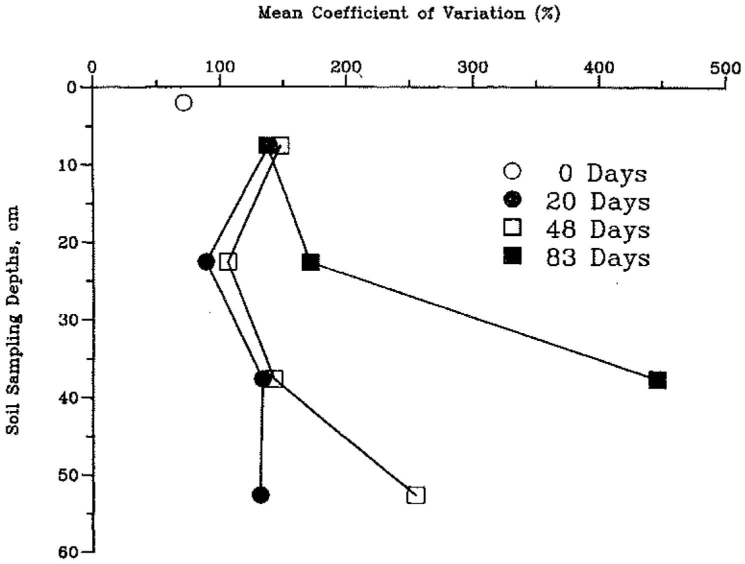

Figure 5.1
Aldicarb-residue variability with depth in a field with loamy-sand and sandy-loam soils and with time after application (Smith et al., 1987; ©John Wiley and Sons, with permission).

In some studies, replicate undisturbed soil columns were taken from a field for lysimeter-station experiments. Bergström and Jarvis (1993) took eight soil columns (0.3 m diam.; 1.0 m long) from a sandy-loam-on-sand profile (Mellby, Sweden). The columns were grown with spring barley and dichlorprop was sprayed on the columns with young plants in the beginning of June. Four of the lysimeters received average precipitation, while the other four received high precipitation (supplemental irrigation). The variation in the leaching of dichlorprop (weakly adsorbed) from the columns with the average precipitation was substantial. This can be the result of differences in the pattern of water flow. However, Bergström and Jarvis (1993) and Bergström et al. (1994) presumed that differences in adsorption and transformation rate in the soil columns contributed much to the variation. The variation in the volume of water flowing from the soil columns was lower than that in the concentrations leached. The authors emphasised the need for including replicates in lysimeter/column studies. The amount of dichlorprop leaching from the columns at high precipitation (0.06% of the dosage) was only double that leaching at the average precipitation (0.03% of the dosage); this difference is lower than expected. Possibly, the rate of transformation of dichlorprop in the wetter soil columns was comparatively high.

Aspects of soil variability in a 10-ha arable field with loamy-sand soil (Germany) were studied by sampling at 66 grid points (Nordmeyer, 1994). The average percentage of organic carbon in the 0-0.3 m layer was 1.44%, while the range was 0.83 - 2.3% (variation coefficient 24%). The variation coefficients for the 0.3-0.6 and 0.6-0.9 m layer were even higher. Coefficients K_d for the adsorption of terbuthylazine were measured for each of the soil samples collected from the 0-0.3 m layer top layer at the grid points. The K_d value was higher as the organic carbon content of the soil sample was higher. Using these K_d values in the model PRZM, the variation in movement of terbuthylazine in the soil profile was calculated. As could be expected, movement in the soil profile was greater when the K_d value was lower.

The thickness of the soil horizons can show substantial variation within a field. Van den Bosch and Boesten (1994) reported the thickness of the humic-sandy (black) top layer of the Vredepeel (NL) arable field to be on average 0.32 m, with a range from 0.27 to 0.40 m. Thickness of the humic top player of a sandy soil (Mellby, Sweden) was on average 0.32 m, with a variation in the field between 0.20 and about 0.43 m (Bergström et al., 1994; Larsson et al., 1999).

Van Wesenbeeck and Kachanoski (1994) described the variation in depth of the transition between the B and C horizons in the sandy soil of a cultivated field (Canada). This depth started at 0.5 m, but increased in the form of regularly-occurring tongues to 1.5 m depth. After spraying chloride ion on the soil surface, the field was trickle-irrigated (randomised positions) at 40 mm per day, up to 131 mm. Movement of chloride ion tracer was measured by soil sampling on transects via the walls of a trench. The chloride tracer moved to a greater depth in the tongue areas (peaks at 0.85 m depth versus at 0.55 m depth). The tongues of the B horizon into the C horizon served as major conduits for water and solute moving through the soil. The Bt horizon at various places (clay enrichment) seemed to promote the lateral flow and transport to the tongues.

Three undisturbed soil monoliths (1 m diam.; 1.3 m high) of sandy-loam soil were collected from the field in lysimeters (Jene, 1998, Chapter 4; Jene et al., 1998). The herbicide benazolin-ethyl (^{14}C labelled) was sprayed on the cultivated soil on 22 November. Natural rainfall was supplemented by sprinkler irrigation to attain at least 800 mm precipitation per year. Leaching of benazolin and its transformation products was strongly different for the three lysimeters: 1.33, 0.38 and 3.83% of the dosage, respectively. The variation of the leaching of bromide ion from the lysimeters was much smaller. The large variation for benazolin is an indication for differences in the extent of transformation in each of the soil monoliths.

Thirty soil batches were collected from the 0.05 m top layer of an arable field (grid pattern in an area of 200 m x 250 m) with sandy-loam soil (England), with seemingly uniform characteristics (Walker et al., 2001). The herbicide isoproturon was incubated in the soils under standard conditions (temperature 15 ^{O}C; water pressure – 33 kPa). Various soil batches showed gradual degradation of isoproturon according to first-order kinetics. In other soil batches, degradation first proceeded gradually but it increased drastically after a certain time of incubation. In a third group of soil batches, degradation was comparatively fast from the beginning, presumably due to adaptation of the micro-organisms. The time for 50% degradation, DT50, of isoproturon in the soil batches ranged from 6.4 to 30.2 days.

The variability in the leaching of three herbicides at field and farm scales (the Netherlands) was calculated by Van Alphen and Stoorvogel (2002), using the WAVE model. Characteristics like the organic matter content of the soil layers were obtained by detailed soil survey. The model calculated a distinctly higher leaching of the moderately-adsorbed metribuzin at the locations with comparatively low amounts of organic matter in the soil profile (as expected) (Figure 5.2). However, the leaching of the weakly-adsorbed bentazone (comparatively high) was quite insensitive to the organic matter level in the soil profiles. Adsorption (and thus extent of leaching) of neutral molecules can be related easily to the amount of organic matter in the soil profile, via the adsorption coefficient Kom.
Remark:
the rate of transformation of a pesticide (much effect on leaching) often cannot be related in a simple way to a soil characteristic.

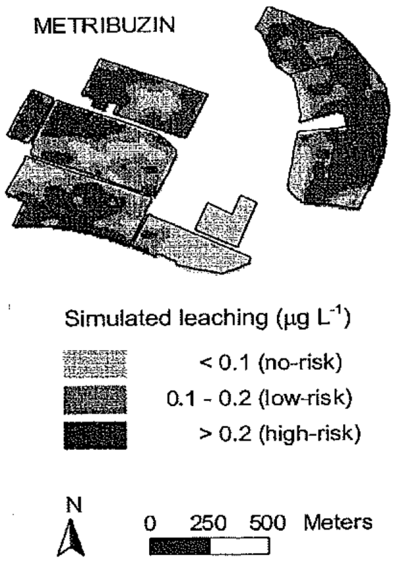

Figure 5.2
Computed effect of the variability in organic matter profile on the leaching of metribuzin (Van Alphen and Stoorvogel, 2002; ©American Society of Agronomy, with permission).

