Pesticides Research Nr. 67 2003
Bekæmpelsesmiddelforskning fra Miljøstyrelsen

Facilitated Transport of Pesticides

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Contents

Preface

The project ”Model Based Tool for Evaluation of Exposure and Effects of Pesticides in Surface Water”, funded by the Danish Environmental Protection Agency, was initiated in 1998. The aim of the project was:

> To develop a model-based tool for evaluation of risk related to pesticide exposure in surface water. The tool must be directly applicable by the Danish Environmental Protection Agency (DEPA) in their approval procedure. As part of this goal, the project had to:
>
> - Develop of guidelines for evaluation of mesocosm experiments based on a system-level perspective of the fresh water environment
> - To develop models for deposition of pesticides on vegetation and soil.
> - To estimate the deposition of pesticides from the air to the aquatic environment.

The project, called ”Pesticides in Surface Water”, consisted of seven subprojects with individual objectives. The sub-projects are listed in Table i.

TABLE i. SUB-PROJECTS OF ”PESTICIDES IN SURFACE WATER”.
TABEL i. OVERSIGT OVER DELPROJEKTER I ”PESTICIDER I OVERFLADEVAND”.

	Title	Participating institutions
A	Development and validation of a model for evaluation of pesticide exposure	DHI Water & Environment
B	Investigation of the importance of plant cover for the deposition of pesticides on soil	Danish Institute of Agricultural Science
C	Estimation of addition of pesticides to surface water via air	National Environmental Research Institute Danish Institute of Agricultural Science
D	Facilitated transport	DHI Water & Environment
E	Development of an operational and validated model for pesticide transport and fate in surface water	DHI Water & Environment National Environmental Research Institute
F	Mesocosm	DHI Water & Environment National Environmental Research Institute
G	Importance of different transport routes in relation to occurrence and effects of pesticides in streams	National Environmental Research Institute County of Funen County of Northern Jutland

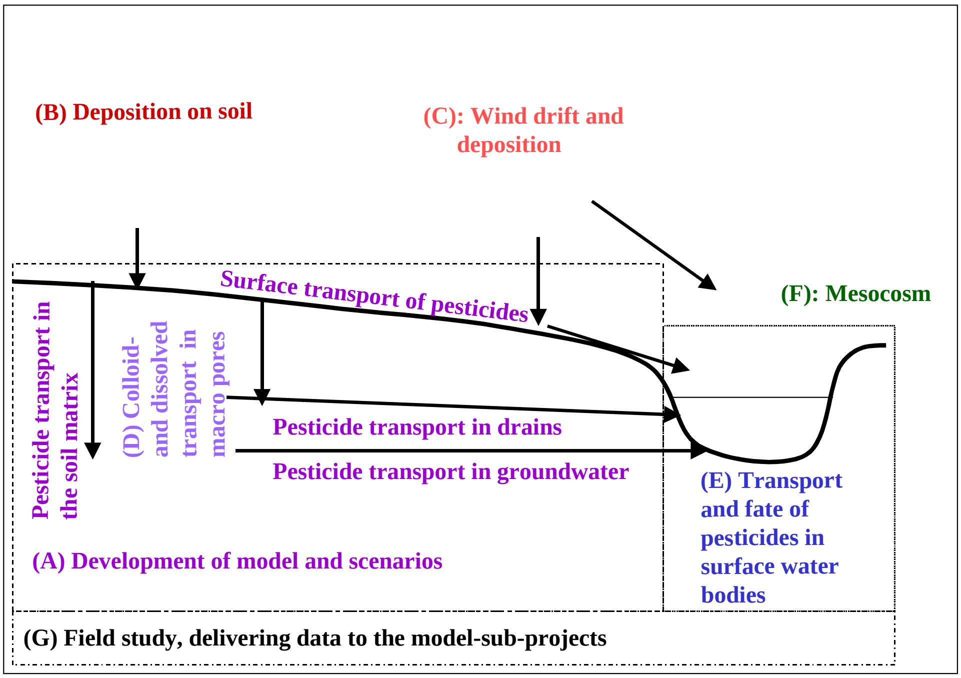

FIGURE i. LINKS BETWEEN THE DIFFERENT SUB-PROJECTS. THE SUB-PROJECTS ARE PLACED ON A CROSS-SECTION OF THE CATCHMENT TO ILLUSTRATE INTERACTIONS.

FIGUR i. SAMMENHÆNG MELLEM DELPROJEKTERNE. DELPROJEKTERNE ER PLACERET PÅ ET TVÆRSNIT AF EN OPLAND FOR AT ILLUSTRERE INTERAKTIONERNE.

Figure i describes the relationship between the sub-projects. Sub-project 1 models the upland part of the catchment, while sub-project 5 models surface water bodies. Sub-project 8 delivers data to both modelling projects. Sub-project 2 and 3 develops process descriptions for wind drift, dry deposition and deposition on soils. Sub-project 4 builds and tests a module for calculation of colloid transport of pesticide in soil. The module is an integrated part of the upland model. Sub-project 6 has mainly concentrated on interpretation of mesocosm-studies. However, it contains elements of possible links between exposure and biological effects.

The reports produced by the project are:

- Styczen, M., Petersen, S., Christensen, M., Jessen, O.Z., Rasmussen, D., Andersen, M.B. and Sørensen, P.B. (2002): Calibration of models describing pesticide fate and transport in Lillebæk and Odder Bæk Catchment. - Ministry of Environment, Danish Environmental Protection Agency, Pesticides Research No. 62.

- Styczen, M., Petersen, S. and Sørensen, P.B., Thomsen, M. and Patrik, F. (2002): Scenarios and model describing fate and transport of pesticides in surface water for Danish conditions. - Ministry of Environment, Danish Environmental Protection Agency, Pesticides Research No. 63.

- Styczen, M., Petersen, S., Olsen, N.K. and Andersen, M.B. (2002): Technical documentation of PestSurf, a model describing fate and transport of pesticides in surface water for Danish Conditions. - Ministry of Environment, Danish Environmental Protection Agency, Pesticides Research No. 64.

- Jensen, P.K. and Spliid, N.H. (2002): Deposition of pesticides on the soil surface. - Ministry of Environment, Danish Environmental Protection Agency, Pesticides Research No. 65.

- Asman, W.A.H., Jørgensen, A. and Jensen, P.K. (2002): Dry deposition and spray drift of pesticides to nearby water bodies. - Ministry of Environment, Danish Environmental Protection Agency, Pesticides Research No. 66.

- Holm, J., Petersen, C., and Koch, C and Villholth, K.G. (2002): Facilitated transport of pesticides. - Ministry of Environment, Danish Environmental Protection Agency, Pesticides Research No. 67.

- Helweg, C., Mogensen, B.B., Sørensen, P.B., Madsen, T., Rasmussen, D. and Petersen, S. (2002): Fate of pesticides in surface waters, Laboratory and Field Experiments. Ministry of Environment, Danish Environmental Protection Agency, Pesticides Research No. 68.

- Møhlenberg, F., Petersen, S., Gustavson, K., Lauridsen, T. and Friberg, N. (2001): Guidelines for evaluating mesocosm experiments in connection with the approval procedure. - Ministry of Environment and Energy, Danish Environmental Protection Agency, Pesticides Research No. 56.

- Iversen, H.L., Kronvang, B., Vejrup, K., Mogensen, B.B., Hansen, A.M. and Hansen, L.B. (2002): Pesticides in streams and subsurface drainage water within two arable catchments in Denmark: Pesticide application, concentration, transport and fate. - Ministry of Environment, Danish Environmental Protection Agency, Pesticides Research No. 69.

The original thoughts behind the project are described in detail in the report "Model Based Tool for Evaluation of Exposure and Effects of Pesticides in Surface Water", Inception Report – J. nr. M 7041-0120, by DHI, VKI, NERI, DIAS and County of Funen, December, 1998.

The project was overseen by a steering committee. The members have made valuable contributions to the project. The committee consisted of:

- Inge Vibeke Hansen, Danish Environmental Protection Agency, chairman 1998-mid 2000.
- Jørn Kirkegaard, Danish Environmental Protection Agency (chairman mid-2000-2002).
- Christian Deibjerg Hansen, Danish Environmental Protection Agency
- Heidi Christiansen Barlebo, The Geological Survey of Denmark and Greenland.
- Mogens Erlandsen, University of Aarhus
- Karl Henrik Vestergaard, Syngenta Crop Protection A/S.
- Valery Forbes, Roskilde University
- Lars Stenvang Hansen, Danish Agricultural Advisory Centre (1998-2001).
- Poul-Henning Petersen, Danish Agricultural Advisory Centre (2002).
- Bitten Bolet, County of Ringkøbing (1988-1999)
- Stig Eggert Pedersen, County of Funen (1999-2002)

- Hanne Bach, The National Environmental Research Institute (1999-2002).

October 2002

Merete Styczen, project co-ordinator

Summary and conclusions

This study combined field investigations with model work to obtain information on the dynamics and the extent of pesticide movement into subsurface drains, and the conditions and transport mechanisms governing pesticide and soil particle losses with drainage water.

The field experiments, performed on two plots (each 16 by 100 m^2), were carried out in corporation with The Royal Veterinary and Agricultural University (KVL) at their test facilities at Rørrendegaard near Høje Tåstrup. Experiments with pesticides were carried out in two winter seasons; 1999-2000 and 2000-2001. The leaching dynamics of two differently sorbing pesticides, Pendimethalin (hydrophobic) and Ioxynil (hydrophilic) was observed through sampling of drain water collected below the two plots.

A model component for MIKE SHE describing the transport of colloids generated at the soil surface through the unsaturated zone and the colloid-facilitated transport of pesticide was developed. The technical documentation for the module can be found in Styczen et al. (2002). In Appendix C of this report, a sensitivity analysis for some of the parameters in the module can be found. Chapter 4 of this report describes the application of MIKE SHE with the colloid-module to the drain-flow- and concentration observations of particles and Pendimethalin at Rørrendegaard for the season 1999-2000.

Based on the observations from the two sampling seasons at the field site and the modelling of the observations, the most significant conclusions drawn from this study were:

From experiments:

- Peak concentrations of soil particles and Pendimethalin occurred shortly after initiation of drain events and before the occurrence of maximum drain flow rates.
- There was a significant correlation between Pendimethalin (with a K_{oc}-value in the range 10000-18000) concentrations and turbidity (particle concentrations) in the drain flow samples.
- The timing of the peak concentrations indicated that macropores were the dominant means of transport for Pendimethalin and soil particles.
- Fractionation analysis (filtering through 0.7 µm filter or centrifugation) on the drain water from the field experiments showed that between 0 and 30 % of the Pendimethalin was associated with particles. Three drain water samples from two other areas (Odderbæk and Lillebæk) showed that 45-65 % of the Pendimethalin was associated with particles.
- Ioxynil (with a K_{oc} value of approx. 170) did not exhibit any sign of correlation between particle content and compound concentration.
- The strong correlation between turbidity and Pendimethlin concentrations implies that turbidity may serve as a guide in determining which samples to analyse for Pendimethalin or other hydrophobic compounds.

From modelling:

- Using a setup calibrated to fit the observed particle concentrations in the drains, the subsequent modelling of colloid-facilitated transport showed that with use of realistic K_d-values for Pendimethalin, colloid-facilitated transport through the macopores completely dominated (97 %) the mass transport of Pendimethalin through the unsaturated zone.
- The observed low values of particle-associated Pendimethalin (0-30 %) in the drain flow samples from Rørrendegaard could be explained by the dilution of the colloidal concentrations and the subsequent release of Pendimethalin to the dissolved state.
- Simulations using different K_d-values for sorption of pesticide showed that for the calibrated model setup for Rørrendegaard, particle-associated transport completely determined the mass transport of pesticides to the saturated zone in the range of K_d-values from 0.1 to 100 l/kg and was a potentially important factor for even lower K_d-values. However, the experimental evidence for Ioxynil did not support that low K_d pesticides should associate considerably with particles.
- The model-approach applied in this study, where the particle-associated pesticide was obtained through sorption of dissolved pesticide could not produce concentrations of particle-associated Pendimethalin and hence total Pendimethalin concentrations that were comparable to the observed ones, since the obtainable concentrations were limited by the solubility of the Pendimethalin.
- It was not possible to simulate concentrations up to the level of the observed concentrations even though Pendimethalin was considered a conservative tracer – again indicating the existence of a very considerable supplementing transport mechanism than dissolved transport.
- Applying a concept, where the particle-associated concentration of the pesticide is unrelated to the solubility of the pesticide will allow for higher pesticide concentrations to be simulated.

In combination between experimental and modelling results, the following conclusions could be drawn:

- The time between leaching events and sampling and between sampling and filtering of samples may be a very important factor in finding proof of particle-associated transport when taking samples from the saturated zone (and from drains), because of dilution of colloidal concentrations and subsequent release of pesticide from the particle associated state.
- Ideally, for determining the importance of particle-association as transport mechanism, samples should be taken directly from the macropores and not from the saturated zone

In conclusion, the study indicates strongly that colloid-facilitated transport through macropores is a very important transport mechanism for strongly sorbing pesticides (K_{oc} in the range of Pendimethalin) from soil surface to saturated zone, at locations where generation of colloidal particles is considerable, and that this should be taken into account when determining the potential leaching of at least strongly sorbing pesticides.

To determine the potential leaching of pesticides from different soil types at least the organic carbon content of the topsoil, the structure of macropores in the soil, and the ease of soil detachment should be considered.

Sammenfatning og konklusioner

I nærværende projekt kombineredes feltundersøgelser med modelarbejde med henblik på at skaffe informationer om dynamikken og omfanget af pesticidtransport til markdræn samt om de transportmekanismer, der styrer udsivningen af pesticider og jordpartikler med drænvand.

Feltforsøgene, som fandt sted på to marker (hver 16x100 m^2), blev udført i samarbejde med Den Kgl. Veterinær- og Landbohøjskole (KVL) på deres testområde, Rørrendegaard, ved Høje Taastrup. Forsøgene med pesticider fandt sted over to vintersæsoner: 1999-2000 og 2000-2001. Transporten af to forskelligt sorberende pesticider, Pendimethalin (hydrofobt) og Ioxynil (hydrofilt), blev observeret ved hjælp af prøvetagning af drænvand fra de to marker.

Der blev udviklet en modelkomponent til MIKE SHE til beskrivelse af transporten af kolloider dannet ved jordens overflade og af den kolloid-faciliterede transport af pesticider. Den tekniske dokumentation for modulet findes i Styczen et al. (2002). Appendiks C til denne rapport indeholder en følsomhedsanalyse for nogle af parametrene til modulet. Kapitel 4 beskriver anvendelsen af MIKE SHE med kolloid-modulet til simulering af indholdet af partikler og pesticider i drænvandet ved Rørrendegaard i sæsonen 1999-2000.

På basis af studierne fra feltområdet i løbet af de to prøvetagningssæsoner samt modelleringen af observationerne blev følgende konkluderet:

Fra eksperimenterne:

- Den højeste koncentration af jordpartikler and Pendimethalin viste sig kort efter starten af drænafstrømningshændelser og før forekomsten af den maksimale drænafstrømning.
- Der var en markant sammenhæng mellem Pendimethalin-koncentrationen og turbiditeten (partikel-koncentrationen) i drænvandsprøverne.
- Tidspunktet for opnåelse af de maksimale koncentrationer indikerede, at makroporer var den dominerende transportvej for Pendimethalin og jordpartikler.
- Fraktioneringsanalyser (filtrering gennem 0.7 μm filter eller centrifugering) af drænvandsprøver fra feltforsøgene viste, at mellem 0 og 30% af Pendimethalin var associeret med partikler. Tre drænvandsprøver fra de to modelområder (Odderbæk og Lillebæk) viste, at 45-65% af Pendimethalinen var forbundet med partikler.
- Ioxynil (med en K_{oc} værdi på ca. 170) viste ingen tegn på sammenhæng mellem partikelindhold og stofkoncentration.
- Den markante sammenhæng mellem turbiditet og Pendimethalin-koncentration antyder, at turbiditeten af prøven kan benyttes til at indikere hvilke prøver, der skal analyseres for Pendimethalin eller andre hydrofobe forbindelser.

Fra modelleringen:

- Med en opsætning, der var kalibreret mod partikelkoncentrationerne i drænene, viste den efterfølgende modellering af partikelbåren transport, at ved brug af realistiske K_d-værdier for Pendimethalin var massetransporten af Pendimethalin til den mættede zone totalt domineret (97%) af den kolloid-bårne transport via makroporer.
- De observerede lave værdier af partikelbunden Pendimethalin i drænvandsprøverne fra Rørrendegaard kunne forklares ud fra fortyndingen af kolloid-koncentrationerne og den deraf følgende frigørelse af Pendimethalin fra kolloider til vandfasen.
- Simuleringer med forskellige K_d-værdier for sorption af pesticider viste, at for den kalibrerede modelopsætning for Rørrendegaard dominerede den partikelbundne transport fuldstændig massetransporten af pesticider til den mættede zone for K_d-værdier i intervallet fra 0.1 til 100 l/kg og var samtidig en potentielt betydningsfuld faktor selv ved endnu lavere K_d-værdier. Imidlertid støttede forsøgsresultaterne ikke direkte, at pesticider med lave K_d-værdier skulle forbindes mærkbart med partikler.
- Den metode, der her er anvendt til at beskrive kolloid-faciliteret transport kunne ikke producere koncentrationer af kolloid-båren Pendimethalin, og derfor heller ikke total-koncentrationer af Pendimethalin, der kunne sammenlignes med de observerede koncentrationer, da den opnåelige koncentration var begrænset af opløseligheden af Pendimethalin.
- Selv ved simulering af Pendimethalin som et konservativt (ikke-sorberende) stof var det ikke muligt at opnå de observerede koncentrationsniveauer, hvilket er stærk indikation af eksistensen af en betydelig transportmekanisme udover opløst transport.
- Ved anvendelse af et alternativt koncept, hvor den kolloid-faciliterede transport ikke er relateret til opløseligheden af pesticidet, vil kunne simuleres højere pesticid-koncentrationer.

Ud fra kombinationen af eksperimentelt og modelmæssigt arbejde kunne følgende konklusioner drages:

- Den tid, der går mellem regnhændelse og prøvetagning og mellem prøvetagning og filtrering af prøven kan være en meget vigtig faktor for bedømmelse af kolloid-faciliteret transport ved udtagning af drænvandsprøver (eller prøver fra mættet zone), p.g.a. fortyndingen af kolloidkoncentrationen og den efterfølgende afgivelse af stof fra kolloiderne.
- For eksperimentelt at kunne bestemme vigtigheden af kolloid-båren transport bør prøverne ideelt set udtages fra makroporerne.