There can be a large variation in the amount of pesticide leached (as fraction of the dosage) from replicate lysimeters/columns from the same field (Boesten, 2007). First of all there is variation in the areic volume of water flowing from the soil monoliths. The coefficient of variation in the leached fraction of pesticide reported in the literature for lysimeter/column studies ranged from 50 to 90%.

Vereecken et al. (1996) stressed the need for more complete data sets for coupled soil-aquifer systems in pesticide studies. They described the build-up of a phreatic aquifer in Germany on the basis of four corings down to 15 to 20 m depth. The local basis of the aquifer consisted of a clay layer at a depth of 11 to 13 m. The aquifer mainly consisted of fluvial sand and gravel, in heterogeneous deposits. Further, there were thin clay layers, thicker layers of silty fine sands, a layer of poorly-sorted gravelly material and a stony layer. The depth of the water table varied between 0.8 m (winter) and 3 m (late summer).

Concluding remarks (variability)
- The concentration of inert tracers at a certain depth in soil shows a wide range of variation due to local differences in transport.
- The extent of pesticide adsorption to soil varies with position in the field, e.g. dependent on the variation in soil organic matter profile.
- The rate of transformation of a pesticide in the top layer of a field shows a (wide) range of variation with position.
- No data were found on the variation in rate of pesticide transformation in the layers below the cultivated top layer.
- The variation in concentration of a pesticide at a certain depth in soil is even higher than that of inert tracers, presumably because of local differences in adsorption and transformation in soil.
- The leaching of pesticide residue from replicate columns/lysimeters taken at a field shows substantial differences, which stresses the need for studying replicates.
- Thickness of the humic top layer of sandy soils can vary substantially at the field scale.
- Variation of the transport of substances in soil can be related to features of soil formation, e.g. tongues of the B-horizon in the C-horizon.

- The few observations on the phreatic-aquifer in combined soil-aquifer studies with pesticides indicate that their build-up can be very heterogeneous.
- The few measurements for deeper layers and their variability will make it difficult to discriminate between preferential-transport models, as there is no clear shape of the breakthrough curve.

6 Limitations of experimental data

6.1 Soil characterization and meteo data

In most field studies on the transport of pesticides in soil, the description of the soil is far from complete. A checklist for characterising the soil in future studies could be:

- Origin of the soil material (geogenesis).
- Processes of soil formation (pedogenesis).
- Soil profile description: soil horizons, soil structure, macropores, rooting depth.
- Characteristics of the soil in layers: mineral fractions, soil organic matter content, bulk density, pH.
- Build-up of the deeper subsoil: layers, size of the materials, packing.
- Regional and local hydrology: depth of the water table, tube drainage, nearby water courses.
- International soil classification.
- Land reclamation in the past: deep ploughing, subsoiling to disturb dense layers (increase of rooting depth), digging and filling drain trenches.
- Soil management: ploughing, seedbed preparation, hilling, etc.
- Crop growth in recent years and during the experiment.

Various attempts were made to predict the soil moisture profiles in field on the basis of the moisture-retention curve measured in the laboratory. In their computations with the MACRO model (matrix-flow option), Larsson et al. (1999) over-estimated the volume fractions of water in the Mellby field with sandy soil. Boesten and Gottesbüren (2000), using laboratory data in the PESTLA model, simulated the soil moisture profiles in the Vredepeel humic-sandy soil to be higher than measured in the field (so also over-estimation). Improved descriptions of the soil moisture profiles had to be obtained by calibration against the field measurements. In the laboratory, moisture-retention measurement starts from completely saturated soil. In the field, however, soil wetting is heterogeneous (Leistra and Boesten, 2010), e.g. due to differences in hydraulic conductivity and hysteresis. No attempts could be found to predict the variation of the groundwater table in time, as influenced by weather conditions, from independent measurements. A reasonable description could be obtained by calibration against measurements for the Vredepeel field (Boesten and Gottesbüren, 2000).

In studying the transport of substances in soils, information on the geometry of the pore system is of great value. Soil micro-morphological features of horizons of loamy soils were studied by Kodesova et al. (2008) and Kodesova (2009) in thin sections. They used the results to explain the nature of water flow and chlorotoluron transport in plots of three loamy soils. The connectiveness of the pores and the degree of filling of the larger pores (dependent on rainfall, etc.) have much effect on flow and transport. Pore geometry of the cultivated top layer can change in time due to the effect of soil management and weather conditions. No such micro-morphological studies were found for humic- and loamy-sandy soils. Besides the micro-morphological method, there are other methods of studying soil-pore geometry (Kodesova, 2009): a) X-ray computer tomography, b) magnetic resonance imaging and c) dye-tracer distribution imaging. Hopefully, soil micromorphology can provide tools to enable independent estimation of parameters for models of non-equilibrium water flow and solute transport.

In many field studies on pesticide transport in soil, the information on precipitation pattern, water flow and water balance is far from complete (e.g. Chapter 3). Precipitation data should be available at least on a daily basis and preferably for shorter time intervals (e.g. one hour) for the fast processes. Measurements on the volume fraction of water as a function of depth and time are needed. Evapotranspiration of the soil-crop combination can be estimated from potential evapotranspiration, which is itself an estimated quantity (meteorological services). Soil temperature as function of depth and time is needed for description of the transformation rate of pesticides.

In lysimeter/column studies, the outflow of water can be measured, but soil moisture profiles are usually not available. Downward water flow in the field (e.g. below 1 m depth) has to be estimated from the water balance of the soil profile. The water intercepted by suction plates at e.g. 1 m depth, as a fraction of field drainage, can be uncertain. Water flow from tube drains can be measured, but part of the water can originate from outside the experimental area and/or be lost from the area. Estimation of downward and upward seepage to/from the deeper groundwater is difficult. The horizontal component of water flow in the upper part of the aquifer is dependent on local and regional hydrology; exchange by inflow and outflow can occur with the surroundings of the experimental area. Many measurements are needed within the field and in its surroundings to characterise groundwater flow.

6.2 Sampling procedures

Until a few decades ago, field researchers were quite optimistic on the possibility of representative sampling of soil and groundwater. Taking many soil cores (e.g. 16) in a field section per time and division of the cores into layers was considered to yield a good approximation of the average concentration per depth, with limited spreading. Sampling of the soil solution with suction cups was considered to be a good alternative for soil sampling: repeated sampling at the same place and more sensitive chemical analysis in water. However, it was found that the spreading in the concentration per depth obtained with a certain sampling method was very great (Chapters 2, 3 and 5). Further, in comparison studies there were great differences in the results of the different sampling methods. It was found that preferential flow and transport pathways in soil can be easily missed by the sampling methods. It was assumed that quite some mixing occurred in the top of the groundwater zone, which would facilitate representative sampling. It became more and more clear that, instead of the expected leveling-out of the concentration per depth, the differences tended to increase because of heterogeneous flow and transport. In this Section, a survey is given of experiences with different sampling methods which should be kept in mind when using the results for model testing.

The nematicide aldicarb applied to a field (Central Sand Area, Wisconsin) was sampled in two ways (Brasino, 1986, referenced by Kung, 1990):

- via suction samplers in the vadose zone;
- via wells in the upper groundwater.

The peak concentrations measured in the groundwater were higher than those in the water of the vadose zone above and they appeared earlier in the groundwater. This was ascribed to transport through preferential flow paths, caused by funneling (Figure 6.1), which were missed by the suction samplers. Such sampling problems hamper the close comparison of the concentrations in the vadose zone with those in groundwater, as well as the testing of transport models.