Sammenfattende er konklusionen på dette arbejde, at kolloid-faciliteret transport gennem makroporer er en meget vigtig transport-mekanisme gennem den umættede zone for stærkt sorberende pesticider (med K_{oc}-værdier i samme interval som Pendimetahlin) på steder, hvor genereringen af kolloider er betragtelig. Dette faktum bør tages med i betragtning, når udvaskeligheden af i hvert fald stærkt sorberende pesticider skal bedømmes.

For at kunne bedømme den potentielle udvaskelighed fra forskellige jordtyper skal som minimum bestemmes indholdet af organisk kulstof i jorden, makropore-strukturen og frigørelsen af partikler fra overfladen.

1 Purpose

The purpose of the project was to contribute to the understanding of colloidal transport in structured soils and the importance of colloid-facilitated transport to the leaching of pesticides to surface waters. Furthermore, the purpose was to develop a component for the MIKE SHE model, which could be used for a quantitative evaluation of colloid-facilitated transport of pesticide through the unsaturated zone.

Following the purpose stated, the project consisted of two main parts: an experimental part and a model-development and testing part.

This report focuses on the experimental results and on the modelling of these results, whereas the model documentation can be found in Styczen et al. (2002).

2 Field experiments

The aim of the present field investigations was to obtain information on the dynamics and the extent of Pendimethalin and Ioxynil movement into subsurface drains, and the conditions and transport mechanisms governing pesticide and soil particle losses with drainage water.

The field experiments were carried out in corporation with The Royal Veterinary and Agricultural University (KVL) at their test facilities at Rørrendegaard near Høje Tåstrup. Experiments were carried in two winter seasons; 1999-2000 and 2000-2001.

2.1 Description of experimental setup

2.1.1 Physical layout

The experimental site consisted of four plots (each 16 by 100 m^2) located adjacent to each other. The four plots were established in such a way that they were drained by lateral tile drain pipes, each 100 m long and each located 1,1 m below ground surface (installed in 1965). A sampling well was established downstream on each drain, allowing for drain flow measurements (tipping bucket system, resolution app. 10 l) and water sampling. The perforated drain line and the sampling well were connected by a 3 m long tight pipe, eliminating the risk of direct contamination along the side walls of the well. The maximum level difference within the field was approximately 0.7 m. Liquid soil water content was determined in an area downstream to the sampling wells using the TDR technique. 32 TDR probes (30 cm long) were installed horisontally with minimal soil disturbance along a transect at 8 and 16 cm depth, 8 probes at each depth in each plot. Precipitation was measured using one centrally located rain gauge (resolution 0,1 mm) and two control gauges. The physical layout is presented in Figure 2.1;the plots A and B on which the experiments have been conducted are plots (3) and (4), respectively.

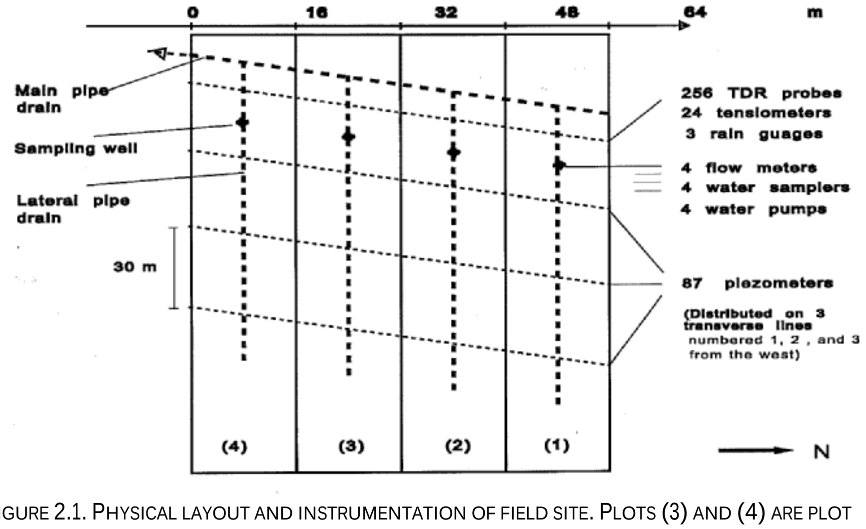

FIGURE 2.1. PHYSICAL LAYOUT AND INSTRUMENTATION OF FIELD SITE. PLOTS (3) AND (4) ARE PLOT A AND B, RESPECTIVELY.
FIGUR 2.1. SKETCH OVER FELTFORSØG, PLOT (3) AND (4) SVARER TIL HHV. PLOT A OG PLOT B.

2.1.2 Soil

The soil was developed on moraine deposits from the Weichselian Glaciation, and was classified as an Agrudalf. It bore the impressions of a long duration of cultivation with an agric horizon located directly below the plow layer at 25-35 cm depth. Aggregates with clay skin had developed in the Bt horizon. The depth to the C horizon (containing calcite) was 110 cm on average. The Bt horizon exhibited a well developed structure with angular to columnar aggregates. The upper horizons were characterised by weak, subangular aggregates, tending towards a platy structure in the agric horizon. Biopores were dominated by root and vertically oriented earthworm channels transecting the aggregates. The root channels were generally smaller than 2 mm diameter, whereas the worm channels were between 3 and 8 mm diameter, extending to 20 mm in the worm cavities. Rough estimates on the number of earthworm channels were made on large lumps of soil taken from the profile. Common numbers found in the Bt horizon at 50 cm depth were 2-6 channels per 100 cm^2 horizontal cross section. There were coatings of clay and humus-rich particles on the pore walls. The number of channels decreased rapidly from about 90 cm depth, though some channels penetrated below 130 cm depth. The entire subsoil below 30 cm depth was relatively compact with mean bulk densities between 1,66 and 1,70 kg/l. Selected soil characteristics are given in Table 2.1

TABLE 2.1. SELECTED SOIL CHARACTERISTICS. MEAN VALUES WITH STANDARD DEVIATIONS IN ().
TABEL 2.1. UDVALGTE KARAKTERISTIKA FOR JORD. MIDDELVÆRDIER MED STANDARDAFVIGELSER I ().

Property		Plot A				Plot B			
		Depth, cm							
		0-5	10-15	30-40	60-80	0-5	10-15	30-40	60-80
Texture kg kg^{-1} †	Clay, <2 µm	0.111 (0.022)		0.122 (0.034)	0.151 (0.049)	0.113 (0.017)		0.128 (0.040)	0.220 (0.020)
	Silt, 2-50 µm	0.217 (0.029)		0.219 (0.046)	0.188 (0.029)	0.227 (0.028)		0.228 (0.054)	0.202 (0.028)
	Sand, 50-2000 µm	0.672 (0.030)		0.659 (0.055)	0.661 (0.070)	0.660 (0.036)		0.644 (0.066)	0.578 (0.044)
Org. Matter, kg/kg		0.030		0.016	0.010	0.032		0.010	0.008
Field capacity ‡, m^3/ m^3		0.276 (0.016)	0.284 (0.024)	0.252 (0.008)	0.278 (0.017)	0.291 (0.027)	0.279 (0.021)	0.266 (0.010)	0.285 (0.016)
Bulk density §, kg/l Autumn		1.26 (0.10)	1.47 (0.06)	1.67 (0.07)	1.69 (0.06)	1.32 (0.13)	1.41 (0.14)	1.66 (0.09)	1.70 (0.04)
Spring		1.35 (0.07)	1.51 (0.08)			1.40 (0.07)	1.48 (0.08)		

† Based either on n=45 (0-15 cm and 30-40 cm depth) or n=8 (60-80 cm depth) samples.

‡ Equilibrium water content at 50 hPa tension (n=10 -18).

§ Determined from 10-18 samples. The plow layer was sampled early in November 1999 (autumn) and in March 2000 (spring).

2.1.3 Tillage treatment

Tillage treatments were both years:

Plot A : ploughing (25-28 cm depth), light subsurface compaction, one intense harrowing with a PTO-driven rotary harrow (5 cm depth), drilling.
Plot B : ploughing (25-28 cm depth), one harrowing with a spring-tooth harrow (4-6 cm depth), drilling.

The two treatments represent conventional soil preparation methods for wheat used in Denmark. Wheat was used as test crop both seasons.

2.1.4 Chemical Application

Pendimethalin (N-(1-ethylpropyl)-3,4 dimethyl-2,6 dinitrobenzenamine) at a dose of 2,00 kg/ha was applied in Stomp SC on November 16 1999. Ioxynil at 0.200 kg ha^{-1} was applied together with Pendimethalin at 2.00 kg ha^{-1} on November 10 in 2000. Both applications were using a pesticide sprayer. The two herbicides were applied in the following commercial formulations: Pendimethalin 400 g l^{-1} (‘Stomp’ SC, BASF) and Ioxynil 200 g l^{-1} (‘Oxitril’ CM, Aventis). The applied doses were maximum doses according to recommendations for practical agriculture. All applications were given uniformly to the entire plot areas, except on a 5 m belt upstream from the sampling well. No Pendimethalin had been applied at the site during the 3 years period up to November 1999.

Pendimethalin and Ioxynil are widely used herbicides in Denmark (Miljøstyrelsen, 2000). Table 2.2 summarises some chemical characteristics for the two compounds.

TABLE 2.2. CHEMICAL CHARACTERISTICS FOR THE TWO PESTICIDES USED IN FIELD INVESTIGATIONS.
TABEL 2.2. KEMISKE KARAKTERISTIKA FOR DE TO PESTICIDER BENYTTET I FELTFORSØG.

Compound	Solubility (mg/l)	K_{oc}	DT_{50} in soil/groundwater (days)
Pendimetahlin	0,3*	10000-18000**	40*** 66**
Ioxynil	50*	170**	8-10*,**

* Tomlin (1996)
** Database PATE, Miljøstyrelsen (2002)
*** Extoxnet (http://ace.orst.edu/info/extoxnet)

Pendimethalin adsorbs strongly to topsoils and has reported soil-water partition coefficients (K_d values) ranging from 99.8 (0.59 % organic carbon) to 1638 (16.9 % organic carbon) (Pedersen et al., 1995; Zheng and Cooper, 1996). Increasing soil organic matter and clay content is associated with increased soil binding capacity (Extoxnet, 2002). Ioxynil adsorbs weakly (Kjær et al., 2001) and is considered to be mobile in soil (Aventis, 2000). However, it may have a fairly low persistency with DT_{50} values for topsoil of about 10 days (Extoxnet, 2002) or less (Kjær et al, 2001).

Based on the strong affinity for the soil, Pendimethalin was not expected to be transported in significant amounts in the traditional perception of dissolved species transport. Thus, any significant leaching of Pendimethalin was expected to be related to particle-facilitated transport. The much more soluble Ioxynil was expected to be transported dissolved in the water phase, given that the low persistency to degradation would allow for any detectable leaching . The two compounds were applied simultaneously in the second season of sampling to compare the leaching dynamics of the two different pesticides.

2.1.5 Sampling of drain water and soil

Drain water sampling was performed on a flow-related basis. The maximum resolution was one separate sample per 0.025 mm drain flow with subsampling for every 0.0063 mm. The minimum resolution was 1 separate sample per 0.2 mm drain flow with subsampling for every 0.05 mm. Both samplers[‡‡] were equipped with teflon tubes and a roundabout with 24 half litre glass vessels. A total of 1913 separate samples were taken in the two plots.

Turbidity (expressed in Nephelometric Turbidity Units, NTU) was measured[†] during the two seasons, plus the preceeding season 1998-1999, in all water samples with visual indications of suspended matter (421 samples in total), and in 24 randomly selected samples without such visible indications. The content of suspended matter was determined by centrifugation in 77 drain water samples with visible indications of suspended matter.

Analyses for pesticides were performed on 50 water samples during the 1999/00 season (Pendimethalin) and on 38 water samples during the 2000/01 season (Pendimethalin and Ioxynil). When selecting samples for pesticide analyses, focus was given to the first drain flow events after application.

Drain water flow was measured continuously using a tipping bucket system (resolution: about 0.0063 mm). Precipitation was registered at the site every 5 minutes (resolution: 0.1 mm). Liquid soil water content at 8 and 16 cm depth was determined from measured dielectric constant using the TDR-technique (Topp et al., 1980; Hayhoe and Bailey, 1985). Measurements were performed every two hours during the first two seasons. Thirty-two TDR-probes (30 cm long) were installed horizontally along a transect downstream to the sampling wells; 8 probes at each depth in each plot (see Figure 2.1).

Soil cores for Pendimethalin analyses were sampled before and right after Pendimethalin application on November 16th 1999 (0-4 cm depth), and on February 24th 2000 (0-35 cm depth). Sixteen randomly located soil cores were taken each date in each plot. The sixteen soil cores were pooled to obtain one composite sample. The soil samples were immediately frozen at –20°C and kept frozen until analysis.

2.1.6 Analyses

Analyses for Pendimethalin for the season 1999-2000 were performed at The Department of Environmental Assessment at The Swedish University of Agricultural Sciences, Uppsala, Sweden according to procedures described by Andersson (1999). Analyses for Pendimethalin and Ioxynil for the season 2000-2001 were performed at DHI.

Drain water samples were separated into an aqueous and a solid phase using a filtration technique (0.7 µm glass micro fibre filter). Pendimethalin and

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[‡‡] Model Epic 1011 from Bühler Montec (http://www.BuhlerMontec.co.uk)

[†] Using a HACH 2100N turbidimeter from Hach Company (http://www.hach.com)

Ioxynil were extracted from solid phases by Soxtec extraction using either a mixture (1:1 v/v) of dichloromethane and acetone (1999/00 season) or acetone (2000/01 season) as solvent. A polystyrene divinylbenzene polymer was used as adsorbent in the aqueous phase. During the 1999/00 season, samples were analysed for Pendimethalin using a Hewlett Packard model 5890A gas chromatograph (detection limit: 0.04 µg l^{-1}). During the 2000/01 season, samples were analysed for Pendimethalin (detection limit: 0.01 µg l^{-1}) and Ioxynil (detection limit: 0.03 µg l^{-1}) using HPLC-technique. Samples were kept at 5^{o} C from the time of sampling until filtration and analyses were performed. This period extended from a few days to weeks.

The content of suspended matter in drain water was determined by centrifugation (30 min at 5000 rpm or 4100 g´s) and drying of the precipitate (110^{o} C).

3 Results

3.1 Rainfall, soil conditions, and drain flow

Drain flow was generated exclusively during the months October - March. Rainfall totals during these 6 months were 280 mm for the 1999/00 season, and 246 mm for the 2000/01 season (see Table 3.1), compared to an average of 274 mm for the years 1961-1990 measured at a nearby climate station (Jensen, 1996). Cumulative drain flow for the 6 months period as related to entire plot areas varied between 4.6 mm and 36.0 mm (Table 3.1). The cumulative flow decreased with the amount of rainfall, and it was larger for plot B than for plot A. The ratio between drainage flow from plot A to that from plot B was fairly similar for the two seasons.

TABLE 3.1. RAINFALL (P) AND DRAIN FLOW DURING THE 1999/00 AND 2000/01 SEASONS. TOTALS FOR THE MONTHS OCTOBER-MARCH.
TABEL 3.1. REGN (P) OG DRÆNFLOW FOR SÆSONERNE 1999/00 OG 2000/01. TOTALER FOR MÅNEDERNE OKTOBER-MARTS.

	1999/00 season		2000/01 season	
P, mm	280		246	
Plot	A	B	A	B
Drain flow, mm	8.4	20.7	4.6	14.7

Drain flow appeared as events, separated by periods with little or no flow (see Fig. 3.1). Liquid soil water content at 8 cm depth ($\theta_{L,8}$) varied in plot A between 10 and 33 % (v/v) during the 1999/00 seasons. Values considerably below the measured field capacities (Table 2.1) did not represent total water contents but showed that some of the soil water was frozen. For plot B, $\theta_{L,8}$ values were similar to the values shown for plot A, whereas fewer distinct frost events occurred at 16 cm depth in both plots (data not shown). During the 2000/01 season, most of the drain flow occurred in periods with soil surface temperatures above 0^{o}C, i.e. periods with an unfrozen soil surface.

3.2 Dynamics of herbicide concentrations in drain water

3.2.1 Pendimethalin, 1999/00 season

Eighty-three percent of the total Pendimethalin loss with drain water from the two plots occurred during the three events that are shown on Figure 3.2 (numbered successively 1-3). The first drain flow occurred during event No. 1 on December 10; 25 days after the application. Maximum Pendimethalin concentration (C_p) values (8.3 µg l^{-1} for plot A and 12.6 µg l^{-1} for plot B) were observed during this event and almost simultaneously (within the same 3-6 hours period) for the two plots after a cumulative drain flow corresponding to 0.05 mm for plot A and 0.06 mm for plot B. The concentrations dropped rapidly as the event continued. However, C_p more than doubled in both plots in response to an extra 2 mm of rainfall about 60 hours after the onset of the event (Fig. 3.2).

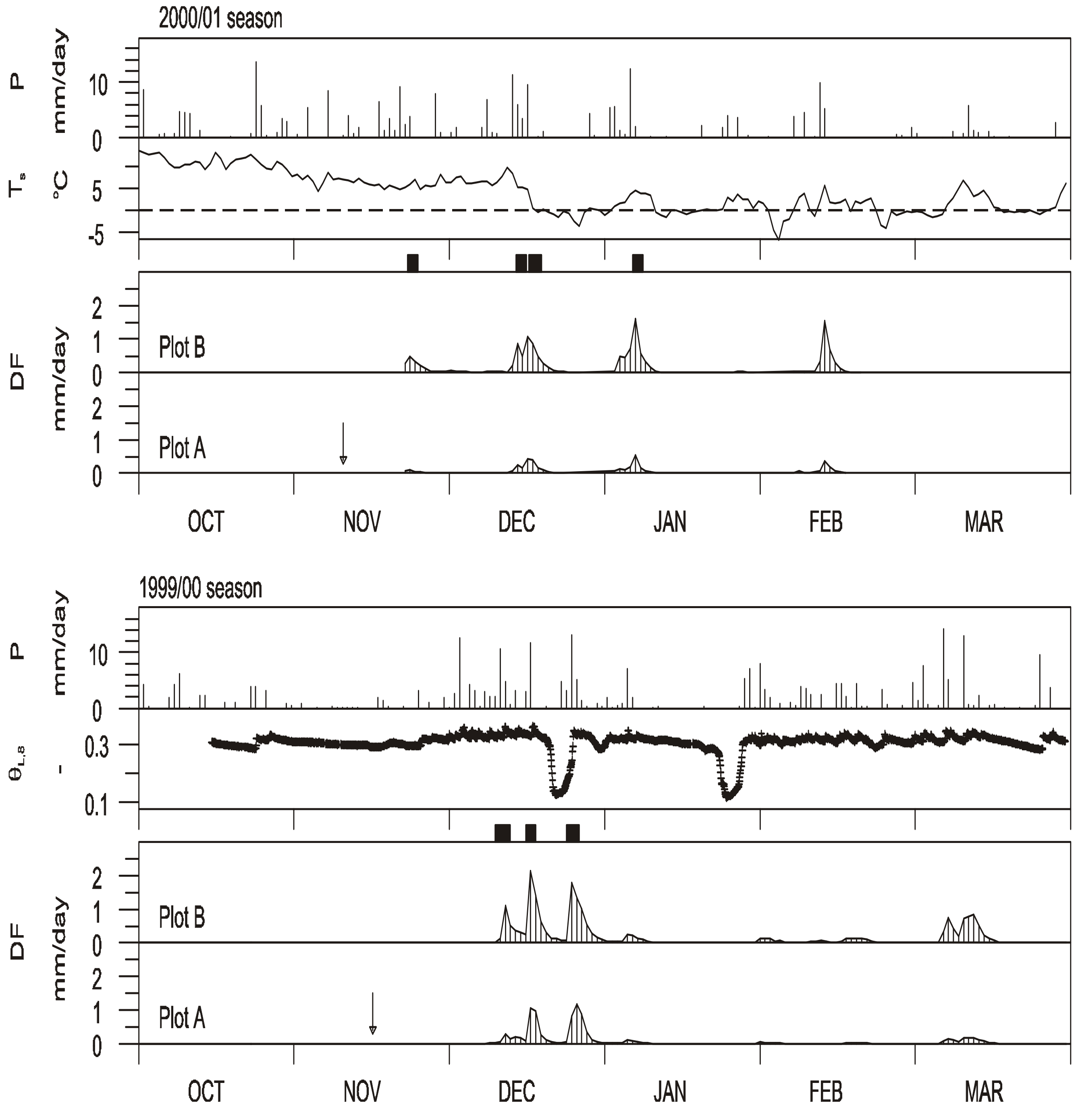

Figure 3.1. Tile drainage flow (DF) and precipitation (P) on a daily basis during both seasons. Daily average liquid water content at 8 cm depth in plot A (θ_{L},8) in 1999/00 season and average soil temperature at 1 cm depth in plot A (T_S, 2000/01 season). Arrows indicate application dates for the herbicides; black columns indicate periods offered special attention in Figs. 3.2 and 3.3.
Figur 3.1. dagsværdier for drænflow (DF) og regn (P) for begge sæsoner. daglige værdier for vandindhold ved 8 cm dybde i plot A (θ_{L},8) i 1999/00-sæsonen og gennemsnitlig temperatur i jorden ved 1 cm dybde i plot a (T_S, 2000/01 season). pile indikerer anvendelsesdage for herbicider; sorte søjler indikerer perioder som vises mere detaljeret i figur 3.2 og 3.3.

The cumulative rainfall from Pendimethalin application until the sampling of peak concentrations in the first drain flow event was about 48 mm.

During all three events and for both plots, peak values for C_P occurred before peak values for the drain flow rates (Fig. 3.2). The peak C_P values were all observed during rain events. During the first two events, peak concentrations

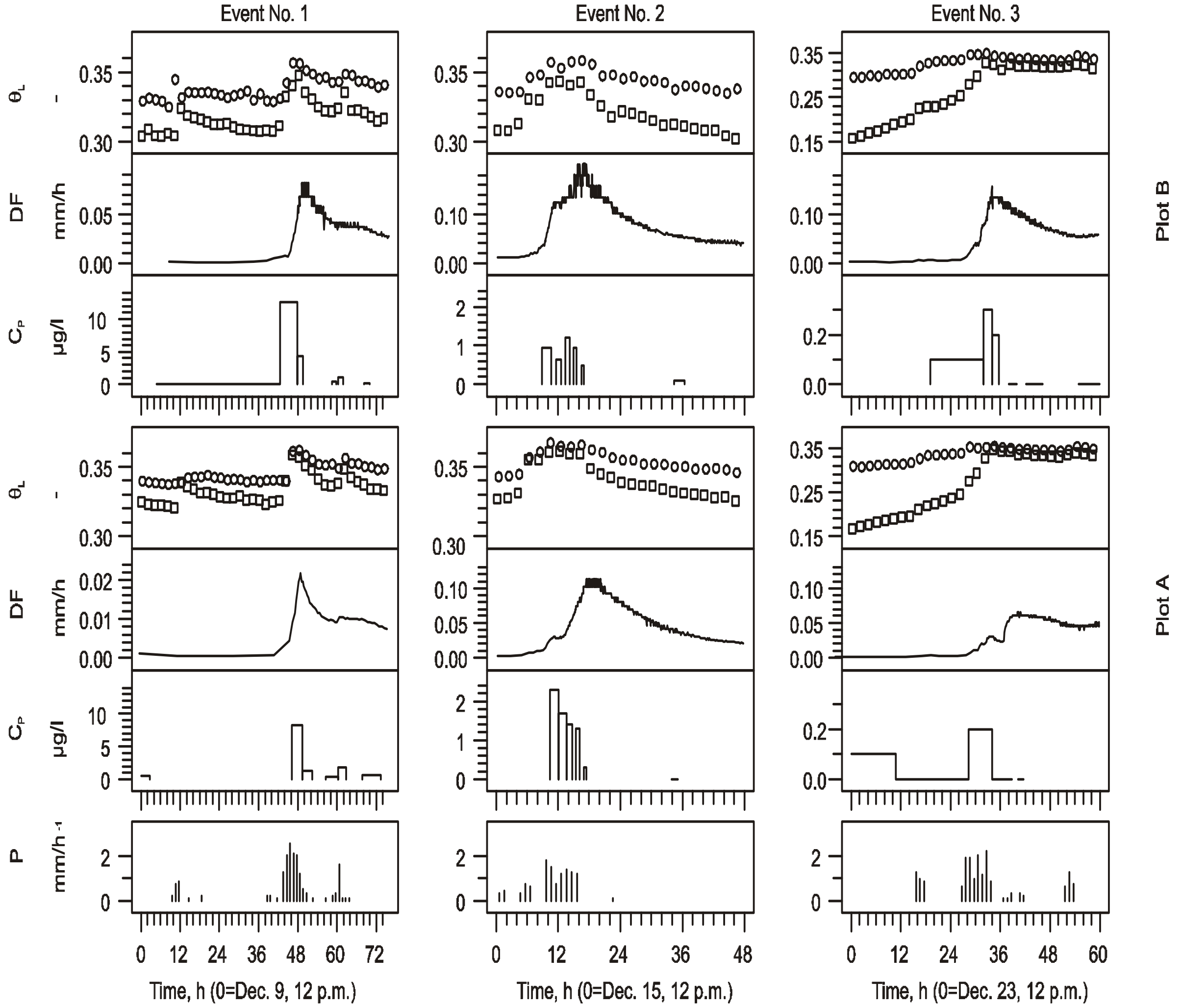

Figure 3.2. Precipitation (P), Pendimethalin concentration (C_P), tile drainage flow (DF), and liquid water content (θ_L) at 8 and 16 cm depth versus time in the two plots (plot A bottom and plot B top) during three runoff events in 1999/00.
Figur 3.2. regn (P), Pendimethalin koncentration (C_P), drænflow (DF) og vandindhold (θ_L) ved 8 og 16 cm dybde plottet mod tiden for de to plots (plot A nederst og plot B øverst) for tre drænflow-hændelser i 1999/00.

coincided with large peak values for soil moisture content at 8 and 16 cm depth. The third event occurred right after or during a break of frost situation as shown by increasing θ_L-values at 8 cm depth from values considerably below field capacity. The observed peak C_P values decreased with event number. No or very little Pendimethalin was detected in drain water sampled after December 25 1999.

3.2.2 Pendimethalin and Ioxynil, 2000/01 season

Seventy-five percent of the total loss of Pendimethalin with drain water, and sixty percent of the loss of Ioxynil, occurred during the four events that are shown on Figure 3.3 (defined successively as event No's. 1-4). As during the 1999/00 season, C_p varied considerably between and within events. Peak C_p-values decreased with event number from the second event. Generally, peak C_p-values were observed during rain events and before peak values for drain flow (Fig. 3.3). While the variation in drain flow was fairly well synchronized between the two plots, peak values for Ioxynil concentration (C_i) did not

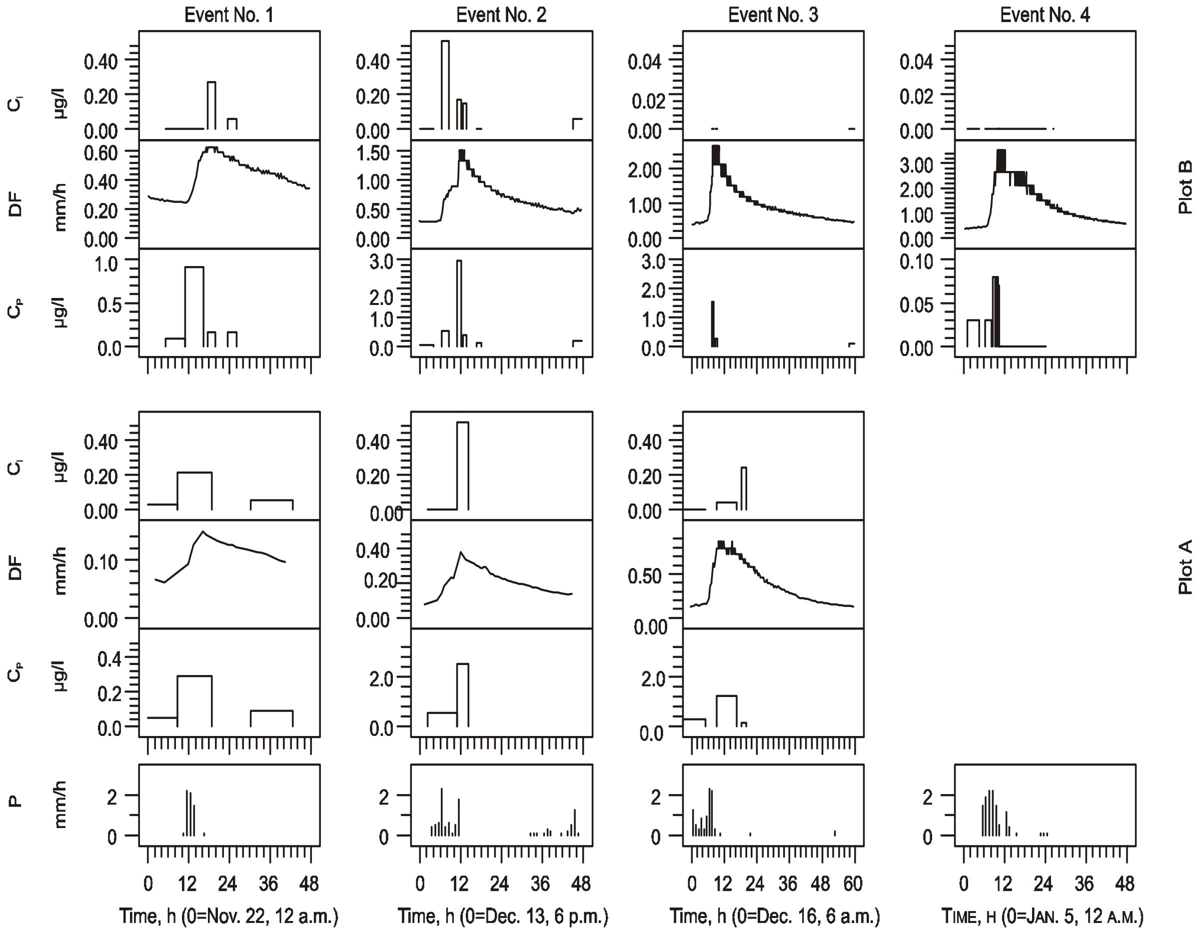

Figure 3.3. Precipitation (P), Pendimethalin concentration (Cp), tile drainage flow (DF), and Ioxynil concentration (C_I) versus time during four runoff events in 2000/01 (plot A bottom, plot B top). No herbicide analyses were performed for plot A during event No. 4.
Figur 3.3. regn (P), Pendimethalin koncentration (C_P), drænflow (DF) og ioxynil koncentration (C_I) plottet mod tiden for de to plots (plot A nederst og plot B øverst). Ingen herbicid-analyser udført for plot A for hændelse nr. 4.

generally occur in the same samples or at the same time as peak values for C_p. No detectable amounts of Ioxynil were found after December 17, 2000 in any of the plots, except from one value just above the detection limit (C_i=0.04 µg l^{-1}) measured in a sample from plot A on February 12 , 2001. Pendimethalin was observed in five samples (up to C_p = 0.18 µg l^{-1}), on February 8, 11, and 13 in 2001 (see appendix A) in connection to heavy rainfall (3,7 mm/d on Feb. 7; 4,5 mm/d on Feb. 9; 9,9 mm/d on Feb. 12; and 5,5 mm/d on Feb. 13).

3.3 Herbicide concentrations and turbidity

Pendimethalin concentration (C_p) was linearly and positively related with turbidity (T) during all the seven drain flow events defined by Figs. 3.2 and 3.3. A summary of the correlations is shown in Table 3.2. An example correlation from the first event of first season, is shown in Figure 3.4.

The coefficients of determination (r^2) for the least squares relationships varies listed in Table 3.2 varies between 0.45 and 0.98. Within each season, r^2 tended to decrease with event number. During the 1999/00 season, the slopes were significantly larger for the first two events than for the third event ($P<0.05$). During the 2000/01 season, the slopes were significantly larger for the first two events than for the last events ($P<0.05$). There were no significant intercepts, except for event No. 1 in 2000/01 (intercept=0.11 µg l^{-1}, cf. Table 3.2). Similar linear relationships between Ioxynil concentration and turbidity could not be established.

TABLE 3.2. PARAMETERS DESCRIBING LINEAR RELATIONSHIPS BETWEEN TURBIDITY (IN NTU) AND HERBICIDE CONCENTRATIONS (PENDIMETHALIN: C_P OR IOXYNIL: C_I), AND BETWEEN TURBIDITY AND CONCENTRATION OF SOIL PARTICLES (C_S): $C = \alpha.\ NTU+ \beta$. N=NUMBER OF OBSERVATIONS, r^2=COEFFICIENT OF DETERMINATION.
TABEL 3.2. BESKRIVELSE AF LINEÆR RELATION MELLEM TURBIDITET (I NTU) OG HERBICID KONCENTRATIONER (PENDIMETHALIN: C_P OG IOXYNIL: C_I), OG MELLEM TURBIDITET OG KONCENTRATION AF JORD-PARTIKLER (C_S): $C = \alpha.\ NTU+ \beta$. N=ANTAL OBSERVATIONER, r^2=KORRELATIONSKOEFFICIENT.

Pesticide – Turbidity							
Dependent variable	Season	Event No.	Concentration range, µg l^{-1}	n	r^2	$\alpha^{\dagger}$ 10^{-2} µg l^{-1} NTU^{-1}	$\beta^{\dagger}$ 10^{-2} µg/l
Pendi-methalin, C_p	1999/00	1	0.00-12.6	12	0.94	3.2 (0.3) ***	-3 (38) ^{ns}
		2	0.00-2.3	12	0.62	1.9 (0.5) **	-13 (29) ^{ns}
		3	0.00-0.30	11	0.45	0.19 (0.07) *	0 (4) ^{ns}
	2000/01	1	0.05-0.91	7	0.98	0.74 (0.05) ***	11 (3) *
		2	0.05-3.0	8	0.91	0.74 (0.10) ***	-9 (19) ^{ns}
		3	0.09-1.5	6	0.74	0.27 (0.08) *	20 (18) ^{ns}
		4	0.00-0.08	6	0.78	0.06 (0.02) *	1 (1) ^{ns}
Ioxynil, C_i	2000/01	1	0.00-0.27	7	0.13	-0.09 (0.13) ^{ns}	10 (6) ^{ns}
		2	0.00-0.51	8	0.30	0.08 (0.05) ^{ns}	7 (10) ^{ns}
		3	0.00-0.24	6	0.10	-0.02 (0.02) ^{ns}	7 (5) ^{ns}
		4	0.00-0.00	6	-	0.00 (0.00)	0 (0)
Particle concentration – turbidity							
Dependent variable			Concentration range, mg l^{-1}	n	r^2	$\alpha^{\dagger}$ mg l^{-1} NTU^{-1}	$\beta^{\dagger}$ mg l^{-1}
Particle conc., C_s			0-685	77	0.95	0.87 (0.02) ***	-3.3 (3.3) ^{ns}

†: Standard errors in (). Suffix shows the result of t-test for the hypothesis: parameter=0. ns: non significant; *, ** or ***: significant at the 95, 99 or 99.9 % level.

Turbidity generally peaked in the beginning of each new drain flow event and generally showed considerable tailing (example shown in Figure 3.5a). Very turbid drain water ($T > 50$ NTU) in one or more consecutive samples from one or both plots appeared in 6 events during the 1999/00 season and in 7 events during the 2000/01 season, see Table 3.3.

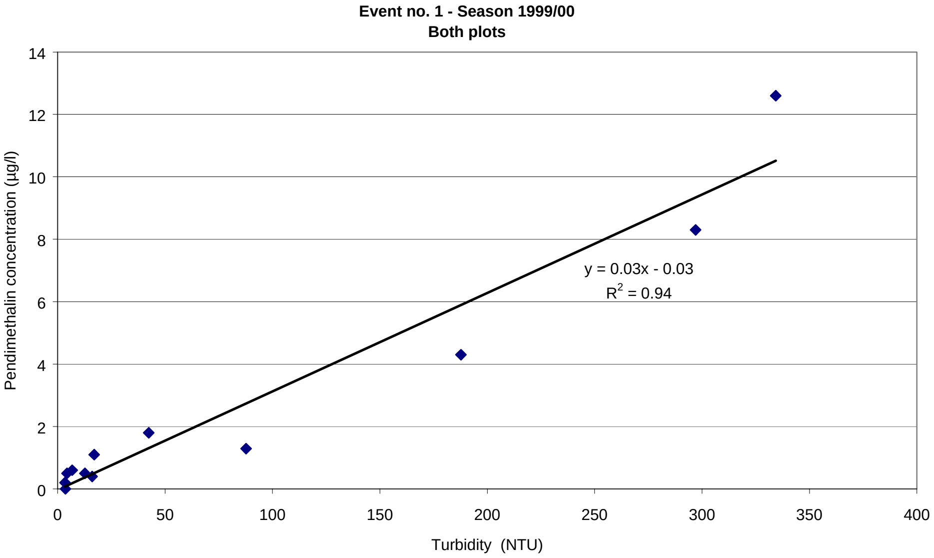

FIGURE. 3.4. EXAMPLE OF CORRELATION BETWEEN TUBIDITY AND PENDIMETHALIN CONCENTRATION IN DRAIN WATER SAMPLES. DATA ARE FROM BOTH PLOT A AND B FROM EVENT NO. 1 OF THE FIRST SEASON, 1999/00.
FIGUR. 3.4. EKSEMPEL PÅ KORRELATION MELLEM TURBIDITET OG PENDIMETHALIN KONCENTRATION I DRÆNVANDSPRØVER. DATA FRA PLOT A OG B FRA DEN FØRSTE DRÆNFLOW-HÆNDELSE I DEN FØRSTE SÆSON 1999/00.