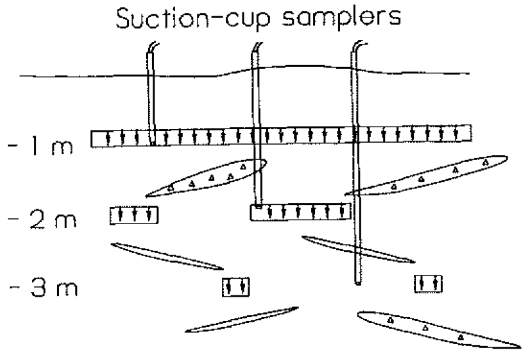

Figure 6.1
Sketch of the influence of funneling on soil-solute sampling in the vadose zone (Kung, 1990; ©Elsevier, with permission).

A data set on the leaching of bromide ion and aldicarb in a deep well-drained sandy soil (Florida) was used to test five simulation models for substance behaviour in soil (Pennell et al., 1990). The soil was sampled by taking sixteen soil cores in each of the four field quadrants, to several metres depth. They found the high variability in the measured substance distributions in soil to be a serious limitation in the testing of the simplified models.
Remark:
The problem of variability in the field measurements can be expected to be even greater when attempting to estimate the parameters of preferential transport models.

When using samplers for soil solution and groundwater (often installed vertically) it is essential to seal the voids around the tubes against short-circuit water flow. This is usually done by filling the voids with the original soil (followed by tamping) and by using seals of bentonite clay (Smith et al., 1990). The soil should be rather wet to obtain adequate volumes of water with the suction samplers.

The herbicides atrazine, napropamide and prometryne were applied to bare field plots of loamy-sand soil (California) (Ghodrati and Jury, 1992). Groups of plots were subjected to different types of water supply (120 mm): continuous ponding, intermittent ponding, continuous sprinkling and intermittent sprinkling. Three soil cores were taken to 1.5 m depth in each of the plots and the samples were combined per layer for analysis. In various plots, incidental concentrations were measured at a certain depth in the subsoil, between zero or much lower concentrations above and below. This was explained from accidental hits of a preferential flow and transport path by the core sampling. Preferential herbicide transport occurred with all types of water supply. Previous cultivation of the soil did not prevent preferential transport to occur.

Steenhuis et al. (1995) described experiences with the sampling of soil solution using suction samplers. They installed the samplers at various depths in sandy-loam soil (New York State) down to 1.8 m. The tracer bromide ion appeared earlier in the samplers at 1.8 m depth (just above the groundwater table at 2 m depth) than in the samplers at 1.2 and 1.5 m depth. The latter samplers had been passed by preferential flow and transport pathways. Volumes of soil solution adequate for chemical analysis can only be obtained if the soil is rather wet, which may be the case only in the capillary zone just above the groundwater table. In most experiments with suction samplers, unrealistically high amounts of water are supplied to make the soil sufficiently wet. The voids between the vertically-placed tubes and the surrounding soil have to be sealed to prevent short-circuit water flow. The question how to sample the preferential flow paths in soil could not be answered.

A two-dimensional hypothetical profile of sandy soil was simulated, using a finite-element numerical method (Ju et al., 1997). Inclined coarse sand lenses were assumed to be embedded in medium sand; they funnelled the uniformly applied water into flow paths. A grid of soil-solution samplers was assumed to be installed in the soil profile (Figure 6.2). After steady-state unsaturated water flow was attained in the computations, an adsorbed and degradable substance was introduced uniformly at the soil surface. The concentrations simulated to be sampled from the soil solution at the various depths (resident concentrations) under-estimated the flux concentration at the same depth. Decreasing the sampling space did not increase sampling accuracy. The substance was computed to be transported in distinct flow paths; only a few paths moved the substance to the bottom of the soil profile. The concentration in the water flowing from the soil profile is representative for substance leaching, but this quantity is difficult to measure under field conditions. The suction samplers in the flow paths tend to collect both, more water and higher concentrations from the leading edge of the distribution than the samplers outside the flow paths.

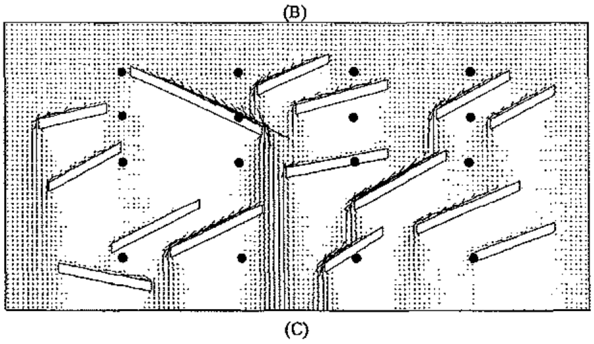

Figure 6.2
Hypothetical sandy-soil profile with location of solution samplers (dots) (Ju et al., 1997; ©Soil Science Society of America, with permission).

Jene (1998) measured the concentration of bromide ion at 1.3 m depth in a sandy-loam soil in two ways: by soil coring and by collecting soil solution with suction plates. In the front part of the distribution with depth, the suction plates collected higher concentrations in solution (flux concentrations) than those calculated for the water phase from soil sampling (resident concentrations) (e.g. 107 versus 62 μg dm^{-3}). On the contrary, in the tailing part of the distribution the concentrations in the collected soil solution were distinctly lower than those calculated from soil sampling (e.g. 11 versus 58 μg dm^{-3}). Between three and six months after application the peak of the bromide breakthrough curve appeared in the suction cells, while the peak of the concentration-distribution in soil was still above 1.3 m depth then.

Sarmah et al. (2004) presented a review of the field studies on pesticide leaching carried out in New Zealand. In various cases, higher concentrations were measured in deeper suction cups than in shallower cups. Apparently, the shallower cups missed the transport pathways. They experienced that preferential transport can also be missed by soil-core sampling. Suction cups samples and soil-core samples can give conflicting results. Using suction cups, deeper leaching was measured than by soil-core sampling

A review of water extraction in soil profiles via suction cups, suction plates, etc. has been presented by Weihermüller et al. (2007). The problem of representative sampling in a heterogeneous soil system is common with soil-sampling systems. When the water-flow pattern is rather irregular (preferential flow), the flow pathways can be easily missed by the samplers. More water may be extracted from the larger pores than from the smaller pores. Care should be taken to select sampling materials that do not adsorb organic compounds.

Plastics are often also unsuitable because they release substances interfering with the very sensitive pesticide analysis. Glass and stainless steel seem to be the materials to be preferred for neutral pesticides. Because suction has to be applied to withdraw water from the unsaturated zone, there will be loss of somewhat volatile compounds.

Bloem (2008) described the further development and testing of multi-compartment soil-solution samplers. These samplers were installed horizontally (from a trench; at 0.25 and 0.31 m depth) below an undisturbed soil volume in a field with humic-sandy soil (Vredepeel, NL). The variable under-pressure in the samplers could be adjusted to the under-pressure of the water in the surrounding soil. The measurements for the tracer chloride ion (applied uniformly) in each suction cell (3.15 x 3.15 cm) provided a breakthrough curve of the substance for each of the 100 cells. They showed a heterogeneous leaching pattern from the field under rainfall conditions in the winter period. The samplers were expected to yield concentrations somewhere between the resident and the flux concentrations. The variable-pressure samplers are an improvement over the earlier zero-pressure and fixed-under-pressure samplers. The method measured the heterogeneities in transport in the field on a rather small scale (fraction of 1 m^2).