TABLE 3.3. SOME CHARACTERISTICS FOR DRAIN FLOW EVENTS WITH VERY TURBID DRAIN WATER (TURBIDITY > 50 NTU IN ONE OR MORE CONSECUTIVE SAMPLES FROM ONE OR BOTH PLOTS). LIQUID SOIL WATER CONTENT WHEN SAMPLING THE PEAK TURBIDITY (θ_L), AND PRECIPITATION DURING THE LAST 8 HOURS BEFORE SAMPLING THE PEAK TURBIDITY (P_8). MEAN VALUES WITH STANDARD DEVIATIONS IN ().
TABEL 3.3. KARAKTERISTIKA FOR DRÆNFLOW-HÆNDELSER MED HØJ TURBIDITET (TURBIDITET > 50 NTU I EN ELLER FLERE PÅ HINANDEN FØLGENDE PRØVER FRA ET ELLER BEGGE PLOT). VANDINDHOLD PÅ TIDSPUNKT FOR UDTAGELSE AF PRØVE MED MAX.-TUBIDITET (θ_L) OG REGN GENNEM DE SIDSTE 8 TIMER FOR PRØVETAGNINGEN AF SAMME (P_8). MIDDELVÆRDIER MED STANDARDAFVIGELSER I ().

	1999/00 season	2000/01 season
Frost indications[†]	No	-
Number of events	6	7
θ_L [‡] ,% (v/v)		
8 cm depth	35.4 (0.8)	-
16 cm depth	33.3 (1.8)	-
P_8, mm	8.2 (2.1)	6.4 (3.0)

[†] θ_L at least 5 % (v/v) less than estimated field capacity in Table 2.1 at one or both depths when sampling the peak turbidity.
[‡] θ_L was not determined during the 2000/01 season.

During the 1999/00 season, the occurrence of the large peak values (peak T > 50 NTU) always coincided with very large θ_L-values in the plow layer, θ_L at each depth and plot being 3-7% (v/v) larger than the estimated field capacity, generally (Tables 3.3 and 2.1). During the 1998/99 season, the large peak T values either coincided with such very large θ_L values (8 events), or with θ_L-values at 8 or 16 cm being clearly lower (at least 5 % v/v) than the estimated field capacities indicating a partly frozen soil. The only two peak T values larger than 1000 NTU were both observed in break of frost situations (data not shown). In all events without frost indications, considerable amounts of precipitation occurred during the last 8 hours before sampling the peak turbidity (Table 3.3). For the break of frost events, the cumulative 8 hours precipitation preceding the large peak T values tended to be somewhat smaller and more variable.

The peak turbidity was generally observed before the peak drain flow rate. In general, turbidity was negatively related to the drain flow rate, i.e. very large turbidity values only occurred at small drain flow rates (Fig. 3.5b).

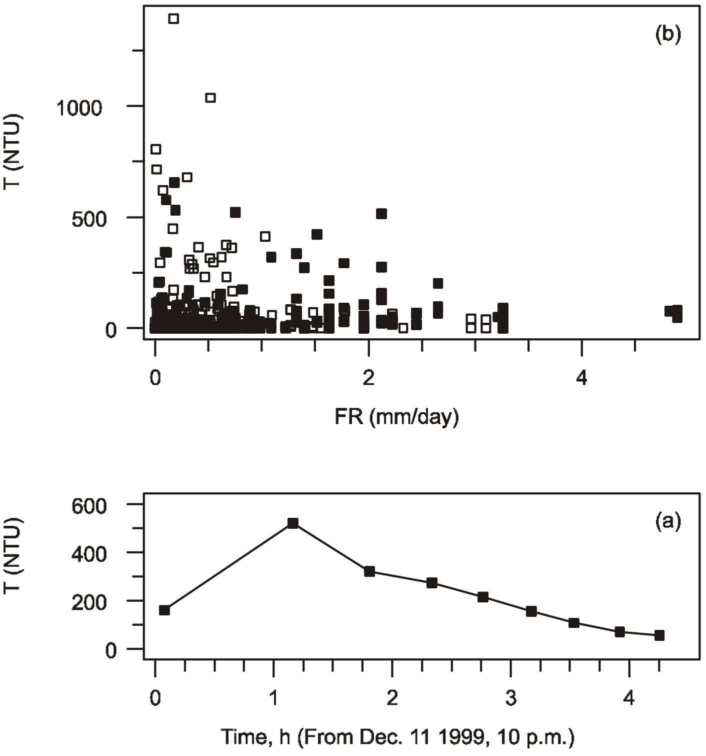

Figure 3.5. (a): Turbidity (T) versus time measured in plot B during 4 hours from December 11 1999 at 10.00 p.m., and (b): Turbidity (T) versus tile drainage flow at the time of sampling (FR). Data for all turbidity measurements performed in plot A () and B (+) during seasons 1998/99, 1999/00, and 2000/01.
Figur 3.5. (a): Turbiditet (T) versus tid målt for plot B over 4 timer fra 11. December,1999 kl. 22.00, og (b): Turbiditet (T) versus drænflow på måletidspunktet (FR). Data for alle turbiditetsmålinger udført i plot A () og B (+) over sæsonerne 1998/99, 1999/00 og 2000/01.

The concentration of soil particles in the drain water as determined by centrifugation (C_s) correlated linearly with T for turbidity levels up to 700 NTU, covering practically all the turbidity observations (r^2=0.95, Table 3.2). The least squares relationship showed a small non-significant intercept (C_s = -3.3 mg l^{-1}) indicating some turbidity in samples where sediments were not produced by the applied centrifugation procedure. Turbidity measurements performed on randomly selected drain water samples without visible indications of suspended matter (representing the major part of the drain flow) showed an average of 2.1 NTU and a standard deviation of 1.3 NTU. A T-value of 2.1 NTU put into the least squares relationship between T and C_s (Table 3.2) would produce a negative C_s value. Thus, it was assumed that samples without visible indications of suspended matter would not produce sediments by centrifugation (C_s=0 mg l^{-1}).The concentrations of soil particles (C_s) were estimated from measured T values using the relationship between T and C_s in Table 3.2 (data not shown). A few negative C_s values produced by following this procedure were converted to zero.

3.4 Fractionation of Pendimethalin

All water samples were filtered through a 0,7 µm glass filter and both the filtrate and the residue on the filter were analysed. This was done to examine the distribution of pesticide in the fractions separated by the 0,7 µm filter.

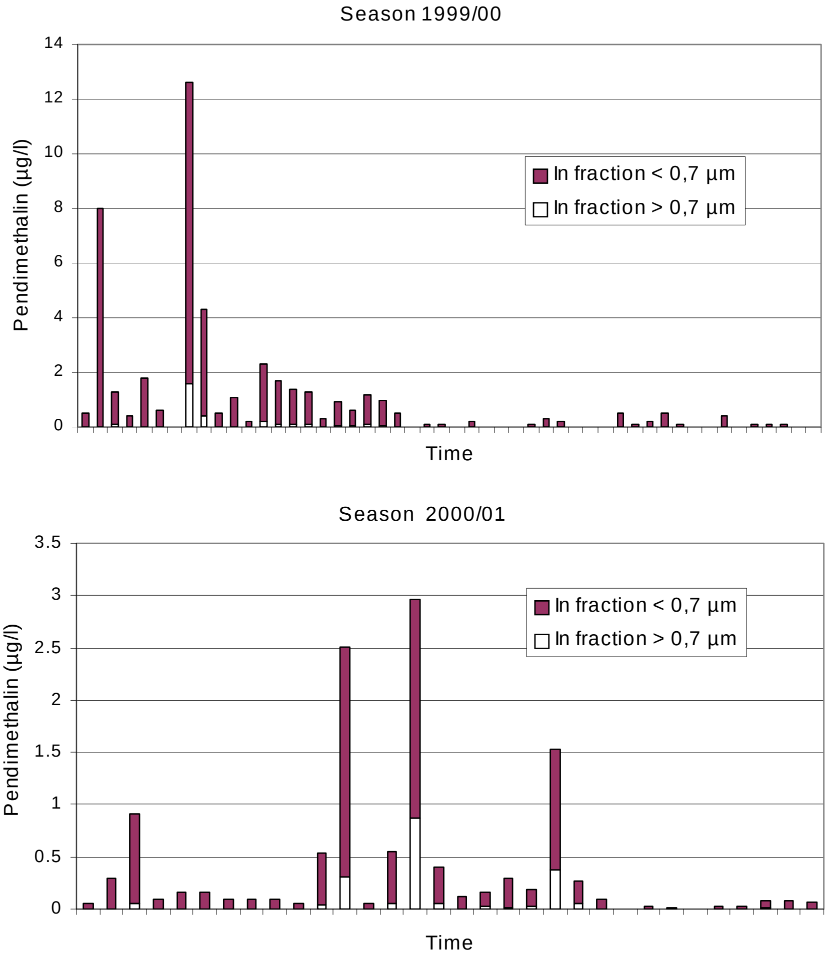

FIGURE 3.6. THE FRACTIONATION OF PENDIMETHALIN BETWEEN SOLID PHASE (FRACTION > 0,7 µm, WHITE) AND AQUEOUS PHASE (FRACTION < 0,7 µm, DARK BROWN) FOR BOTH SEASONS. EACH BAR REPRESENTS ONE SAMPLE.

FIGUR 3.6. FRACTIONERING AF PENDIMETHALIN MELLEM FAST FASE (FRAKTION > 0,7 µm, HVID) OG VANDIG FASE (FRAKTION < 0,7 µm, MØRKEBRUN) FOR BEGGE SÆSONER. HVER KOLONNE REPRÆSENTERER EN PRØVE.

The fractionation above and below 0,7 µm for both seasons and both plots is shown in Figure 3.6.

Far the most of the Pendimethalin in the drain water was found in the filtrate (fraction below 0,7 µm), not in the solid phase on the 0.7 µm filter. In the first season, the percentage of Pendimethalin found in the solid phase on the 0,7 µm filter varied between 0 and 10 %. In the second season this percentage varied between 0 and 30 %. For the 28 samples with the largest C_p-values and clearly detectable amounts in both phases, the ratio of Pendimethalin concentration found in the water phase to that in the solid phase averaged 11 with a standard deviation of 8.

For Ioxynil the detection limit of 0,03 µg/l was never exceeded in the solid phase, thus all Ioxynil was found in the filtrate.

Based on the low findings of particle-associated Pendimethalin in the first season, it was speculated whether the cut-off value of 0,7 µm was possibly to high. Therefore, the water samples from the second season were filtered through both the 0,7 µm filter and a 0,2 µm Polysep filter. However, because of laboratory error, the results from the filtration of Pendimethalin could not be used, since it turned out that the filter actively adsorbed Pendimethalin. For Ioxynil, again the detection limit was not exceeded in the solid phase from the 0,2 µm filter.

One single five liter sample was taken out on December 18, 2000. Following the unsuccessful filtration through the 0,2 µm filter, a procedure of combined filtration and centrifugation was followed (illustrated in Figure 3.7) to determine the distribution between solid and aqueous phase. Centrifugation was performed for 30 minutes at 5000 rpm. corresponding to 4100 times g-force. This should essentially remove all particles from solution. The results of the different analyses are presented in Figure 3.7. The figure shows that the estimated total concentration in the original sample is 1,20 – 1,23 µg/l and that 20 % of the Pendimethalin is in the fraction above 0,7 µm, whereas virtually no Pendimethalin is removed through centrifugation. The figure also shows the problem of Pendimethalin adsorption to the Polysep 0,2 µm filter.

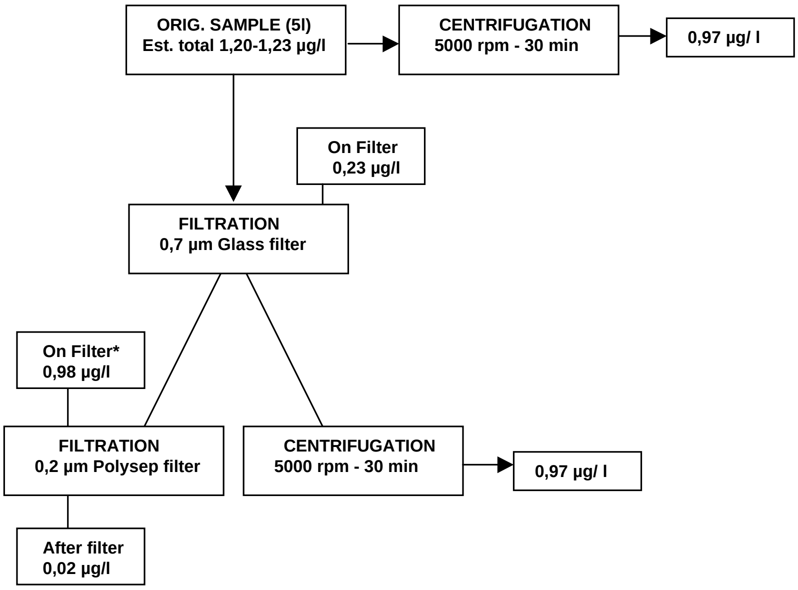

Figure 3.7. Results from analysing filterred and centrifuged samples from 5 liter drain water sample. The estimate on total contents of the original sample is based on contents found in the other analyses. *: Polysep filter adsorbs Pendimethalin; hence this result is not valid.
Figur 3.7. resultater fra analyser af filtrerede og centrifugerede prøver fra 5-liters drænvandsprøve. estimatet på totalindholdet er baseret på indholdet i de øvrige prøver.*: Polysep filter adsorberer Pendimethalin; derfor er resultatet ukorrekt.

3.5 Cumulative losses

In general, there was little detectable herbicide in drainage outflow sampled after December in both seasons. Almost all the herbicide mass losses to drainage occurred in short time intervals during the first 1-2 months after application, whenever there was a large enough rainfall to generate drain flow (Figure 3.8). The total loss of Pendimethalin with drainage was larger for the 1999/00 season than for the 2000/01 season (Table 3.4). The relative amount of herbicide lost with drainage water during the 2000/01 season for Ioxynil was about twice that of Pendimethalin.

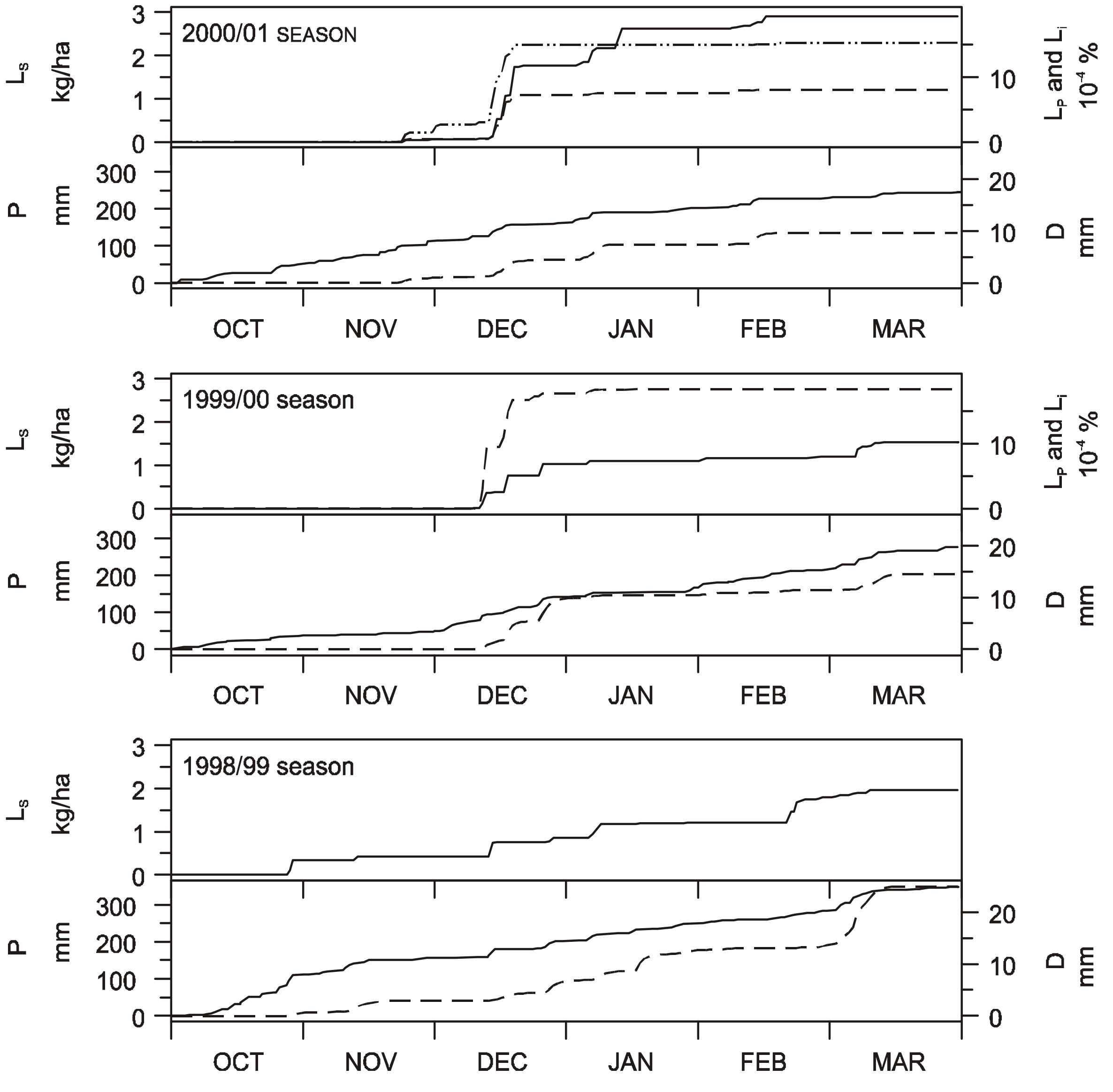

Figure 3.8. Cumulative losses of soil particles (L_S: solid lines), Pendimethalin (L_P: dashed lines), and Ioxynil (L_I: dashed and dotted line) with drain flow relative to the applied amount and averaged for the two plots. Cumulative precipitation (P: solid lines) and cumulative drainage (D: dashed lines) averaged for the two plots.