<u>Concluding remarks</u> (sampling)

- In attempts to sample deeper soil layers, the front part of the concentration distribution can be missed, e.g. due to wet soil flowing from the core tube.
- In soil and soil solution sampling of the unsaturated soil zone, preferential flow and transport pathways can be easily missed.
- Soil-core sampling and suction-cup sampling can give conflicting results.
- In various cases, the substance was measured earlier in soil-solution samples taken near the groundwater table than in less-deep samples.
- Effective sealing of the voids around access tubes for soil solution and groundwater sampling is essential to prevent short-circuit flow.
- The comparatively high amounts of pesticide at the surfaces (especially shortly after spraying: soil surface, plants, sampling heads) may lead to contamination of the samples.
- Suction sampling of an adequate volume of soil solution for chemical analysis is only possible when the soil is rather wet (triggers the used of much irrigation water).
- In the sampling of soil solution, the materials used should be checked for adsorption of the pesticides and for release of substances interfering in chemical analysis.
- Multi-compartment suction-plate sampling is only possible for a small surface area (of the order of 1 m^2).
- In the interpretation of measurements, it is important to distinguish resident concentrations (often measured) and flux concentrations (relevant for leaching).
- The question how to sample a field with preferential water flow and substance transport remains.
- The high variation of substance concentration per depth is an obstacle in the close comparison between computations and measurements.
- Because there is no clear shape of the breakthrough curve, it will be difficult to discriminate between the performance of different preferential-transport models.

6.3 Analytical methods

In their review, Jarvis et al. (1995) emphasised that the leading edge of the pesticide distribution in soil is of great interest. They noticed that the determination limit of pesticides in soil samples is often rather high (low sensitivity). Consequently, the leaching of relevant concentrations to groundwater can be missed by soil sampling. The determination limit for soil samples can be one or two orders of magnitude too high, as compared to the EC limit for drinking water. Concentrations in water (suction cups, lysimeter outflow, groundwater, tube-drain water) are needed to test computation models at the low concentrations of regulatory interest. Some examples of the limitations of analytical methods are discussed below.

In a field experiment for isoproturon (autumn application) in humic-sandy soil (Traub-Eberhard et al., 1995) the determination limit in soil (HPLC) was 10 μg kg^{-1}, while that in water was 0.02 μg dm^{-3}. The estimated concentration of isoproturon in soil solution at the determination limit for soil is 12 μg dm^{-3} (Appendix A). This is much higher than the determination limit for water. Tile-drainage (0.7 to 0.9 m deep) of water through the sandy soil was only 3.3 mm in a year; discharge to groundwater was not considered. Isoproturon was measured to remain in the top 0.3 m of the soil (no further information). The maximum concentration in tile-drain water was measured to be 1.4 μg dm^{-3}.

In a study on atrazine movement in a humic-sandy soil (Australia), Patterson et al. (2000) analysed soil (coring) and water (suction) samples by GC-MS. The limit of determination for the soil samples was 25 μg kg^{-1} while the limit for water samples was 5 μg dm^{-3}. The limit of determination in soil can be estimated to correspond to a concentration in the water phase of 145 μg dm^{-3} (Appendix A). So substantial atrazine leaching could occur below the limit of determination in soil. Vertical installation of the suction cups in soil resulted in earlier breakthrough and higher soil-solution concentrations than horizontal installation at the same depth. The authors supposed that disturbance of the soil by the vertical installation produced preferential flow and transport pathways to the suction cups.

The herbicide methabenzthiazuron was applied to a bare arable field (Germany) with silt loam-soil in November (Kasteel et al., 2010). It was also applied to lysimeters with undisturbed soil monoliths of the same soil (1.2 m deep) installed at the same site. Concentrations of methabenzthiazuron in the field soil (33 core samples per time) could be measured only in the top 0.15 m of the soil profile. Nevertheless, some fast (preferential) leaching of the herbicide from the monoliths in the lysimeters was measured to occur (e.g. up to 0.7 μg dm^{-3}). Apparently, the preferential transport paths were missed by soil sampling. The limit of determination of methabenzthiazuron in soil (HPLC with MS/MS detection) was 9 μg kg^{-1}. This corresponds to an estimated concentration in soil solution of 4.9 μg dm^{-3} (Appendix A). For comparison: the limit of determination in the water leached from the lysimeter was 0.05 μg dm^{-3}.

Concluding remarks (analytical methods)

- The determination limit for pesticides in soil samples is usually much higher (less sensitive) than that in water samples.
- The low sensitivity of the measurements in soil hamper the comparison with the concentrations in groundwater and tube-drain water.
- Measurement of pesticide residues by certain analytical methods gives a high risk of false-positive or too high results, if not checked by a second, more specific, method.

7 General aspects of transport-model testing

In the field, physical non-equilibrium (preferential transport) can occur simultaneously with chemical non-equilibrium (adsorption-desorption kinetics) (Leistra and Boesten, 2011). The mathematical equations derived for both processes can be converted to the same type of equation. Both theoretical approaches give the same calculated shape of the breakthrough curve of substances in soil column studies with high water fluxes: early arrival and long tailing. The possibility to describe the transport of an inert tracer with the convection-dispersion equation does not imply that physical equilibrium is approached for adsorbed pesticides (Boesten, 1986). A relatively small fraction of stagnant water can contain a substantial fraction of the adsorbing sites, which can make the effect of physical non-equilibrium much stronger for pesticides. This is an interesting topic for a computer simulation study. It is thus a difficult task to distinguish the effects of physical and chemical non-equilibrium processes under field conditions. Weakly-adsorbed pesticides are most suitable to study the isolated effect of preferential transport.

It remains to be investigated whether a dispersion length derived for a non-adsorbed tracer can also be used for adsorbed pesticides (as is often done). Because of the adsorption, the transverse equilibration can be expected to be slower for pesticides. In field studies there can be accelerated transport of the front part of the distribution and long tailing, caused by both physical and chemical non-equilibrium.

In field experiments, checks are needed on the amount of tracer/pesticide that reaches the soil. First of all it has to be checked whether the calculated amount (spray volume, concentration) actually reaches the field. Part of the dosage may be intercepted by plants, which is followed by dissipation processes and wash-off to the soil surface. Specific dissipation processes can also occur at the soil surface, e.g. volatilisation and photochemical transformation. In various field experiments, the net load of the soil is uncertain. In other cases, a much lower deposition on the field was measured than calculated from the application. Uncertainty in net soil load makes the testing of computation models problematic. Uneven application on the field, e.g. in rows, can be expected to increase the variability in concentration in soil, which hinders model testing. Similarly, uncertainty in the uptake of pesticide by crop roots is an obstacle in transport-model testing.

Chemical analyses are rather labour-demanding and costly, so the number of chemical analyses has been reduced in most experiments. One way of reducing the number of analyses is by combining samples from the same depth in soil. However, much information on the spreading of the concentration is missed in this way. Even when several samples are analysed per depth in heterogeneous distributions, the variability of the concentration remains great. Various possible model concepts for preferential transport have been discussed by Leistra and Boesten (2011). At large variation in the concentration per depth it will be difficult to discriminate between the model concepts. Then the shape of the breakthrough curve from the soil profile cannot easily be distinguished. Therefore the use of a high value of the dispersion length in convection-dispersion models (Boesten, 2007; Leistra and Boesten, 2011) could be first step to account for preferential pesticide transport in soil.

A first step in the simulation of field experiments is the correct description of water flow and water balance. Some terms of the water balance can be measured directly, such as precipitation and outflow from lysimeters. Various other terms have to be estimated, like actual evapotranspiration and downward water flow in the field. The latter terms are based on other estimates such as the reference evaporation (from meteorological services). Regular measurement of the volume fraction of water in soil is essential. However such measurements are usually missing in lysimeter and column experiments.