Figur 3.8 akkumulerede tab af jordpartikler (L_S: solid lines), Pendimethalin (L_P: stiplet linie) og Ioxynil (L_I: stiplet og prikket linie) med drænflowow relativt til den anvendte mængde og midlet for de to plots. Akkumuleret regn (P: fuldt optrukket linie) og akkumuleret drænvandsmængde (D: stiplet linie) midlet for de to plots.

TABLE 3.4. TOTAL LOSS OF PENDIMETHALIN (L_P), IOXYNIL (L_I), AND SOIL PARTICLES (L_S) WITH DRAINAGE FROM THE TWO PLOTS. AMOUNTS ARE ESTIMATED BY INTEGRATING MEASURED OR ESTIMATED CONCENTRATIONS OVER THE MEASURED DRAIN WATER DISCHARGE PERIOD. ESTIMATED CONCENTRATIONS WERE AVERAGED BETWEEN THE PRECEDING AND THE SUCCEEDING MEASUREMENTS DURING PERIOD WITH DRAIN FLOW BUT WITHOUT SAMPLE ANALYSES.
TABEL 3.4. TOTALT TAB AF PENDIMETHALIN (L_P), IOXYNIL (L_I) OG JORDPARTIKLER (L_S) MED DRÆNVAND FRA DE TO PLOTS. MÆNGDER ER ESTIMERET VED AT INTEGRERE MÅLTE ELLER ESTIMEREDE KONCENTRATIONER OVER DEN MÅLTE DRÆNFLOW-PERIODE. ESTIMEREDE KONCENTRATIONER BLEV MIDLET MELLEM DEN FOREGÅENDE OG DEN FØLGENDE MÅLING UNDER PERIODER MED DRÆNFLOW, MEN UDEN DRÆNVANDSANALYSER.

	Season	Plot		Average
		A	B	
L_s, kg/ha	1999/00	1.1	2.0	1.5
	2000/01	1.5	4.3	2.9
L_p, % of applied	1999/00	0.0010	0.0027	0.0018
	2000/01	0.0007	0.0009	0.0008
L_i, % of applied	2000/01	0.0014	0.0016	0.0015

The losses of soil particles occurred during short time intervals throughout the seasons (Fig. 3.8). In general, the correspondence between cumulative drainage line flow and loss of soil particles was poor. The seasonal losses of soil particles with drainage varied between 0.9 and 4.3 kg ha^{-1}. On average for the two plots and three seasons (including 1998/99), 2.1 kg ha^{-1} year^{-1} of soil particles was lost with drain water. Eighty-one percent of the amount of Pendimethalin found in the soil right after application on November 16 1999 was still present in the soil (0-35 cm depth) on February 24, 2000. No detectable amounts of Pendimethalin was found in the soil before application in 1999.

3.6 Investigation of fractionation in model areas

To further investigate the fractionation of pesticides between dissolved and particle associated states supplementary drain water samples were taken from the two model areas. From one drain in each model area two samples were taken during the same rain event. The samples were centrifuged in the same manner as previously (5000 rpm for 30 minutes) and both the supernatant and the centrifuged solid phase were analysed for a suite of 31 pesticides, including Pendimethalin. In fact, the only pesticide found in the samples was Pendimethalin and the results for that compound are given in Table 3.5.

The analysis showed that between 36 and 66 % of the Pendimethalin was in a particle-associated state. This compares to approximately 20 % in the particle-associated state found for the five liter centrifuged sample from Rørrendegaard shown in Figure 3.7, and to 0-30 % for the 0,7 µm filtered samples from the two sampling seasons at Rørrendegard shown in Figure 3.6.

Table 3.5 Results for fractionation of Pendimethalin in drain water samples from model areas. Samples were analysed before centrifuging and after centrifuging at 5000 rpm (4100 times g-force) for 30 minutes. Pendimethalin was the only pesticide of 31 included in the analysis that was found in concentrations above detection limit.
Tabel 3.5. Resultater for fraktionering af Pendimethalin i drænvandsprøver fra model-oplande. Prøver blev analyseret før og efter centrifugering ved 5000 omdrejninger per minut (4100 gange tyngdekraften) i 30 minutter. Pendimethalin var det eneste pesticid af 31 inkluderet i analysen, som blev fundet i koncentrationer over detektionsgrænsen.

Conc. in µg/l	Lillebæk – Drain 2 October 1, 2001		Odderbæk – Main drain – St. 51 November 11, 2001	
	Sample 1	Sample 2	Sample 1	Sample 2
Total content	< 0,026	0,09	0,063	0,083
After centrifuge	< 0,026	0,03	0,034	0,053
Percentage in solid fraction	-	66	46	36

3.7 Sorption of Pendimethalin

The sorption of Pendimethalin to different soil fractions was investigated in order to better be able to understand what controls the sorption. It was hypothesised that clay minerals would have larger sorption capacity (see e.g. Ghadiri and Rose (1991a+b)) and that possibly surface-oxides and hydroxides might also contribute to increasing sorption capacity. Fractions of clay and silt were sieved; one fraction of fine clay was DCB-extracted to remove Fe- and Mn-oxides. Refractory soil organic matter samples from the plow layer at Rørrendegaard were prepared. One refractory soil organic matter sample from a different site (in Northern Jutland) was also included in the experiment. The sorption experiments were performed with radioactively marked Pendimethalin and only the equilibrium state was investigated. Results are shown in Table 3.6.

Table 3.6. Equilibrium sorption-coefficient values for different fraction of soil from the test site Rørrendegård. One refractory soil organic matter sample from a different site (in Northern Jutland) included.
Tabel 3.6. Ligevægts-sorptions-koefficienter for forskellige fraktioner af jord fra test-faciliteten Rørrendegaard. Én prøve af svært nedbrydeligt organisk stof fra jorden fra en anden feltlokalitet (i Nordjylland) inkluderet.

Fraction	Organic C content %	Average K_d-value (l/kg)	Stdv. (no. of samples) (l/kg)
Top soil (5–10 cm); < 2 mm	1,20	268	11 (n=3)
Silt; 2-20 µm	2,95	668	50 (n=3)
Course clay; 0,2-2 µm	4,27	607	33 (n=3)
Fine clay; < 0,2 µm	4,28	476	24 (n=3)
Fine clay – DCB extracted < 0,2 µm	4,28	484	27 (n=3)
Refractory soil org. matter – HCl and HF treated. From plow layer.	47,3	14182	390 (n=3)
Refractory soil org. matter – HCl and HF treated. From plow layer.	54,1	18098	323 (n=2)
Refractory soil org. matter – HCl and HF treated. From plow layer. (Northern Jutland)	59-61	20771	879 (n= 3)

Results show that the high organic carbon content fractions have sorption coefficients that are around 60 times higher than that of the original top soil, indicating that soil organic carbon is the primary factor in determining the sorption capacity of the soil. The K_{oc}- values deducted from the measured K_d-values and the relation $K_d=f_{oc}\cdot K_{oc}$ range from 11.000 for the fine clay to

30.000 for the soil organic matter samples. The estimated value for K_{oc} for the top soil (22.000) is slightly above the range given in Table 2.2.

Results also show that the pure clay fractions have a larger sorption capacity than the original soil (a factor 2.5), and that the DCB treatment does not influence the sorption capacity of the clay, meaning that the hypothesis of prevalent oxide-sorption was not proven by the experiment.

4 Modelling of experiments

4.1 Application of MIKE SHE with colloid module to data from Rørrendegaard

The colloid and colloid-facilitated transport module developed for MIKE SHE in this study was applied to the field experiments at Rørrendegaard to further investigate the possible importance of colloid-facilitated transport of Pendimethalin.

The technical documentation for the new module can be found in Styczen et al. (2002). A sensitivity analysis on some of the parameters in the module is given in Appendix C of this report.

4.2 Flow setup and calibration

Firstly, the model was calibrated to the flow conditions at plot B on Rørrendegaard. There were no measurements to support a spatial division of the plot into more than one single homogeneous area. Hence, to simplify and speed up calculations, the whole area of plot B was represented by one single column with a drainage line at a depth of 1.1 meter and a neighbouring constant head cell to let some of the infiltrating water escape as it would under natural conditions. The soil column was divided into 3 compartments with characteristics corresponding to Table 2.1 (see also Figure 4.1):

TYPE 1 : 0 - 15 cm : Characteristics as 0-15 cm in Table 2.1
TYPE 2 : 15 - 35 cm : Characteristics as 30-40 cm in Table 2.1
TYPE 3 : 35 - 110 cm : Characteristics as 60-80 cm in Table 2.1

In the calibration, the timing of the events and the level of drain flow were the main objectives, since these would be imperative in the comparison with the obtained particle and pesticide concentrations in the drain flow. Because of variation in groundwater table, topography, and depth to the tile drain at the field site, there could be variations in what parts of the drain that contributed to the drain flow. Consequently, the observed drain flow in ***mm/day*** (converted from ***volume/day*** by division by the full plot area upstream of the sampling well) could underestimate the drain flow in the parts of the drain where it actually occurred, making matching of the modelled drain flow to observed drain flow more difficult.

Retention curve characteristics and hydraulic conductivity were calculated from the soil characteristics in Table 2.1 using the Hypress solution scheme (Wösten et al., 1998). Subsequently, the retention curve characteristics were adjusted slightly, so that the initial situation was approximately a no-flow situation.

Rainfall series with discretisation of 0.1 mm and daily potential evaporation series were obtained from the site and used in the simulations. Time series for

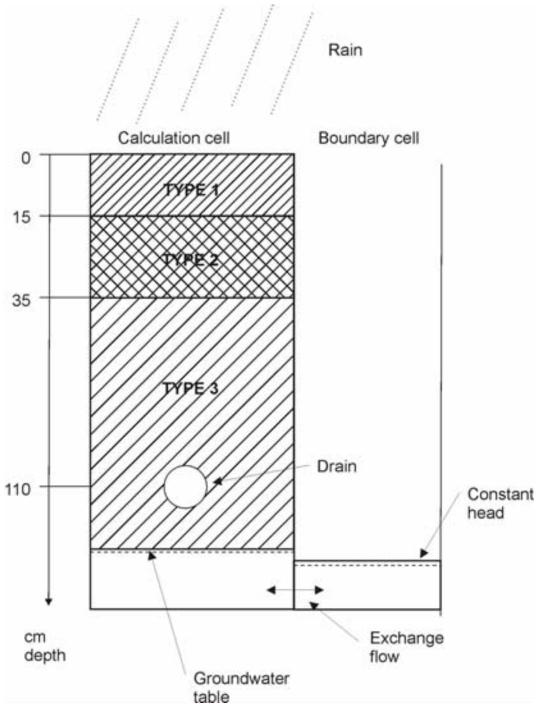

FIGURE 4.1. SKETCH OF FLOW SETUP. CALCULATION COLUMN NEXT TO A CONSTANT HEAD COLUMN. REGULATION OF THE CONSTANT HEAD WILL REGULATE WATER LEVEL IN CALCULATION CELL AND THEREBY IMITATE THE GROUNDWATER FLOW AT THE FIELD SITE.
FIGUR 4.1. SKETCH AF FLOW SETUP. BEREGNINGSKOLONNE VED SIDEN AF EN KOLONNE MED KONSTANT TRYKNIVEAU. REGULERING AF DET KONSTANTE TRYK OG DEN HYDRAULISKE LEDNINGSEVNE REGULERER TRUKNIVEAUET I BEREGNINGSKOLONNEN OG EFTERLIGNER DERMED GRUNDVANDSSTRØMNINGEN PÅ FELTLOKALITETEN.

winter wheat for crop coverage, plant height and interception storage were used in the simulation.

The constant head level of the neighbouring cell was calibrated to fit the onset of the first occurrence of drain flow and the hydraulic conductivity for the exchange of water between these two cells was calibrated to fit later occurrences.

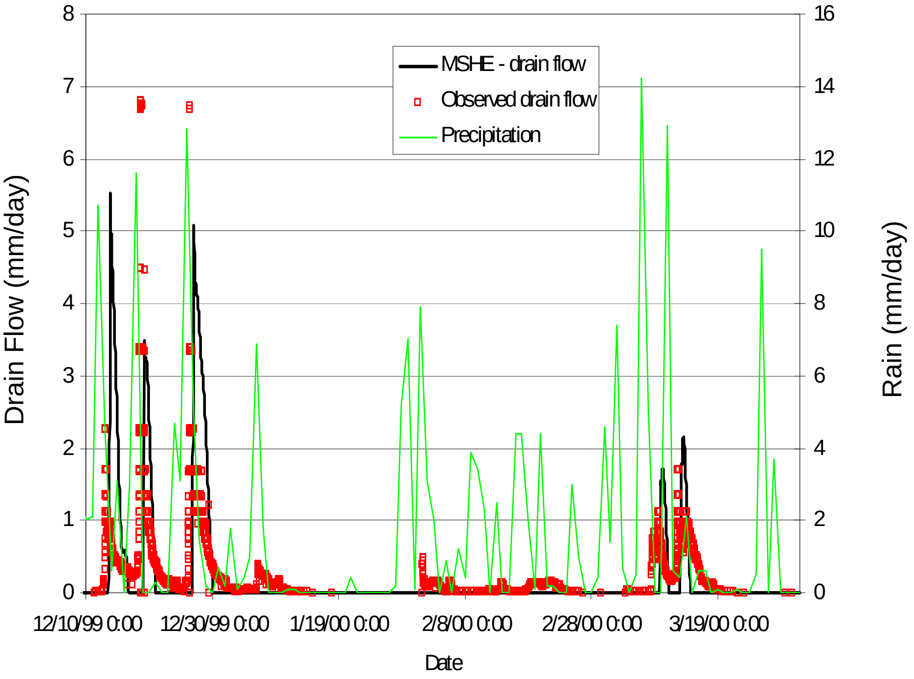

FIGURE 4.2. RAINFALL (RIGHT Y-AXIS), SIMULATED AND OBSERVED DRAIN FLOW (LEFT AXIS).
FIGUR 4.2. REGN (HØJRE Y-AKSE), SIMULERET OG OBSERVERET DRÆNFLOW (VENSTRE Y-AKSE).

The simulated drain flow in Figure 4.2 finds the timing and the drain flow levels fairly well for the five most pronounced events. The smaller drain flow occurrences are not simulated. The simulation in Figure 4.2 uses a macroporosity of 0,01 throughout the unsaturated column.

Results were not very sensitive towards the macropore flow initiation pressure or the hydraulic conductivity of the macropores. The sensitivity towards the macropore porosity is shown in Figure 4.3 below. The simulated drain flow was not very sensitive towards the macropore porosity, but having no macropores in the simulation gave rise to slightly higher peaks on the drain flow events (except one event). For transport simulations, the flow results from the simulation using a macropore porosity of 0,01 was used.

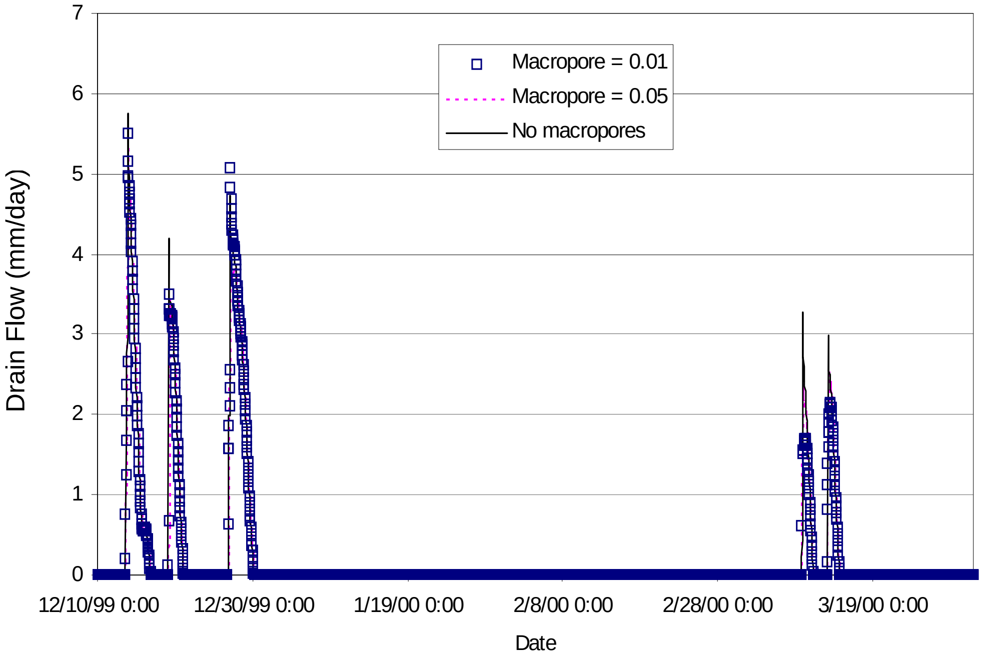

FIGURE 4.3. SENSITIVITY OF SIMULATED DRAIN FLOW ON THE MACROPORE POROSITY.
FIGUR 4.3. DET SIMULEREDE DRÆNFLOWS FØLSOMHED OVERFOR MAKROPORE-PORØSITETEN.

4.3 Calibration and sensitivity analysis of colloid transport

Most of the measurements on particle contents in the drain flow were made during the 98-99 season. However, from the linear relation between turbidity and particle content made from these measurements (see Table 3.2), the particle contents for the 99-00 season were extrapolated from the turbidity measurements of the season. These extrapolated values were used for comparison with the simulated values for colloids to adjust the colloid generation parameters and the filtration coefficients.

The occurrence of colloid breakthrough in the drain pipes was very much event-based, and happened very close in time to heavy rainfall. In the model, event-based breakthrough was obtained by emphasising macropore transport. Macropore transport was emphasised by directing the flow interaction between matrix and macropores to only take place from matrix and into macropores, and not from macropores into the unsaturated matrix (see also Styczen et al. 2002).

The estimated concentration to be compared with the measured value was the concentration in the top calculation layer in the saturated zone. Because of the horizontal discretisation, this entailed dilution of the colloidal concentration before comparison to the measured value. At the same time, it also allowed for filtering of the colloidal particles to take place in the top calculation layer of the saturated zone before comparison. This was not how the transport was thought to happen in reality, where transport of colloidal particles was believed to take place from macropores to the very top of the groundwater table and into the drain pipes, and at least only experiencing a minor dilution and filtering in the saturated zone. This artificial dilution impact was minimised by minimising the vertical extent of the top calculation layer to only extent 10 centimetres below the depth of the drain pipe.

The MACRO description (see Styczen et al., 2002) for generation of colloidal particles was used and the EUROSEM model (Morgan et al., 1998) was used for water depth correction. Macropore distribution was assumed to be the same from the top to the drain depth (macropore porosity of 0,01). The basic parameters used for the simulations are shown in Table 4.1. Variations from the values shown in the table will be indicated in the relevant plots.

TABLE 4.1. BASIC PARAMETERS FOR SIMULATIONS FOR CALIBRATION OF COLLOID TRANSPORT.
TABEL 4.1. BASIS-PARAMETRE FOR SIMULERINGER TIL KALIBRERING AF KOLLOID-TRANSPORT.

Parameter	Value	Unit
e_{ma}, macropore porosity	0,01	-
c_{ma}, saturated hydr. cond. of macropores	1E-3	m/s
n*, hydr. cond. function exponent	2.0	-
β_{mp}, water transfer coeff. matrix-macropores	0	m^{-2}
β_c, diffusion transfer coeff. Matrix-macropores	1E-8	s^{-1}
ψ_t, pressure at macropore flow initiation	-0,1	m
k_d, soil detachability	7E+8	mg/J
k_r, replenishment rate	1E+5	$mg/m^2/s$
z_i, influence depth	0,01	m
M_{max}, max. fraction detachable soil	0,10	-
f_{macro}, filter coeff. Macropores	1E-5	s^{-1}
f_{matrix}, filter coeff. matrix (unsat)	1E-3	s^{-1}
f_{sat}, filter coeff. saturated zone	7.5E-4	s^{-1}

The resulting particle concentrations using the parameters listed in Table 4.1 are compared to the observed ones in Figure 4.4.

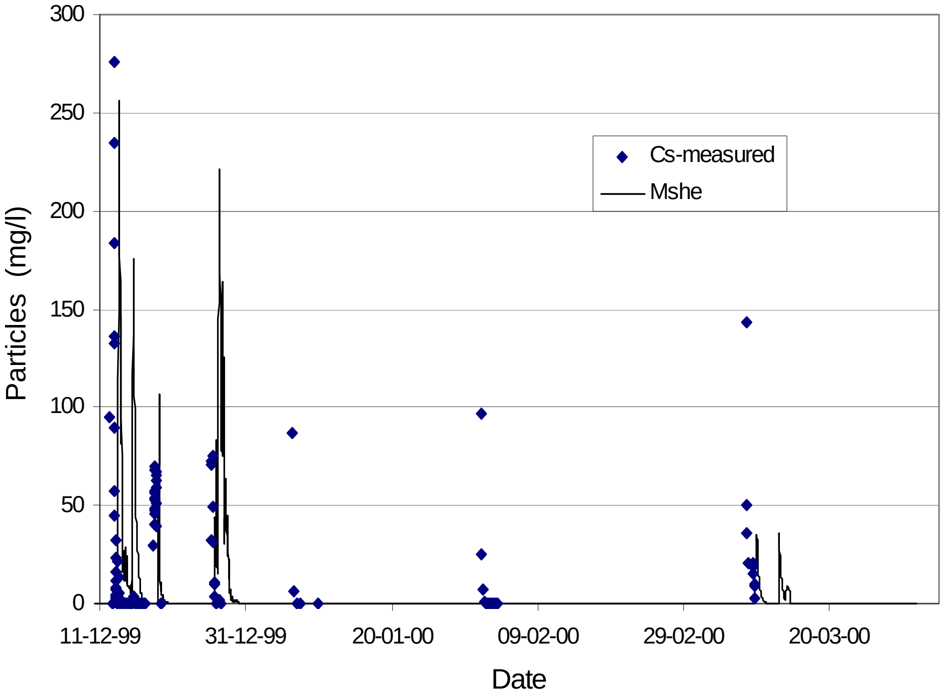

FIGURE 4.4. OBSERVED (EXTRAPOLATED) PARTICLE CONCENTRATIONS IN DRAIN FLOW COMPARED TO SIMULATION RESULTS FOR PARAMETERS LISTED IN TABLE 4.1. THE MODELLED CONCENTRATIONS ARE ONLY SHOWED FOR TIMES WHERE DRAIN FLOW TAKES PLACE IN THE SIMULATIONS.
FIGUR 4.4. OBSERVEREDE (EXTRAPOLEREDE) PARTIKEL-KONCENTRATIONER I DRÆNVANDET SAMMENLIGNET MED SIMULEREDE VÆRDIER FOR PARAMETERVÆRDIERNE LISTET I TABEL 4.1. SIMULEREDE KONCENTRATIONER KUN VIST FOR TIDSPUNKTER HVOR DRÆNFLOW FOREGÅR I SIMULERINGERNE.

The maximum level of the first drain flow event is matched fairly well, whereas the second and third event are overestimated somewhat.

The value of the detachability coefficient k_d (700 kg/J) is higher than the reported values between 8 and 44 kg/J for compacted soils (Morgan et al., 1998). However, the formulation of detachment used here, incorporates the coefficient M_s, which has a maximum value of 0,10 g/g and therefore the detachability coefficient should be reduced accordingly when comparing to other values.

For the simulation shown in Figure 4.4, the total generation of colloidal particles over the season from October till April was $3.8 \cdot 10^5$ kg/m^2, out of which almost all was filtered out from suspension in the top of the unsaturated matrix. A total of 65 kg/m^2 was put in to the macropores and out of these 48 kg/m^2 (70 %) reached the saturated zone. No particles reached the saturated zone through the unsaturated matrix. The amount of particles washed out in the simulation is approximately a factor 10.000 higher than the cumulative leaching of particles to drain flow estimated from measurements of particles contents at the site (see Table 3.4). This discrepancy can be partly explained by the fact that in the simulation all particles leached to the saturated zone, and just those led away by drain flow, are accounted for. For comparison, amounts of soil lost by erosion processes in Denmark are typically on the order of 0,1-25 tons/ha/year (=0,01-2,5 kg/m^2/year) depending on soil types and other conditions. The amount of particles lost through the macropores is a factor of approximately 30 higher than this. Obviously, the generation of particles could be lowered by 30 %, if at the same time filtering in the macropores was set to zero (all particles transported through the macropores would the reach the saturated zone, not only 70 %). However, the combination of parameters combination of parameters listed in Table 4.1 was deemed the most physically plausible in simulating concentration levels comparable the observed ones.

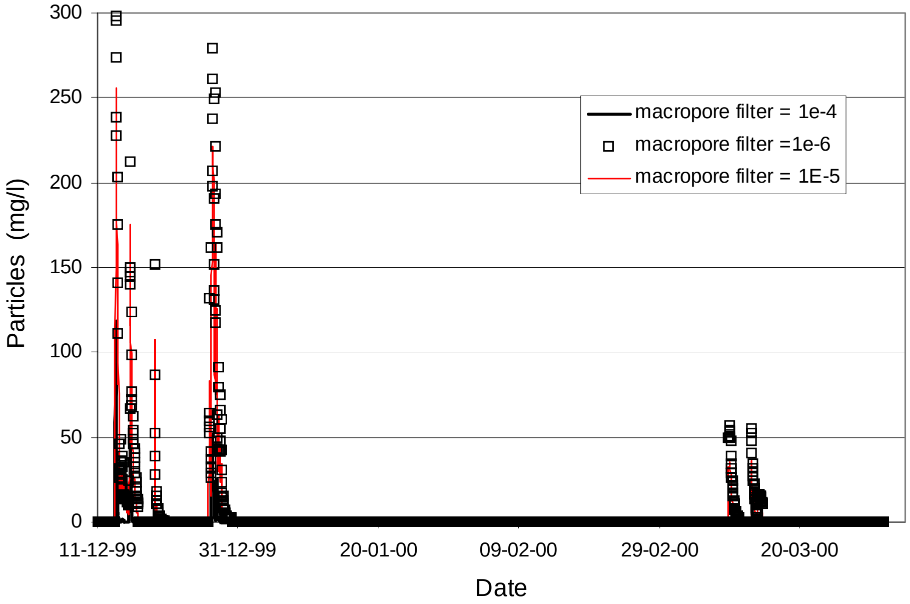

FIGURE 4.5.SENSITIVITY ON MACROPORE FILTER COEFFICIENT FOR PARTICLE CONCENTRATION IN DRAIN FLOW; HIGHER FILTRATION LEADS TO LOWER CONCENTRATIONS.
FIGUR 4.5. PARTIKEL-KONCENTRATIONEN I DRÆNVANDETS FØLSOMHED OVER FOR FILTER-KOEFFICIENTEN I MAKROPORERNE; STØRRE FILTRERING GIVER LAVERE KONCENTRATIONER.

Simulation results were not very sensitive towards the macropore porosity or the diffusion mass transfer coefficient (β_c)(see Styczen et al., 2002). Figure 4.5 shows the sensitivity on the macropore filter coefficient. Results are fairly sensitive towards the filtration coefficient of the macropores, since only the macropores led particles to the saturated zone.

4.4 Calibration of Pendimethalin transport

The next step was the simulation of the observed Pendimethalin concentrations. Pendimethalin was applied in the maximum allowed dose of 2,0 kg/ha, corresponding to 200 mg/m^2. This was used as the initial concentration in the overland compartment of the model.

At first, two simulations not including colloid-facilitated transport were performed; one simulation where Pendimethalin was treated as a conservative tracer (K_d = 0) and one where a K_d-value 100 l/kg was used. A Kd-value of 100 l/kg corresponds to the Koc-value for Pendimethalin of 10.000-18.000 reported in Table 2.2 and a f_{oc} of approximately 1 %, which is in the low end of the values for f_{oc} reported in Table 2.1 for the soil at Rørrendegaard. The results of this simulation are shown in Figure 4.6.

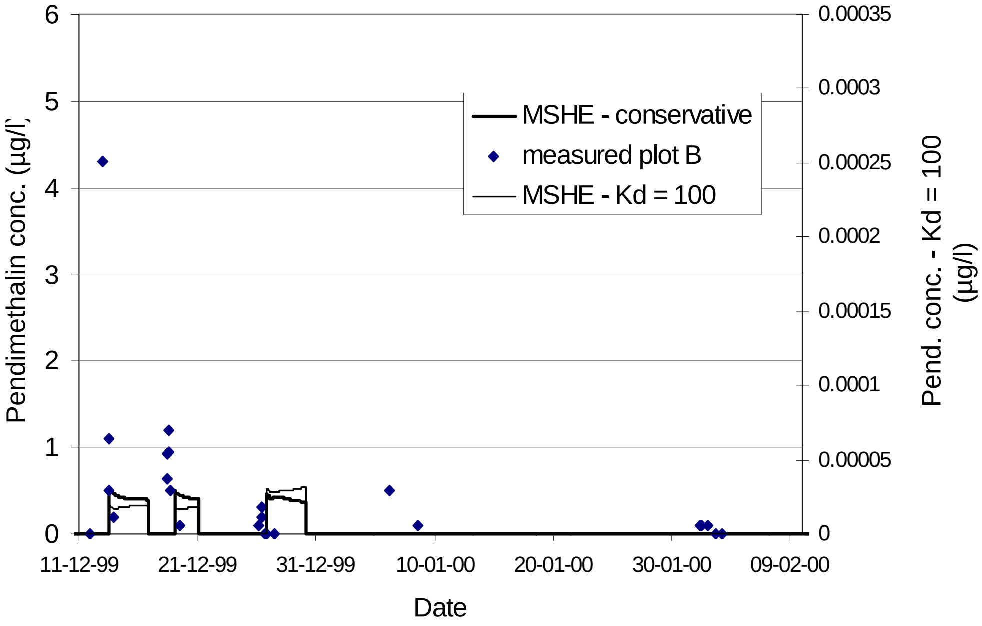

FIGURE 4.6. CONSERVATIVE AND $K_D = 100$ l/kg SIMULATION OF PENDIMETHALIN TRANSPORT WITH INITIAL INPUT OF 2,0 KG/HA. THE MAXIMUM OBSERVED CONCENTRATION OF 12 µg/l IS NOT SHOWN. THE $K_D = 100$ l/kg SIMULATION VALUES ARE SHOWN ON THE SECONDARY Y-AXIS.
FIGUR 4.6. KONSERVATIV ($K_D = 0$) OG SORBERENDE ($K_D = 100$ l/kg) SIMULERING AF PENDIMETHALIN TRANSPORT MED INITIELT INPUT PÅ 2,0 KG/HA. DEN MAKSIMALE OBSERVEREDE KONCENTRATION PÅ 12 µg/l ER IKKE VIST. RESULTATERNE FOR SIMULERINGEN MED $K_D = 100$ l/kg ER VIST PÅ DEN HØJRE Y-AKSE.

Even though Pendimethalin was handled as a conservative tracer with a reported solubility of 0,3 mg/l (Extoxnet at http://ace.orst.edu/cgi-bin/mfs/01/pips/pendimet. htm), the observed concentrations at the times of drain flow in December 1999 could not be achieved. At later times in the simulation, concentrations of 2-3 µg/l were obtained in the saturated zone but not at times of drain flow occurrences. The low simulation concentrations were not caused by dilution from the neighbouring cell, since flow was directed from the middle cell and outwards at times of drain flow events. As stated before, the lower level of the upper calculation layer was only 10 cm below the drainage level, so the artificial dilution was also limited.

In these simulations a maximum timestep of 60 seconds was used and results were stored (momentarily)every hour. When comparing concentrations from the simulations to concentrations from the field site, it should be noted that field site concentrations were averaged over the time it took to fill one sampling bottle, whereas the concentration from the simulations were momentary (averaged over the timestep length). During the rain events, the averaging (time to fill sampling bottle) was on the order of one to two hours. Using smaller time steps or saving results more frequently did not alter simulated concentrations significantly.

The observed concentrations of Pendimethalin could not be achieved, since solubility controlled the amount of Pendimethalin that could be put into the model. By increasing the solubility to 30 mg/l (100 times the reported solubility), concentrations of 9 µg/l could be obtained at later stages in the simulation, but the concentrations at the time of drain flow still did not match the observed levels.

The simulation using K_d = 100 l/kg shows how low simulated concentrations become when sorption is included without colloid-facilitated transport (simulated concentrations are approximately a factor of 20.000 lower than for the conservative simulation).

4.4.1 Colloid-facilitated transport of pesticide

Since the colloid transport had already been calibrated, the calibration of the colloid-facilitated transport should imply only the adjustment of the sorption parameter for sorption of Pendimethalin onto colloids, which should in turn be a relatively well determined parameter depending on the composition of the colloids. Figure 4.7 shows the results of a simulation using a K_d-value of 50 l/kg for sorption onto soil and a K_d-value of 200 l/kg for sorption onto colloids. The concentration levels achieved were orders of magnitude lower than the levels observed. However, by comparison the results obtained for the K_d=100 l/kg without colloid-facilitated transport in Figure 4.6, it can be seen that incorporating colloid-facilitated transport leads to significantly higher simulated concentrations.

In the macropores, the concentration of pesticide sorbed onto colloids was on the order of 200 µg/l, whereas the dissolved pesticide concentrations in macrpores and matrix were orders of maginitude lower. Over the simulation period (October-April), 97 % (!) of the total input of Pendimethalin to the saturated zone came through colloid-facilitated transport through macropores. So, even though the observed concentrations were not reached, the simulation showed that the colloid-facilitated transport without comparison was the most important transport mechanism for the Pendimethalin through the unsaturated zone. The large concentrations of colloid-associated Pendimethalin in the macopores were caused by the also very large concentrations of colloids in the macropores.
In the saturated zone, however, the colloid-concentrations were diluted and the colloid-associated Pendimethalin transferred to the dissolved state to maintain equilibrium, since the macropore water input to the saturated zone was only a small fraction of the total amount of water present. In fact, simple hand calculations using the following parameter-values:

Colloid concentration:	350 mg colloids/l
Dissolved pesticide conc:	10 µg/l
K_d for sorption onto colloids:	200 l/kg

show that the corresponding concentration of pesticide sorbed onto colloids is only 0.7 µg/l (less than 10 % of the dissolved concentration). The colloid concentration of 350 mg/l is approximately equal to the maximum observed colloid concentration in the drain flow. These percentages correspond well to the observed distributions between particle-associated and dissolved Pendimethalin seen in the drain water samples from Rørrendegaard.

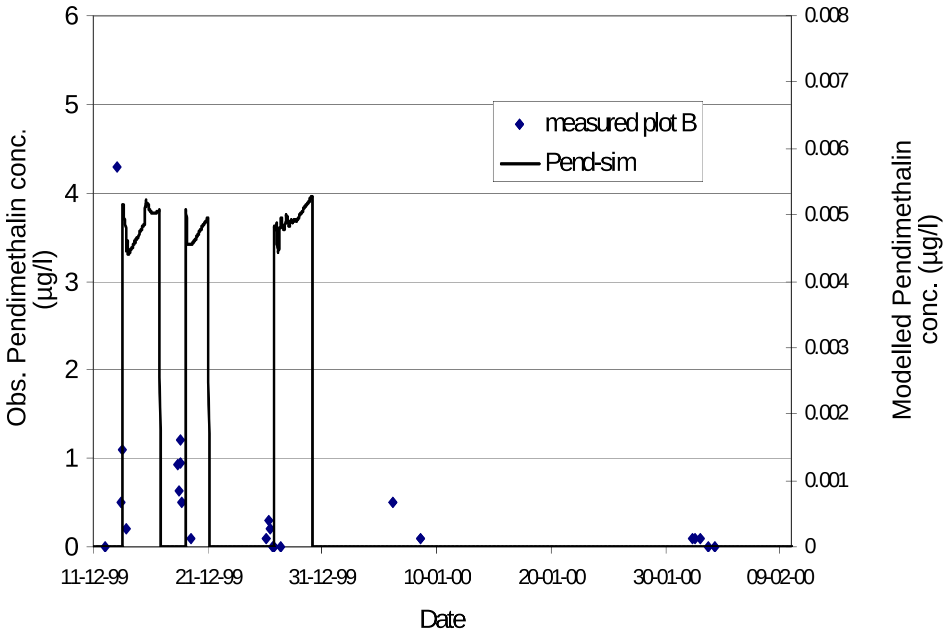

FIGURE 4.7.OBSERVED (LEFT AXIS) AND SIMULATED (RIGHT AXIS) PENDIMETHALIN CONCENTRATION FOR SIMULATION WITH K_D FOR SOIL = 50 l/kg AND K_D FOR SORPTION ONTO COLLOIDS = 200 l/kg.
FIGUR 4.7.OBSERVEREDE (VENSTE Y-AKSE) OG SIMULEREDE (HØJRE Y-AKSE) PENDIMETHALIN KONCENTRATIONER FOR SIMULERING MED K_D FOR SOIL = 50 l/kg OG K_D FOR SORPTION TIL KOLLOIDER = 200 l/kg.

By eliminating filtration of colloids in the macropores, slightly higher concentrations of Pendimethalin could be obtained. Increasing the K_d-value for the sorption of pesticide onto colloids would obviously increase the transport of pesticide to the saturated zone, but only slightly, since concentrations of colloid-associated Pendimethalin in the macropores almost reached the solubility of Pendimethalin in the simulation in Figure 4.7.