Comparison of transport computations with measurements for tracers like bromide ion are relatively uncomplicated; the ions are not adsorbed nor transformed. For substances like pesticides showing interactions with the soil, the comparison can be expected to be more complicated. Besides heterogeneities in water flow and substance transport, other process can be expected to proceed in a heterogeneous way. The adsorption of pesticides per depth in the soil can be heterogeneous, e.g. due to differences in organic matter content. Further, the rate of transformation in soil can vary in horizontal direction. This causes the variation in measured concentration of pesticides per depth to be comparative large. As a result, accurate comparison of computations for pesticides with measuring results to estimate transport parameters is even more problematic than for inert tracers.

In various model-test studies, there was a discrepancy between the pesticide transformation rate in the field and that in the laboratory. The transformation in a certain layer in the field can be faster or slower than expected on the basis of lab data. A possible explanation is a difference in microbial activity in field and lab. Even the derivation of input parameters by different model users can result in different rate coefficients. Such discrepancies and uncertainties hamper the testing of the transport part of the model.

A general limitation is that the publications on leaching experiments with pesticides under practical conditions contain little detailed information, e.g. on soil and weather conditions. In journal articles, the experiments can be described only briefly. E.g. the reconstruction of rainfall patters from figures is cumbersome and inaccurate. Some journals provide the possibility to attach supplementary information (in digital form) to the article. The detailed data on the experiments should be made available for continued model testing, preferably in digital form. An example of exchange of detailed digital data on field/lysimeter experiments is given in the concerted model-testing project, as described by Vanclooster et al. (2000).

It is generally recognised that preferential transport of pesticides in soil should be included in the evaluation of the risk of leaching from soil (Vanclooster et al., 2004). Various model concepts have been proposed, both for soils with macropores and soils without macropores. However, confidence in a model depends on thorough testing under representative field conditions. Transport models often perform badly when used in a purely predictive mode (blind validation). Often, detailed field experiments are used as the starting point of such scenarios. On the basis of the first field experiments, various parameters and relationships can be calibrated to obtain a better description. Gradually, the parameters values could converge to certain values by continued testing. It is expected that prediction of preferential transport of pesticides will be impossible for several years to come. In the use of a model for leaching evaluation, representative scenarios have to be defined, with instructions on the derivation of input parameters. Otherwise the computations will be much influenced by subjective choices of the user.

8 General discussion and conclusions

Much of the water used for drinking water supply is extracted from groundwater and water courses in areas with intensive agriculture (e.g. in the Netherlands), in which crop protection chemicals (pesticides) are used. Environmental policy is focused on the prevention and reduction of the contamination of this water with pesticides. Usually it is supposed that water flow and pesticide transport in cultivated sandy soils (a major soil type in the extraction areas) proceed rather uniformly. However, it was shown that preferential water flow and pesticide transport can occur also in cultivated sandy soils. Such complicated transport leads to pesticide leaching to groundwater and water courses to be higher than expected from computer simulations with models assuming rather uniform transport (convection-dispersion approach).

Concepts for the modelling of preferential water flow and substance transport in sandy soils have been developed. In the present study, the question is whether there are data sets published/available to test models for preferential transport in sandy soils. In such testing it is especially interesting to have both, measurements in the soil profile and in the upper groundwater or tube-drain water for comparison. The present report discusses results of field experiments with tracers and pesticides in cultivated humic-sandy and loamy-sandy soils that may be suitable for testing preferential transport models.

In the Hupsel (NL) study for a field with loamy-sand soil, water flow and bromide-ion transport were studied. The upper part of the distributions of bromide ion in soil could be described reasonably well by the convection-dispersion approach. The front (deepest) parts of the distribution were missing for testing. The concentration pattern in shallow groundwater was too erratic for model testing.

The Vredepeel (NL) field experiment for bromide ion and bentazone in humic-sandy soil was carried out by our own research groups. The high variation of the concentration of bromide ion measured per depth in soil shows that water flow and substance transport were very heterogeneous. The high variation of the concentration of bentazone per depth in soil (composite of four samples) indicates that local differences in adsorption and transformation rate increased the variation. Because of problems with the sampling of wet subsoil, the earlier testing of convection-dispersion models was confined to the upper part of the unsaturated zone. The few measurements available to compare the concentrations in the subsoil with those in the upper groundwater indicate that complicated transport occurred.

In the literature, only few measurements are available on tracers and pesticides throughout the soil profile into the upper groundwater. Site-specific data on the adsorption and rate of transformation of the pesticides are often not available. In other cases there was a discrepancy in the transformation rates in the laboratory and in the field. The high variation in concentration measured per depth (which tends to increase with depth in the soil) is expected to hamper model testing. Concentration patterns in groundwater could not be reconstructed (too erratic). Only one experiment was reported which included chemical analysis of tube-drain water from a field with sandy soil.

In lysimeter and column studies with undisturbed sandy soil (relevant for the present study), only the leaching of a small fraction of the dosage was measured in a limited period after application of the substances. Measurements on the water and the concentrations within the soil are often not available (soil monolith considered as black box). Conclusions of the authors on preferential leaching from lysimeters/ columns seem to be premature and they need further study. Lysimeter studies should be simulated in detail (as far as possible) with an appropriate model to check whether preferential transport actually occurred.

The concentration of inert tracers at a certain depth in soil shows a wide range of variation due to local differences in transport. Both the extent of adsorption and the rate of transformation of pesticides vary substantially in the soil of a field. These variations contribute to the variation of the concentration of pesticides at a certain depth in the soil. The leaching of pesticide residue from replicated columns/lysimeters taken from a field shows substantial differences. Variation in the transport of substances in soil can be related to features of soil formation, e.g. thickness of the soil horizons. The few observations on aquifer build-up in combined soil-groundwater studies indicate that they can be very heterogeneous.

Uncertainties in the accompanying processes in an experimental data set hamper its use in the testing of transport models. Spraying on plant and soil surfaces raises the question on the extent of the surface-dissipation processes and thus on the net load of the soil system. The uptake of some groups of substances by the crop roots is highly uncertain. Discrepancies in the rate of pesticide transformation in the lab and in the field also make transport-model testing problematic.

Many field studies suffer from imperfections in the characterisation of the soil and of the meteorological conditions; suggestions are given to improve this situation. Problems were encountered with the sampling of the (rather wet) soil deeper in the soil profile (water and soil flowing out of the sampling tube). In soil and soil solution sampling, preferential flow and transport pathways can be easily missed. In various cases the substance was measured earlier in samples taken near the groundwater table than in shallower samples (so part of the soil matrix was by-passed). Soil-core sampling and suction-cup sampling can give conflicting results. The question remains on how to sample a field with preferential water flow and substance transport in a representative way. The determination limit in the chemical analysis of pesticides in soil samples is usually much higher (less sensitive) than that in water samples. This low sensitivity hampers the comparison of the concentrations in (sub)soil with those in groundwater. Checks of the measurements by a second (independent) method of analysis is often highly desirable to prevent false-positive and too high values.

In conclusion, all field experiments have their (serious) imperfections. The very heterogeneous nature of sandy soils and of the processes in these soils lead to large variations in the concentrations. Technical problems, e.g. in sampling and chemical analysis, lead to incomplete and confusing data sets. In general, the experimental techniques have to be improved. Only a few data sets may be adequate for the testing of models for preferential water flow and substance transport in sandy soils. The present literature study can serve as the starting point for a) selection of the most suitable data sets for model testing and b) the design of more complete and detailed data sets.