The real bond on the concentrations that could be achieved was the solubility of the Pendimethalin, because it controlled how much pesticide could be put into the model. since the pesticide was transferred through the aqueous state to the particle-sorbed state. The methodology is explained in Figure 4.8: Rainfall detaches an amount of particles, which is put into the overland compartment. The pesticide on the soil surface is transferred to the rainwater at a concentration equal to the solubility as long as there is pesticide enough present to maintain this concentration in the water. In the overland compartment, the pesticide is distributed between the three possible states (adsorbed to the soil, adsorbed to colloids, and dissolved). Hence, the obtainable concentration of mobile pesticide is limited by the solubility of the pesticide, since this controls the input of pesticide into the overland compartment.

Increasing the solubility of Pendimethalin by a factor 100 (to 30 mg/l) and increasing the K_d-value for sorption onto colloids to 400 l/kg produced a maximum concentration of Pendimethalin in the saturated zone of 1.8 µg/l.

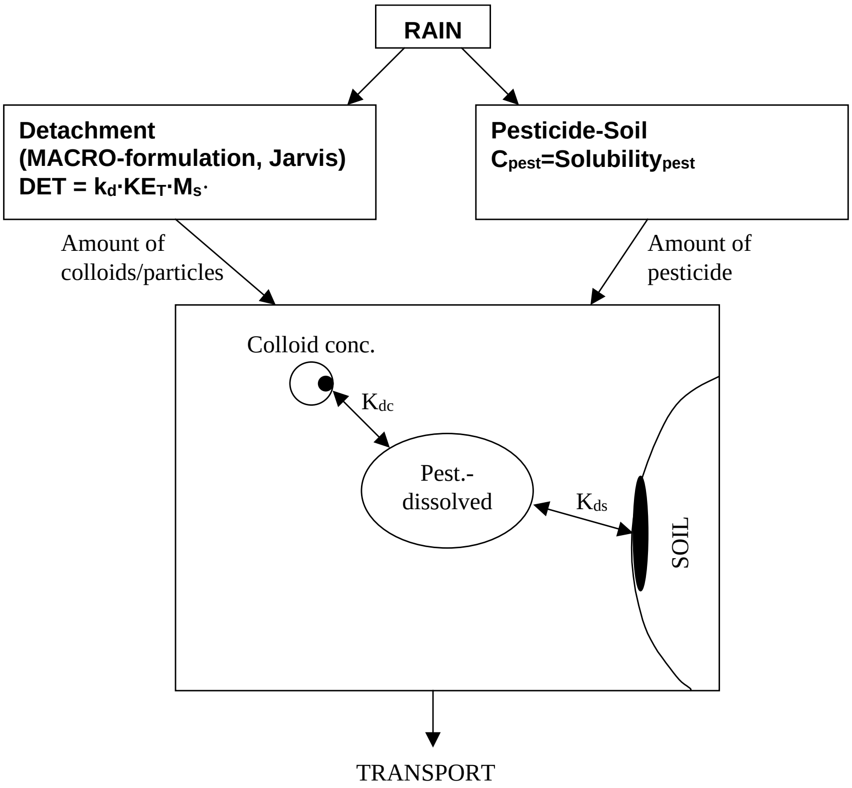

Figure 4.8.Sketch of how concentrations are assigned in the overland compartment. Rainfall detaches an amount of particles, which are put into the overland compartment. The pesticide on the soil surface is transferred to the rainwater at a concentration equal to the solubility as long as there is pesticide enough present to maintain this concentration. In the overland compartment the pesticide is distributed between the three possible states. Hence, the obtainable concentration of mobile pesticide is limited by the solubility of the pesticide.
Figure 4.8.Skitse af hvorledes pesticidet fordeles i "overland compartment" i modellen. Regnen frigør en vis mængde partikler som tilføres overland compartment. Pesticidet afsat på overfladen overføres til regnvandet i en koncentration svarende til mærningskoncentrationen, så længe der er pesticid nok til at opretholde mætningskoncentrationen i vandet. I overland compartment fordeles pesticidet mellem de tre mulige tilstande. Som konsekvens af denne procedure er mængden af mobilt pesticid begrænset af opløseligheden af pesticidet.

The maximum concentrations of pesticide sorbed onto colloids seen in the macropores were now on the order of 5000 µg/l and concentrations of dissolved pesticide in the macropores were on the order of 0,1 µg/l. Input of pesticide through the matrix was still insignificant. However, larger concentrations could not be obtained because further increase in solubility and K_d led to depletion of the Pendimethalin initially put on the soil surface within the first month of the simulation.

4.5 Evaluation of colloid-facilitated transport

The conclusion for the modelling of the Pendimethalin concentrations was that significantly large (compared to observed) concentrations could not be obtained using the approach applied in this study. The approach chosen is still valid in principle and can be used to study the importance of colloid-facilitated transport to concentrations obtained in the saturated zone. A number of simulations, using the parameter-values in Table 4.1 and variable K_d-values (identical for sorption onto soil and to particles in each simulation) were performed. The resulting maximum concentrations obtained in the saturated zone and the total input of pesticide into the saturated zone are given in Table 4.2 below.

Table 4.2 shows, that for the given flow- and transport configuration, colloid-facilitated transport could play an important role in transport of pesticides even though they are not very strongly sorbing. Obviously, the importance increases with increasing K_d-value. At K_d = 100 l/kg, the maximum concentration is a factor 10 higher and the total input to SZ is a factor 100 higher when colloid-facilitated transport is incorporated. Still, even at low K_d-values, the colloid-facilitated transport increases maximum concentrations and total input considerably. It should be noted that these proportions are completely dependent on the colloidal concentrations, meaning that the colloid-facilitated input is linearly dependent on the colloid concentrations. It should also be noted, that for the lightly sorbing compounds, the storage in the unsaturated matrix may dominate the total mass of pesticide present, meaning that matrix flow could become the determining factor for the total input to the saturated zone if simulations were run for a longer period of time.

Table 4.2. Maximum simulated concentration in saturated zone (SZ) and total input to SZ during simulation lasting from October 13 1999 till April 1 2000. K_D-values the same for sorption onto soil and colloids. The model setup was identical to the one calibrated to observed particle concentrations.

Tabel 4.2. simulerede maksimale koncentrationer i mættet zone (SZ) og maksimale input til mættet zone over en simulering fra 13. Oktober 1999 til 1. April 2000. samme K_D-værdi for soprtion til matrix og kolloider. samme modelopsætning, som kalibreret til observerede partikel-koncentrationer.

Kd (l/kg)	With colloid-facilitated transport		No colloid-facilitated transport	
	Max conc. in SZ (μg/l)	Tot. input to SZ (mg)	Max conc. in SZ (μg/l)	Tot. input to SZ (mg)
0	-	-	3.65	0.19
0.01	5.53	0.34	3.48	0.16
0.1	3.35	0.24	0.37	0.019
1	2.1	0.16	0.18	0.0060
5	0.64	0.11	0.05	0.0022
100	0.05	0.094	0.006	0.0009

4.5.1 Future development of model

The approach chosen here was not adequate to reach the observed concentration levels. The limiting factor for the achievable concentrations was the concept of transfer of Pendimethalin from the aqueous state to the colloid-associated state, making the solubility of the compound the limiting factor. Other factors not incorporated in the model could play a role, such as generation of colloids below the soil surface, the possibility of some colloid transport through the matrix, uneven spreading of the compound on the surface, and non-equilibrium division between sorbed and dissolved states (especially in the macropores). However, none of these mechanisms would be able to explain the lack in concentrations of orders of magnitude as the solubility constraint can. A possible explanation for the discrepancies between observed and modelled concentrations could be that the pesticide does not ‘obey’ the reported solubility, but might form crystals leading to higher aqueous concentrations than dictated by reported solubility.

A different approach for modelling the generation of colloid-associated pesticides (or other compounds) at the soil surface must be employed, in which the concentration of colloid-facilitated pesticide is unrelated to the solubility of the compound. The model could conceptualise the generation of particles with very high contents of pesticide being peeled from the top sediment using e.g. the work of C.W. Rose and co-workers in describing the chemical enrichment seen in erosion modelling (see e.g. Ghadiri & Rose, 1991a+b and Rose, 1993). The concentration levels obtained by this technique could be significantly larger in the short periods where heavy rainfall occurs. These ‘supersaturated’ particles should then be allowed to pass through the macropores undergoing a kinetic desoription allowing them to still be carrying a large amount of pesticide as they reach the saturated zone.

5 Discussion

5.1 Pesticide leaching

The estimated total losses of Pendimethalin to the drains (0.0013 % of the applied amount on average for the two seasons) are in fair agreement with losses reported elsewhere for structured field soils. The quantities of Pendimethalin lost with drain water from tile drains range from 0 to 0.040 % of the applied dose (Czapar et al., 1994; Jones et al., 1995; Traub-Eberhard et al.,1995; Vencill et al., 1999). Traub-Eberhard et al. (1995) investigated the movement of Pendimethalin into tile drains in a one year experiment involving two soil types. The estimated total Pendimethalin loss following autumn application was less than 0.001% of the applied dose on a silt loam soil, whereas no Pendimethalin was detected in drain water collected from a sandy soil. They attributed the absence of Pendimethalin in drain water from the sandy soil to less occurrence of preferential flow due to low stability and lack of continuity of macropores. Between 0.009 and 0.040 % of the applied Pendimethalin dose was lost with drain water in a one year field study on a cracking, intensively drained heavy clay soil in England (Jones et al., 1995). Czapar et al. (1992) studied the movement of Pendimethalin in packed soil columns with and without artificially made continuous macropores. Following heavy irrigation, Pendimethalin was detected in drainage from columns with a continuous macropore but not in columns without macropores. Starret et al. (1996) studied the movement of Pendimethalin in 50 cm long undisturbed soil columns. Traces of the herbicide were found in leachate from the columns following heavy irrigation (four 2.54-cm applications) but not after light irrigation (sixteen 0.64-cm applications). On average, 0.2 % of the applied Pendimethalin was found in leachate from the columns after heavy irrigation.

The maximum Pendimethalin concentration reported by Traub-Eberhard et al. (1995) (0.7 µg l^{-1}) was more than ten times smaller than the maximum concentration found in the present study. This difference may be caused by natural variations between the soils in the two studies. It could also be caused by different lag periods between application and first rainfall generating drain flow. However, in the present study the leaching of Pendimethalin was first detected 25 days after application in the season 1999-2000 and after 13-14 days in 2000-2001. This and the moderate amounts of precipitation in the two seasons does not make the present study a “worst case scenario”. The difference in maximum concentration of the present study and that of Traub-Eberhard et al. (1995) may also be due to the analytical methods, the results of Traub-Eberhard et al. (1995) being based on filtered water samples alone (undefined pore size), or it may be due to a differing sampling strategy.

The large amount of Pendimethalin remaining in the soil in February 2000 (81 %) indicates that only a small part of the applied Pendimethalin has been degraded. This is in agreement with the results of Traub-Eberhard et al. (1995), who reported an estimated time to 50 % dissipation (DT_{50} value) for Pendimethalin of more than 300 days following autumn application on a silty loam soil. It also confirms with earlier reported DT_{50} values of 3-4 months

(Walker and Bond, 1977). The investigation for remaining Pendimethalin was based on soil coring in February 2000 to a depth of 35 cm. This depth was chosen mainly in consequence of the findings of Traub-Eberhard et al. (1995). They sampled the soil intensively to a depth of 90 cm but were unable to detect Pendimethalin below ploughing depth.

5.2 Leaching dynamics

5.2.1 Soil particles

Soil particle concentrations (expressed by turbidity) generally peaked shortly after initiation of the drain flow events and before the occurrence of maximum drain flow rates. This is in agreement with observations from similar field experiments (Villholth et al., 2000) and erosion experiments showing that the sediment concentrations peak within the first 3-5 minutes of a rainfall event (Sander et al., 1996).

On unfrozen soil, large peak values for turbidity (T > 50 NTU) always occurred during or shortly after (within 8 hours) relatively strong rain events, coinciding with the occurrence of large moisture contents (θ_L) at 8 and 16 cm depth. Very large turbidity values were observed in break of frost situations where the soil was still partly frozen. These are both conditions (very wet conditions and frozen soil) that favour macropore flow and most likely also reduce reattachment/filtering of particles since pores will be fully wetted and flow will be fast.

Thus, in order to sample these peak values, focus should be given to drain flow events occurring in break of frost situations, and on rain events creating soil moisture contents considerably above field capacity in the entire plow layer.

5.2.2 Pendimethalin and Ioxynil

Pendimethalin concentrations as turbidity generally peaked shortly after initiation of the drain flow events and before the occurrence of maximum drain flow rates.
A similar pattern of pesticide concentrations in flow from tile drains have been reported elsewhere (Brown et al., 1995; Kladivko et al., 1991; Villholth et al., 2000). The early breakthrough of Pendimethalin indicates, that the primary means of transport of Pendimethalin from the surface to the drains is through macropore transport. The hydraulic conductivity of macropores is mostly decades higher than the hydraulic conductivity of the matrix. The very fast transport through the macropores could cause equilibrium sorption conditions to not be reached, hence allowing for a relatively greater portion of the hydrophobic pesticide to pass through the soil. In the matrix, transport is slower and sorption equilibrium can be reached. Also the filtering capacity to soil particles is significantly (infinitely) higher in matrix than in macropores, which would also explain the early findings of maximum concentrations of particles in drain water. Because of the limited water transport capacity of the macropores (macropores only make up a small percentage of the overall porosity), maximum concentrations of hydrophilic compounds will only occur after breakthrough of matrix transport has been reached (see e.g. Addiscott et al., 1978). Any drain flow originating from the soil matrix is expected to reduce rather than increase turbidity and Pendimethalin concentrations. For Ioxynil, the main transport is expected to occur through the matrix.

Breakthrough of Ioxynil could be to some extent controlled by earlier events, in the sense that Ioxynil could be stored in the pore water of the unsaturated zone and in the saturated zone, until a new rainfall strong enough to generate drain flow occurs.

5.3 Particle-facilitated transport

5.3.1 Correlation between turbidity and Pendimethalin

Results showed a strong correlation between turbidity and Pendimethalin concentration during the first most important drain flow events after Pendimethalin application in both seasons. The correlation declined somewhat over time (with event no.), see Table 3.2. This decline is most likely due to the fact that the accessibility of Pendimethalin available for transportation on the soil surface declines with event no., whereas the supply of soil particles is more or less infinite. Gharidi and Rose (1991) by peeling of soil aggregates found, as would be expected, that outer fractions of soil aggregates contained considerably more pesticides than inner fractions. They also found that the enrichment (with pesticides) of the particles detached by rainfall decreased with time (30 and 50 minutes) over a rainfall event, in accordance with the outer fractions of the aggregates being detached before inner fractions.

Even though the correlation is fairly convincing, this does not prove that Pendimethalin is transported associated to colloidal particles. The correlation could be an indirect one, in the sense that Pendimethalin and particle concentrations could both be positively correlated to another phenomenon. This phenomenon could be the flow rate and the mechanism would be that a high flow rate would lead to a rinsing effect of drain tiles, in which particles and Pendimethalin were deposited in a porous deposit on the bottom of the tiles. However, since particle content, and hence Pendimethalin concentrations were inversely correlated to flow rate, this was not the case.

The underlying phenomenon could also be macropore transport. As argued in the preceding section, there is a physically plausible reason why macropore transport would correlate positively with both particle and Pendimethalin concentrations. The decreasing correlation factor with event no. could then be further explained by the fact that in the areas surrounding the ‘openings’ of the macropores in the top soil, Pendimethalin would be washed out to the maximum extent during the first events, leaving behind only more strongly bound Pendimethalin.

However, since Pendimethalin sorbs so strongly to bulk soil and soil particles, it is also very likely that some of the soil particles observed to be washed out through the drains carry Pendimethalin with them. Also, the modelling showed that colloid-facilitated transport through macropores was the totally dominant transport mechanism for a strongly sorbing pesticide, such as Pendimethalin, and even modelling Pendimethalin as a conservative tracer, the observed concentration levels were not achieved, again indicating that a supplementing transport mechanism was acting.

For Ioxynil there was no correlation between particle content (turbidity) and Ioxynil concentration, indicating that particle-associated transport was not an important mechanism for Ioxynil. The modelling exercise, employing different K_d-values, showed however, that even for lightly sorbing compounds such as Ioxynil (K_{oc} ~100), particle-facilitated transport may be an important additional transport mechanism together with dissolved transport (see Table 4.2). In this case this was not supported by the experimental evidence, that was collected in the current study.

5.3.2 Fractionation analysis

The fractionation analysis for Pendimethalin performed in the present study indicated that particle-facilitated transport of Pendimethalin takes place, but is unclear in quantifying it.

The total mass of Pendimethalin found in the fraction above 0,7 μm filter size was 6 % in the season 1999-2000 and 15 % in the season 2000-2001 at Rørrendegaard. For the single 5 liter sample the same fraction was 19 % and no Pendimethalin appeared to be separated out of the water phase through the subsequent centrifugation (see Figure 3.7). In the samples taken from the model areas, between 30 and 60 % of the total Pendimethalin content was found in the solid phase extracted via the centrifugation. This significant difference in particle associated Pendimethalin could possibly be explained by differences in the composition of the soils at the different places. According to the sorption experiments (Table 3.6), the soil from the model areas should then be richer in organic carbon or clay content. The average clay content for the top soil of the three localities is Lillebæk: ~16%; Rørrendegaard: ~12%; Odderbæk: ~6% and the organic C content is Odderbæk: ~2,3-2,5%, Lillebæk: ~1-1,8%; Rørrendegaard: ~1,2%. The topsoil of the model areas are somewhat richer in organic carbon, but the same hypothesis can not explain the variation between the two model areas. The difference in results could also be caused by the experimental procedure. The samples were stored for periods of days to weeks before filtration and centrifugation. The five liter sample from Rørrendegaard was taken out on December 18, 2000 and centrifuged almost 7 months later on July 12, 2001. The samples from the model areas were centrifuged the day after the sampling.

The modelling was a very important addition to the samples of drain water, since it showed that even though the division between dissolved and particle-associated phases may be strongly shifted towards the dissolved phase, this could be caused by the dilution of the water coming to the saturated zone through the macropores and following dissolution of particle-associated pesticide. Hence, particle-associated transport may still very well be the overall determining factor for the transport of pesticides through the unsaturated zone, even though samples from the drain water or from the saturated zone in general show that only 10-15 % or less of the pesticide is found in a particle-associated form. The residence time in the drains, the time to fill the sampling bottle, and the subsequent handling time before filtration/centrifuging of the sample may be very important in determining the distribution of the pesticides between dissolved and particle-associated states, if the sorption/desorption of the pesticides takes a while to find equilibrium. In this context, it is interesting to note, that in the samples from the two model areas, where considerably higher contents of particle-associated Pendimethalin were found than in the experiments at Rørrendgaard, the handling time before filtration was lower than the average handling time before filtration for the samples taken from Rørrendegaard.