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References

Alphen, B.J. van and J.J. Stoorvogel, 2002. Effects of soil variability and weather conditions on pesticide leaching – A farm-level evaluation. J. Environ. Qual. 31: 797-805.

Bergström, L., 1992. Leaching of bentazon in Swedish soils using field lysimeters. Swedish J. Agric. Res. 22: 103-109.

Bergström, L.F. and N.J. Jarvis, 1993. Leaching of dichlorprop, bentazon, and ^{36}Cl in undisturbed field lysimeters of different agricultural soils. Weed Sci. 41: 251-261.

Bergström, L., N. Jarvis and J. Stenström, 1994. Pesticide leaching data to validate simulation models for registration purposes. J. Environ. Sci. Health A29: 1073-1104.

Bloem, E., 2008. Variation in space and time of water flow and solute transport in heterogeneous soils and aquifers. A new multi-compartment percolation sampler and a new parameterization of the spatio-temporal solute distribution. Doctoral thesis, Wageningen University, The Netherlands.

Boesten, J.J.T.I., 1986. Behaviour of herbicides in soil: simulation and experimental assessment. Doctoral thesis, Institute of Pesticide Research and Agricultural University, Wageningen, The Netherlands.

Boesten, J.J.T.I. and L.J.T. van der Pas, 1999. Movement of water, bromide ion and the pesticides ethoprophos and bentazone in a sandy soil in Vredepeel (The Netherlands). Report 122. Winand Staring Centre for Integrated Land, Soil and Water Research, Wageningen, The Netherlands.

Boesten, J.J.T.I. and L.J.T. van der Pas, 2000. Movement of water, bromide and the pesticides ethoprophos and bentazone in a sandy soil: the Vredepeel data set. Agric. Water Manage. 44: 21-42.

Boesten, J.J.T.I. and B. Gottesbüren, 2000. Testing PESTLA using two modellers for bentazone and ethoprophos in a sandy soil. Agric. Water Manage. 44: 283-305.

Boesten, J.J.T.I., 2007. Simulation of pesticide leaching in the field and in zero-tension lysimeters. Vadose Zone J. 6: 793-804.

Bosch, H. van den and J.J.T.I. Boesten, 1994. Validation of the PESTLA model: Field test for leaching of two pesticides in a humic sandy soil in Vredepeel (The Netherlands). Report 82. The Winand Staring Centre for Integrated Land, Soil and Water Research, Wageningen, The Netherlands.

Bosch, H. van den, C.J. Ritsema, J.J.T.I. Boesten, L.W. Dekker and W. Hamminga, 1999. Simulation of water flow and bromide transport in a water repellent sandy soil using a one-dimensional conve ction-dispersion model. J. Hydrol. 215: 172-187.

Brasino, J.S., 1986. A simple stochastic model predicting conservative mass transport through the unsaturated zone into groundwater. PhD thesis, University of Wisconsin, Madison.

Brown, C.D., J.M. Hollis, R.J. Bettinson and A. Walker, 2000. Leaching of pesticides and a bromide tracer through lysimeters from five contrasting soils. Pest Manag. Sci. 56: 83-93.

Brown, C.D. and W. van Beinum, 2009. Pesticide transport via sub-surface drains in Europe. Environ. Pollution 157: 3314-3324.

Fent, G., 2000. Significance of preferential flow as transport mechanism for pesticides in lysimeters containing sandy soil cores. Poster. State Education and Research Centre, Neustadt/W, Germany.

Ghodrati, M. and W.A. Jury, 1992. A field study of the effects of soil structure and irrigation method on preferential flow of pesticides in unsaturated soil. J. Contam. Hydrol. 11: 101-125.

Griffioen, J.W., D.A. Barry and J.Y.Parlange, 1998. Interpretation of two-region model parameters. Water Resources Res. 34: 373-384.

Hamminga, W., C.J. Ritsema and L.W. Dekker, 1994. Transport van water en bromide in waterafstotende zandgrond, onderzocht in een bouwlandperceel bij Vredepeel. Rapport 274, DLO Staring Centrum, Wageningen.

Heatwole, C.D., S. Zacharias, S. Mostaghimi and T.A. Dillaha, 1997. Movement of field-applied atrazine, metolachlor, and bromide in a sandy loam soil. Transactions ASAE 40: 1267-1276.

Jarvis, N.J., M. Stähli, L. Bergström and H. Johnsson, 1994. Simulation of dichlorprop and bentazon leaching in soils of contrasting texture using the MACRO model. J. Environ. Sci. Health A29: 1255-1277.

Jarvis, N.J., L.F. Bergström and C.D. Brown, 1995. Pesticide leaching models and their use for management purposes. In; Environmental behaviour of agrochemicals. Chapter 4, pages 185-220. T.R. Roberts & P.C. Kearney (eds). John Wiley & Sons, New York.

Jene, B., 1998. Transport of bromide and benazolin in lysimeters and a field plot with grid suction bases in a sandy soil. PhD. Thesis, University of Hohenheim. Verlag Ulrich E. Grauer, Stuttgart, Germany.

Jene, B., G. Fent and R. Kubiak, 1998. The movement of ^{14}-C benazolin and bromide in large zero-tension outdoor lysimeters and the undisturbed field. In: The lysimeter concept. Environmental behavior of pesticides. Chapter 10, pages 136-151. F. Führ, R.J. Hance, J.R. Plimmer & J.O. Nelson (eds). ACS Symposium Series 699. American Chemical Society, Washington DC.

Ju, S.H., K.S.J. Kung and C.S. Helling, 1997. Simulating impact of funnel flow on contaminant sampling. Soil. Sci. Soc. Am. J. 61: 427-435.

Jury, W.A., H. Elabd and M. Resketo, 1986. Field study of napropamide movement through unsaturated soil. Water Resources Res. 22: 749-755.

Jury, W.A., G.L. Butters, L.D. Clendening, F.F. Ernst, H. Elabd, T.R. Ellsworth and L.W. Stolzy, 1988. Validation of solute transport models at the field scale. In: Validation of flow and transport models for the unsaturated zone, pages 206-218. P.J. Wierenga and D. Bachelet (eds). New Mexico State University.

Kasteel, R., T. Pütz, J. Vanderborght and H. Vereecken, 2010. Fate of two herbicides in zero-tension lysimeters and in field soil. J. Environ. Qual. 39: 1451-1466.

Kodesova, R., M. Kocarek, V. Kodes, J. Simunek and J Kozak, 2008. Impact of soil micromorphological features on water flow and herbicide transport in soils. Vadose Zone J. 7: 798-809.

Kodesova, R., 2009. Soil micromorphology use for modeling of a non-equilibrium water and solute movement. Plant Soil Environ. 55: 424-428.

Kung, K.J.S., 1990. Preferential flow in a sandy vadose zone: 2. Mechanism and implications. Geoderma 46: 59-71.

Larsson, M.H., N.J. Jarvis, G. Torstensson and R. Kasteel, 1999. Quantifying the impact of preferential flow on solute transport to tile drains in a sandy field soil. J. Hydrol. 215: 116-134.

Leistra, M., A.M.A. van der Linden, J.J.T.I. Boesten, A. Tiktak and F. van den Berg, 2000. PEARL model for pesticide behaviour and emissions in soil-plant systems. Descriptions of the processes in FOCUS PEARL v 1.1.1. Alterra rapport 13. RIVM report 711401009. Alterra Green World Research, Wageningen, The Netherlands.

Leistra, M. and J.J.T.I. Boesten, 2010. Water flow and pesticide transport in cultivated sandy soils. Experimental data on complications. Alterra report 2063. Alterra, Wageningen UR, The Netherlands.

Leistra, M. and J.J.T.I. Boesten, 2011. Heterogeneous water flow and pesticide transport in cultivated sandy soils. Description of model concepts. Alterra report 2182. Alterra, Wageningen UR, The Netherlands.

Nordmeyer, H., 1994. Bodenvariabilität und Verhalten von Pflanzenschutzmitteln. J. Plant Nutr. Soil Sci. 157: 283-288.

Ommen, H.C. van and R. Dijksma, 1988. Analysis of transport in a coupled unsaturated-saturated system. In: Validation of flow and transport models for the unsaturated zone. Pages 447-462. P.J. Wierenga & D. Bachelet (eds). New Mexico State University, Las Cruces NM, USA.

Ommen, H.C. van , M.Th. van Genuchten, W.H. van der Molen, R. Dijksma and J. Hulshof, 1989a. Experimental and theoretical analysis of solute transport from a diffuse source of pollution. J. Hydrol. 105: 225-251.

Ommen, H.C. van, R. Dijksma, J.M.H. Hendrickx, L.W. Dekker, J. Hulshof and M. van den Heuvel, 1989b. Experimental assessment of preferential flow paths on a field soil. J. Hydrol. 105: 253-262.

Öhrström, P., Y. Hamed, M. Persson and R. Berndtsson, 2004. Characterizing unsaturated solute transport by simultaneous use of dye and bromide. J. Hydrol. 289: 23-35.

Parsons, R.G., R.J. Wicks, E.W. Gatzweiler and R.L. Jones, 1995. Variability in lysimeter results. BCPC Monograph No 62: 257-262. Pesticide movement to water. British Crop Protection Council.

Pas, L.J.T. van der, J.H. Smelt and J.J.T.I. Boesten, 1993. Veldexperiment te Vredepeel (1990-1992) naar transport van water en de uitspoeling van bestrijdingsmiddelen naar grondwater. II Analyse van de bodem en grondwater monsters. Interne mededeling 276. DLO-Staring Centrum, Wageningen.

Patterson, B.M., P.D. Franzmann, J.L. Rayner and G.B. Davis, 2000. Combining coring and suction cup data to improve the monitoring of pesticides in sandy vadose zones: a field-release experiment. J. Contam. Hydrol. 46: 187-204.

Pennell, K.D., A.G. Hornsby, R.E. Jessup and P.S.C. Rao, 1990. Evaluation of five simulation models for predicting aldicarb and bromide behavior under field conditions. Water Resources Res. 26: 2679-2693.

Sarmah, A.K., K. Müller and R. Ahmad, 2004. Fate and behaviour of pesticides in the agroecosystem – a review with a New Zealand perspective. Austr. J. Soil. Res. 42: 125-154.

Smelt, J.H., C.J. Schut and M. Leistra, 1983. Movement and conversion of aldicarb and its oxidation products in columns of grassed and fallow soil. J. Environ. Sci. Health B18: 645-665.

Smith, C.N., R.S. Parrish and R.F. Carsel, 1987. Estimating sample requirements for field evaluations of pesticide leaching. Environ. Toxicol. Chem. 6: 343-357.

Smith, M.C., D.L. Thomas, A.B. Bottcher and K.L. Campbell, 1990. Measurement of pesticide transport to shallow ground water. Transactions ASAE 33: 1573-1582.

Smith, C.N. and R.S. Parrish, 1993. A field study to evaluate leaching of aldicarb, metolachlor, and bromide in a sandy loam soil. J. Environ. Qual. 22: 562-577.

Steenhuis, T.S., J.Y. Parlange and S.A. Aburime, 1995. Preferential flow in structured and sandy soils: Consequences for modeling and monitoring. In: Handbook of vadose zone characterization & monitoring. L.G. Wilson, L.G. Everett & S.J. Cullen (eds). Lewis Publishers, Boca Raton Fl.

Tiktak, A., A.M.A. van der Linden and L.J.T. van der Pas, 1998. Application of the Pesticide Transport Assessment Model to a field study in a humic sandy soil in Vredepeel, The Netherlands. Pestic. Sci. 52: 321-336.

Tiktak, A., F. van den Berg, J.J.T.I. Boesten, D. van Kraalingen, M. Leistra and A.M.A. van der Linden, 2000. Manual of FOCUS [PEARL version 1.1.1. RIVM report 711401008. Alterra report 28. National Institute of Public Health and the Environment, Bilthoven, The Netherlands.

Trap, G., S. Meyer-Windel and B. Lennartz, 1995. Cell lysimeter for studying solute movement as influenced by soil heterogeneity. In: BCPC Monograph No 62: 123-128. Pesticide movement to water. A. Walker et al. (eds). British Crop Protection Council, Farnham, UK.

Traub-Eberhard, U., K.P. Henschel, W. Kördel and W. Klein, 1995. Influence of different field sites on pesticide movement into subsurface drains. Pestic. Sci. 43: 121-129.

Vanclooster, M., J.J.T.I. Boesten, M. Trevisan, C.D. Brown, E. Capri, O.M. Eklo, B. Gottesbüren, V. Gouy and A.M.A. van der Linden, 2000. A European test of pesticide-leaching models: methodology and major recommendations. Agric. Water Manag. 44: 1-19.

Vanclooster, M., J. Boesten, A. Tiktak, N. Jarvis, J.G. Kroes, R. Muñoz-Carpena, B.E. Clothier and S.R. Green, 2004. On the use of unsaturated flow and transport models in nutrient and pesticide management. In: Unsaturated-zone modelling: 331-361. R.A. Feddes et al. (eds). Kluwer Academic Publishers, Dordrecht, The Netherlands.

Vanderborght, J., 1997. Experimental and numerical study on non-reactive solute transport in soils. Chapter 9. Dissertationes de Agricultura, Katholieke Universiteit Leuven, Belgium.

Vereecken, H., U. Jaekel, C. Mouvet, C. Moreau, P. Burauel, M. Dust, D.J. Kim, D. Jacques, J. Feyen, A. Georgescu, N. Suciu and G. Marinoschi, 1996. Critical parameters governing the mobility and fate of pesticides in soil/aquifer systems. In: X Symposium Pesticide Chemistry: 627-648. Piacenza, Italia.

Walker, A. and P.A. Brown, 1983. Spatial variability in herbicide degradation rates and residues in soil. Crop Protection 2: 17-25.

Walker, A., M. Jurado-Exposito, G.D. Bending and V.R.J. Smith, 2001. Spatial variability in the degradation rate of isoproturon in soil. Environ. Pollution 111: 407-415

Weihermüller, L., J. Siemens, M. Deurer, S. Knoblauch, H. Rupp, A. Göttlein and T. Pütz, 2007. In situ soil water extraction: A review. J. Environ. Qual. 36: 1735-1748.

Wesenbeeck, I.J. van and R.G. Kachanoski, 1994. Effect of variable horizon thickness on solute transport. Soil Sci. Soc. Am. J. 58: 1307-1316.

Zander, C., T. Streck, T. Kumke, S. Altfelder and J. Richter,1999. Field-scale study of chlortoluron movement in a sandy soil over winter: I. Experiments. J. Environ. Qual. 28: 1817-1823.

Appendix A Measured pesticide contents in the subsoil converted to concentrations in the water phase

In this Appendix, measured contents of pesticides in the (deeper) soil layers are converted to concentrations in the water phase using Equation 1 (Chapter 2, Section 2.2.4).