Ideally, samples for determining the extent of particle-associated transport through the unsaturated zone should be taken directly from macropores and should be centrifuged immediately.

6 Conclusion

Two seasons of field experiments sampling drain flow for Pendimethalin, Ioxynil (one season) and turbidity were carried out. The following conclusions could be drawn from the experiments:

- For Pendimethalin the estimated total losses to drains was on average 0.0013 % of the applied dose (2.0 kg/ha).
- The maximum concentration of Pendimethalin found in the drain flow samples was 12.3 µg/l in the first season and 2.97 µg/l in the second season. In the first season, the maximum concentration occurred in the first drain flow event after application. In the second season the maximum concentration occurred in the second drain flow event after application.
- The maximum concentration of Ioxynil was 0.51 µg/l, found in the second drain flow event in the second season (same event as for Pendimethalin).
- Peak concentrations of soil particles and Pendimethalin occurred shortly after initiation of drain events and before the occurrence of maximum drain flow rates.
- There was a significant correlation between Pendimethalin (with a K_{oc}-value in the range 10000-18000) concentrations and turbidity (particle concentrations) in the drain flow samples.
- The timing of the peak concentrations indicated that macropores were the dominant means of transport for Pendimethalin and soil particles.
- Fractionation analysis (filtering through 0.7 µm filter or centrifugation) on drain water from the field experiments showed that between 0 and 30 % of the Pendimethalin was associated with particles. Three drain water samples from two other areas (Odderbæk and Lillebæk) showed that 45-65 % of the Pendimethalin was associated with particles.
- Sorption experiments showed a clear correlation between organic carbon content of soil and sorption of Pendimethalin.
- Ioxynil (with a K_{oc} value of approx. 170) did not exhibit any sign of correlation between particle content and compound concentration.
- The strong correlation between turbidity and Pendimethlin concentrations implies that turbidity may serve as a guide in determining which samples to analyse for Pendimethalin or other hydrophobic compounds.

From the modelling of the experiments, the following conclusions could be drawn:

- The model was reasonably calibrated to fit the drain flow and the particle concentrations observed in the drains.
- Using this calibrated setup, the subsequent modelling of particle-facilitated transport showed that with use of realistic K_d-values for Pendimethalin, colloid-facilitated transport through the macopores completely dominated (97 %) the mass transport of Pendimethalin through the unsaturated zone.
- The observed low values of particle-associated Pendimethalin (0-30 %) in the drain flow samples from Rørrendegaard could be explained by the

dilution of the colloidal concentrations and the subsequent release of Pendimethalin to the dissolved state.

- Simulations using different K_d-values for sorption of pesticide showed that for the calibrated model setup for Rørrendegaard, particle-associated transport completely determined the mass transport of pesticides to the saturated zone in the range of K_d-values from 0.1 to 100 l/kg and was a potentially important factor for even lower K_d-values. However, the experimental evidence for Ioxynil did not support that low K_d pesticides should associate considerably with particles.
- The model-approach applied in this study, where the particle-associated pesticide was obtained through sorption of dissolved pesticide could not produce concentrations of particle-associated Pendimethalin and hence total Pendimethalin concentrations that were comparable to the observed ones, since the obtainable concentrations were limited by the solubility of the Pendimethalin.
- It was not possible to simulate concentrations up to the level of the observed concentrations even though Pendimethalin was considered a conservative tracer – again indicating the existence of a very considerable supplementing transport mechanism than dissolved transport.
- Applying a concept, where the particle-associated concentration of the pesticide is unrelated to the solubility of the pesticide will allow for higher pesticide concentrations to be simulated.

In combination between experimental and modelling results, the following conclusions could be drawn:

- The time between leaching events and sampling and between sampling and filtering of samples may be a very important factor in finding proof of particle-associated transport when taking samples from the saturated zone (and from drains), because of dilution of colloidal concentrations and subsequent release of pesticide from the particle associated state.
- Ideally, for determining the importance of particle-association as transport mechanism, samples should be taken directly from the macropores and not from the saturated zone

In conclusion, the study indicates strongly that colloid-facilitated transport through macropores is a very important transport mechanism for strongly sorbing pesticides (K_{oc} in the range of Pendimethalin) from soil surface to saturated zone, at locations where generation of colloidal particles is considerable, and that this should be taken into account when determining the potential leaching of at least strongly sorbing pesticides.

To determine the potential leaching of pesticides from different soil types at least the organic carbon content of the topsoil, the structure of macropores in the soil, and the ease of soil detachment should be considered.

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Appendix A.
Measured concentrations of pesticide

Appendix A - Part 1

Measured concentration of Pendimethalin in plot A and B
Season 1999/2000

	PLOT A				**PLOT B**	
Date/time		Pendimethalin		Date/time		Pendimethalin
		µg/l				µg/l
12/10/99 17:54		0.5		12/11/99 23:46		0
12/13/99 0:04		8.3		12/12/99 21:42		12.6
12/13/99 3:00		1.29		12/13/99 0:45		4.3
12/13/99 11:25		0.4		12/13/99 11:09		0.5
12/13/99 13:54		1.8		12/13/99 13:13		1.1
12/13/99 22:48		0.6		12/13/99 21:12		0.2
12/18/99 11:20		2.3		12/18/99 9:55		0.93
12/18/99 12:58		1.7		12/18/99 12:07		0.64
12/18/99 14:14		1.4		12/18/99 13:50		1.2
12/18/99 15:50		1.3		12/18/99 15:14		0.95
12/18/99 17:12		0.3		12/18/99 16:44		0.5
12/19/99 10:34		0		12/19/99 11:31		0.1
12/24/99 15:42		0.1		12/26/99 3:53		0.1
12/25/99 22:02		0		12/26/99 9:09		0.3
12/26/99 7:54		0.2		12/26/99 10:53		0.2
12/26/99 11:52		0		12/26/99 15:07		0
12/26/99 14:06		0		12/26/99 20:21		0
12/26/99 16:59		0		12/27/99 9:56		0
1/6/00 9:48		0.5		1/6/00 2:54		0.5
1/7/00 23:53		0.1		1/8/00 13:09		0.1
2/1/00 16:58		0		2/1/00 7:24		0.1
2/3/00 0:01		0		2/1/00 13:26		0.1
				2/2/00 0:08		0.1
				2/2/00 17:00		0
				2/3/00 6:46		0

Appendix A - Part 2

Measured concentration of Pendimethalin and Ioxynil in plot A and B
Season 2000/2001

	PLOT A				**PLOT B**	
Date/time	Pendimethalin	Ioxynil		Date/time	Pendimethalin	Ioxynil
	µg/l	µg/l			µg/l	µg/l
11/23/00 16:04	0.05	0.03		11/23/00 21:30	0.09	0
11/24/00 4:42	0.29	0.21		11/24/00 2:55	0.91	0
11/25/00 3:37	0.09	0.05		11/24/00 7:14	0.16	0.27
12/1/00 14:33	0.1	0.39		11/24/00 13:23	0.16	0.06
12/12/00 20:05	0.09	0		12/14/00 8:30	0.05	0.13
12/15/00 3:34	0.54	0		12/14/00 20:38	0.05	0
12/15/00 7:22	2.51	0.5		12/15/00 2:04	0.55	0.51
12/17/00 9:05	0.3	0		12/15/00 5:52	2.97	0.17
12/17/00 19:13	1.23	0.04		12/15/00 7:23	0.40	0.15
12/18/00 1:28	0.16	0.24		12/15/00 11:43	0.12	0
2/8/01 3:09	0.18	0		12/16/00 17:17	0.19	0.06
2/11/01 7:50	0.08	0		12/17/00 13:58	1.53	0
2/13/01 2:45	0.07	0		12/17/00 15:09	0.27	0
2/13/01 11:30	0.06	0		12/19/00 18:12	0.09	0
2/13/01 20:15	0.06	0.04		1/3/01 18:04	0	0
				1/4/01 2:31	0.03	0
				1/4/01 8:54	0.02	0
				1/6/01 15:44	0.03	0
				1/6/01 19:51	0.03	0
				1/6/01 21:08	0.08	0
				1/6/01 21:56	0.08	0
				1/6/01 22:26	0.07	0
				1/7/01 11:48	0	0

Appendix B.

Measured turbidity and extrapolated soil particle concentrations

Appendix B		
Values for particle concentrations based on turbidity measurements		
Extrapolation based on relation Cs = 0,87*NTU - 3,3 (mg/l)		
Date	Turbidity, NTU	Cs (mg/l)
12/11/99 2:41	12.7	7.749
12/12/99 22:07	37.2	29.064
12/13/99 0:07	363	312.51
12/13/99 1:20	231	197.67
12/13/99 2:42	105	88.05
12/13/99 4:22	70.4	57.948
12/13/99 6:21	32.3	24.801
12/13/99 9:47	16.1	10.707
12/13/99 14:48	42.4	33.588
12/13/99 17:15	18.3	12.621
12/13/99 19:43	7.7	3.399
12/13/99 22:20	7.96	3.6252
12/14/99 1:14	5.61	1.5807
12/14/99 8:13	2.24	0
12/14/99 12:11	1.49	0
12/14/99 15:31	1.5	0
12/14/99 22:55	1.28	0
12/15/99 4:26	1.68	0
12/15/99 12:05	2.55	0
12/15/99 18:14	12	7.14
12/16/99 0:40	6.96	2.7552
12/16/99 16:52	3.5	0
12/17/99 2:15	1.92	0
12/17/99 8:45	1.98	0
12/18/99 8:49	23.8	17.406
12/18/99 10:22	40.1	31.587
12/18/99 11:13	75.7	62.559
12/18/99 12:04	67.6	55.512
12/18/99 12:54	65	53.25
12/18/99 13:39	80.4	66.648
12/18/99 14:12	84.9	70.563
12/18/99 14:41	84	69.78
12/18/99 15:05	70.7	58.209
12/18/99 15:27	74.3	61.341
12/18/99 15:47	79.7	66.039
Date	Turbidity, NTU	Cs (mg/l)
12/18/99 16:07	81.4	67.518

12/18/99 16:23	64.9	53.163
12/18/99 16:40	52.9	42.723
12/18/99 16:56	41.8	33.066
12/18/99 17:11	41.5	32.805
12/18/99 17:25	35.7	27.759
12/18/99 17:39	22.8	16.536
12/18/99 17:54	20.3	14.361
12/18/99 18:08	18.1	12.447
12/18/99 18:21	17.1	11.577
12/18/99 18:36	28.9	21.843
12/19/99 10:30	3.68	0
12/19/99 11:08	2.4	0
12/25/99 10:45	1.98	0
12/26/99 4:23	20.8	14.796
12/26/99 8:12	98.2	82.134
12/26/99 10:00	98.2	82.134
12/26/99 11:51	103	86.31
12/26/99 13:20	57.4	46.638
12/26/99 14:03	5.74	1.6938
12/26/99 14:42	12.8	7.836
12/26/99 16:59	6.81	2.6247
12/26/99 17:35	6.94	2.7378
1/6/00 8:28	128	108.06
1/6/00 23:06	35.9	27.933
1/7/00 17:11	3.64	0
1/8/00 20:28	3.19	0
1/10/00 3:24	2.18	0
2/1/00 10:39	344	295.98
2/2/00 3:33	78	64.56
2/2/00 21:25	14.8	9.576
2/3/00 10:20	13.5	8.445
3/8/00 16:16	447	385.59
3/8/00 19:26	173	147.21
3/8/00 23:34	88.6	73.782
3/9/00 5:02	40.1	31.587
3/9/00 10:27	50.5	40.635
3/9/00 13:17	104	87.18
3/9/00 16:10	57.6	46.812
3/9/00 19:24	37.3	29.151
3/9/00 23:08	21.3	15.231
3/10/00 3:27	14.9	9.663
3/11/00 3:47	6.94	2.7378

Appendix C.
Sensitivity analysis for colloid-module

At first, some preliminary tests were conducted. The detachment module was tested against a spreadsheet solution of the same equations and produced identical values for DET. Following the integration of the colloid module in the MSHE setup, some simple tests were made to determine whether the module behaved as could be expected. The flow setup was a simple one-column setup with a constant infiltration rate of 0,1 mm/h, and drainage lines at 1,1 meter depth. Two flow simulations were made, one including and one excluding macropores.

The first transport setup included only colloids. All initial concentrations were equal to zero, and the colloids were generated by the colloid generation module and transported through the unsaturated zone. At first, filter coefficients in both domains was set to zero and the transport including and excluding macropores was compared. Following this the effect of the filtration coefficient was investigated.

Figure 1 shows the concentration of colloids in the upper groundwater layer (corresponding to the concentration in drain pipe) for a simulation including macropores and the same simulation excluding macropores (dispersivity in unsaturated zone is zero). As can be seen, the macropores give rise to very

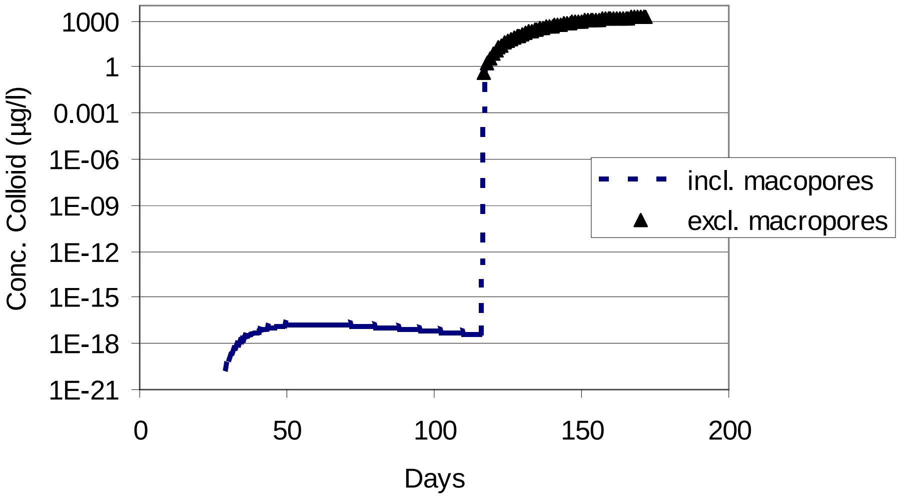

FIGURE 1. COMPARISON OF BREAKTHROUGH CONCENTRATIONS IN SIMULATION INCLUDING AND EXCLUDING MACROPORES. THE TWO CURVES ONLY DIFFER IN THE PART, WHERE VERY LOW CONCENTRATIONS ARE FOUND FOR THE MACROPORE SIMULATION.

FIGUR 1. SAMMENLIGNING AF GENNEMBRUDSKURVER I SIMULERING MED OG UDEN MAKROPORER. DE TO KURVER ADSKILLER SIG KUN I DEN FØRSTE DEL, HVOR DER FINDES MEGET SMÅ KONCENTRATIONER I SIMULERINGEN MED MAKROPORER.

small concentrations before any concentrations are seen without macropores. After breakthrough in matrix the two follow each other.

The same simulation was now performed with a longitudinal dispersivity of 0,05 m in the unsaturated zone. Because of the changed dispersivity, the breakthrough from matrix now occurs much earlier, however still the macropore breakthrough is the fastest (see Figure 2).

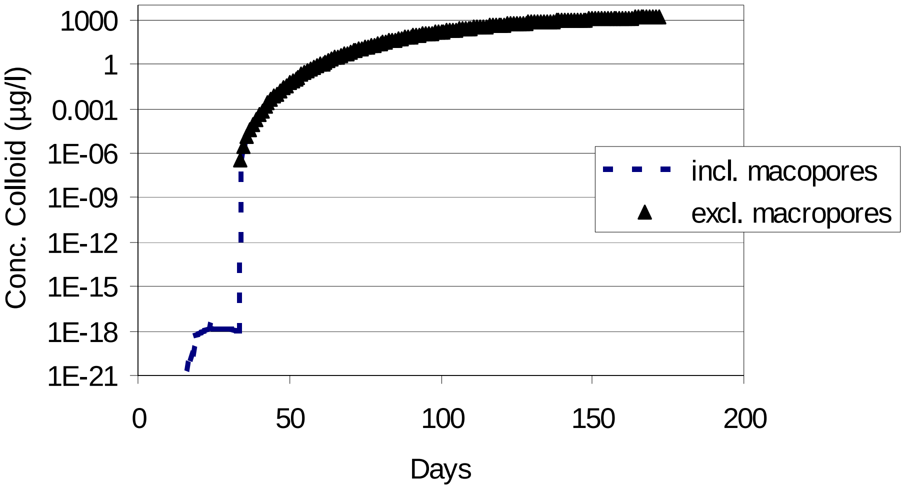

FIGURE 2. COMPARISON OF BREAKTHROUGH CONCENTRATIONS IN SIMULATION INCLUDING AND EXCLUDING MACROPORES, WITH A DISPERSIVITY IN THE UNSATURATED ZONE OF 0,05 m. THE MATRIX BREAKTHROUGH NOW OCCURS MUCH EARLIER, BUT STILL MACROPORE TRANSPORT PROVIDES THE INITIAL BREAKTHROUGH.

FIGUR 2. SAMMENLIGNING AF GENNEMBRUDSKURVER I SIMULERING MED OG UDEN MAKROPORER OG MED EN DISPERSIVITET I DEN UMÆTTEDE ZONE PÅ 0.05 m. MATRIX-GENNEMBRUDDET SKER NU BETYDELIGT TIDLIGERE, MEN DET ER STADIG MAKROPORE-TRANSPORTEN, DER GIVER DET INITIELLE GENNEMBRUD.

The macropore setup was maintained, and a sensitivity analysis on the colloid generation parameters was performed. The values from which variations were made is shown in Table 1 below.

TABLE 1. BASE PARAMETERS FOR SENSITIVITY ANALYSIS

Parameter	Value
Detachment, k_d (mg/J)	100
Replenishment, k_r (mg/m^2/s)	100
Influence depth, z_i (m)	0,01
Max. dispersable soil, M_{max} (g/g$_{soil}$)	0,05
Precipitation, P (mm/h)	0,1

With respect to the detachment coefficient k_d, there is a linear relation between the coefficient and the concentration of colloids. In situations where M_s reaches values around M_{max}, there is also a linear relation between M_{max} and the concentration of colloids (not shown). For the replenishment coefficient k_r, the sensitivity is the highest, when values are small, since at this point the fraction M_s/M_{max} will not dominate the replenishment expression.

With regards to the precipitation, the kinetic energy of the rain will become larger than zero only when the precipitation exceeds an intensity of 0,09 mm/h.

Results with regards to breakthrough time are not very sensitive towards the diffusion coefficient β_c.