Traub-Eberhard et al. (1995)
In a field experiment for isoproturon in humic-sandy soil, the determination limit for isoproturon in soil (HPLC with UV detection) was 10 µg kg^{-1}. The concentration of isoproturon in soil solution corresponding to this content in soil is estimated here using the following assumptions:

- bulk density of the soil is 1.7 kg dm^{-3};
- volume fraction of water in soil is 0.10 dm^3 dm^{-3};
- content of organic carbon (oc) in soil is 0.006 kg kg^{-1} ((Traub-Eberhard et al., 1995).
- adsorption coefficient Koc = 130 dm^3 kg^{-1} (Traub-Eberhard et al., 1995);

The estimated concentration of isoproturon in soil solution at the determination limit for soil is then 12 µg dm^{-3}. This is much higher than the determination limit for isoproturon in water of 0.02 µg dm^{-3}.

Heatwole et al. (1997)
The authors considered the contents around 0.01 mg/kg measured for atrazine in the soil of the 1.2 to 1.5 m layer to be an indication of little leaching. For a better evaluation this content in soil was converted to the concentration in the water phase using the following assumptions:

- dry bulk density in the loamy-sand subsoil was 1.6 kg dm^{-3};
- organic matter content is 0.002 kg kg^{-1} (Heatwole et al., 1997);
- organic carbon content is 0.57 * organic matter content;
- adsorption coefficient Koc = 100 dm^3 kg^{-1} (Heatwole et al., 1997);
- volume fraction of water is 0.15 dm^3 dm^{-3}.

This yields a concentration of atrazine in the water phase at 1.2 to 1.5 m depth of 30 µg dm^{-3}, which is high in view of the EU drinking water limit.

Smith and Parrish (1993)
In their study on the movement of aldicarb residues in soil (Smith and Parrish, 1993), total carbamate concentrations were shown in the figures down to the level of 0.01 kg ha^{-1} per 0.15 m thick soil layer. The authors concluded that transport was minimal. The amounts in the layers can be translated to concentrations in the water phase, assuming that a) dry soil bulk density is 1.72 kg dm^{-3} (measured), b) volume fraction of water is 0.234 dm^3 dm^{-3} (measured field capacity), and c) negligible adsorption of the carbamates to the subsoil material. The resulting concentration of carbamates in the water phase at the limit of presentation is 29 µg dm^{-3}.

Patterson et al. (2000)
The limit of determination of atrazine in soil samples (GC-MS) was 25 μg kg^{-1}. The corresponding concentration in the water phase at 0.5 m depth is estimated here using the following data, all given by Patterson et al. (2000):

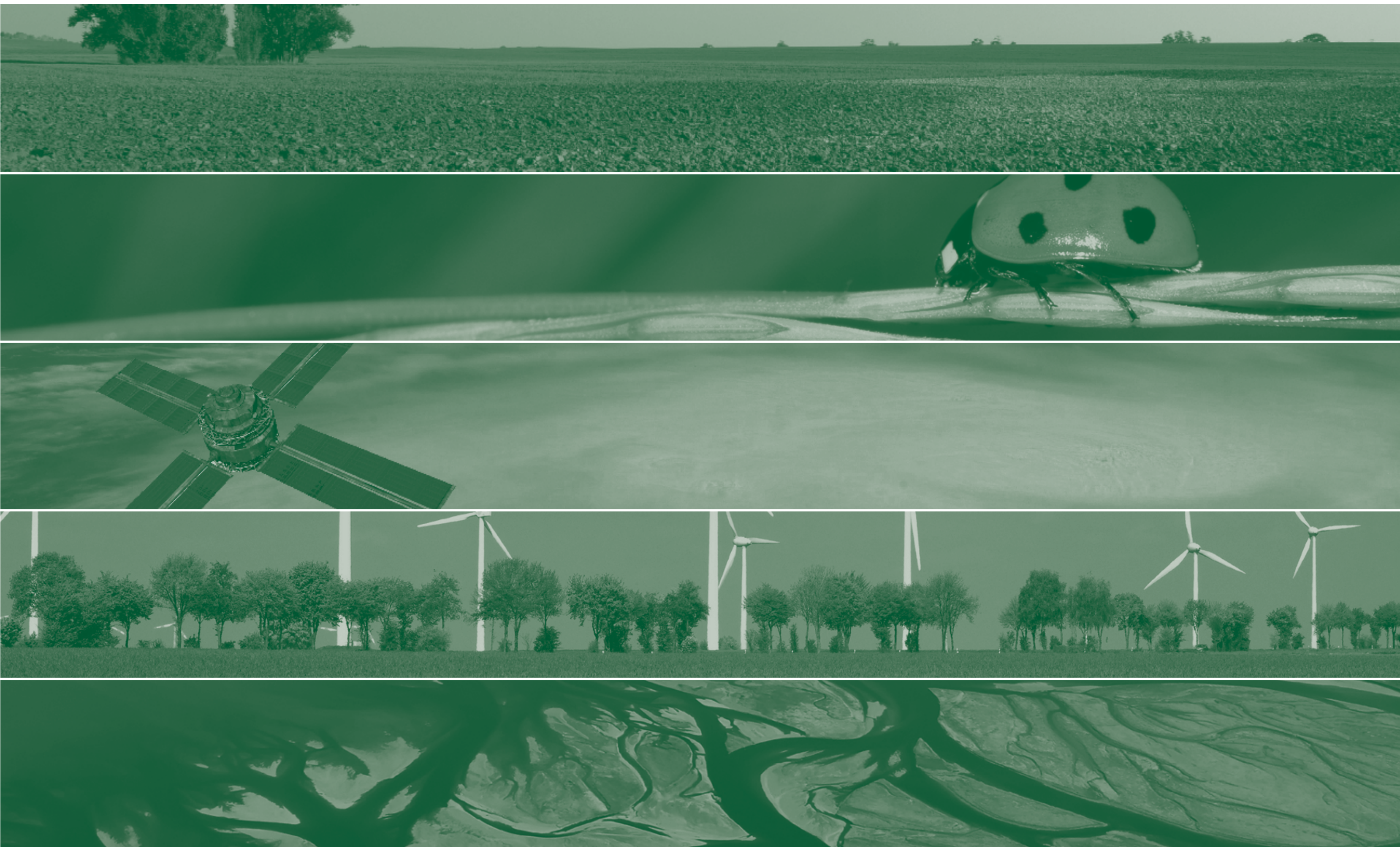
- soil bulk density = 1.73 kg dm^{-3};
- volume fraction of water = 0.05 dm^3 dm^{-3};
- adsorption coefficient Koc = 180 dm^3 kg^{-1};
- soil organic carbon (oc) content = 0.0008 kg kg^{-1}.

The calculated concentration in the water phase is then 145 μg dm^{-3}. The limit of determination in the water phase (suction cups) was 5 μg dm^{-3}.

Kasteel et al. (2010)
The limit of determination of methabenzthiazuron in silt-loam soil was 9 μg kg^{-1} (HPLC with MS/MS detection). The corresponding concentration in soil solution in the 0.35 to 0.70 m layer is calculated here using the following assumptions:

- bulk density of the soil = 1.59 kg dm^{-3} (Kasteel et al., 2010);
- volume fraction of water = 0.30 dm^3 dm^{-3} (estimate);
- organic carbon content in soil = 0.0031 kg kg^{-1} (Kasteel et al., 2010);
- coefficient of adsorption to organic carbon (oc) Koc = 527 dm^3 kg^{-1} (Kasteel et al., 2010).

The equivalent concentration of methabenzthiazuron in the water phase is then 4.9 μg dm^{-3}. For comparison: the determination limit for methabenzthiazuron in the water flowing from the lysimeter was 0.05 μg dm^{-3}.



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