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Fate of Pesticides in Surface Waters, Laboraty and Field Experiments

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Danish Environmental Protection Agency
Danish Ministry of the Environment

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Contents

Preface

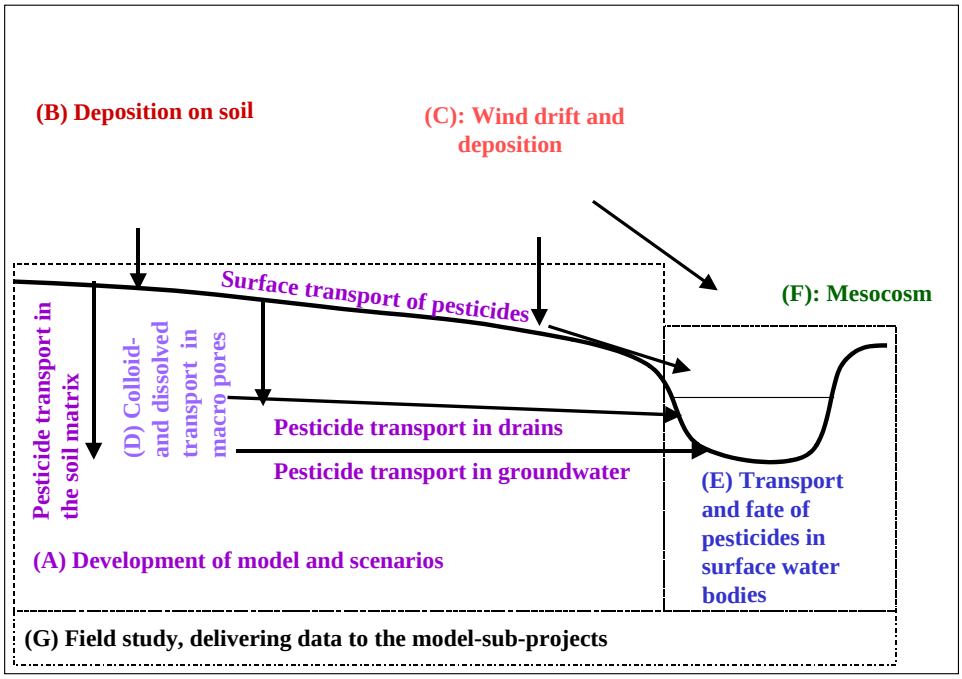
The project "Model Based Tool for Evaluation of Exposure and Effects of Pesticides in Surface Water", funded by the Danish Environmental Protection Agency, was initiated in 1998. The aim of the project was:

- 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 (Danish EPA) in their approval procedure. As part of this goal, the project had to:
    - To develop guidelines for evaluation of mesocosm experiments based on a system-level perspective of the freshwater 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 subprojects are listed in the table below.

Subprojects of "Pesticides in Surface Water"

No.	Title	Participating institutions
1	Development and validation of a model for evaluation of pesticide exposure	DHI Water & Environment
2	Investigation of the importance of plant cover for the deposition of pesticides on soil	Danish Institute of Agricultural Science
3	Estimation of addition of pesticides to surface water via air	National Environmental Research Institute Danish Institute of Agricultural Science
4	Facilitated transport	DHI Water & Environment
5	Development of an operational and validated model for pesticide transport and fate in surface water	DHI Water & Environment National Environmental Research Institute
6	Mesocosm	DHI Water & Environment National Environmental Research Institute
8	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



Links between the subprojects. The subprojects are placed on a cross-section of the catchment to illustrate interactions.

The above figure describes the relationship between the subprojects. Subproject 1 models the upland part of the catchment while subproject 5 models surface water bodies. Subproject 8 delivers data for both modelling projects. Subprojects 2 and 3 develop process descriptions for wind drift, dry deposition and deposition on soils. Subproject 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. Subproject 6 has mainly concentrated on interpretation of mesocosm studies. It contains, however, elements of possible links between exposure and biological effects.

The reports produced by the project are:

- Styczen, M., S Petersen, M. Christensen, A.Z. Jessen, D. Rasmussen, M.B. Andersen & P.B. Sørensen (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., S. Petersen & P.B. Sørensen (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., S. Petersen, N.K. Olsen & M.B. Andersen (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. & N.H. Spliid (2002): Deposition of pesticides on the soil surface. Ministry of Environment, Danish Environmental Protection Agency, Pesticides Research No. 65.

- Asman, W.A.H., A. Jørgensen & P.K. Jensen (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., C. Petersen & C. Koch (2002): Facilitated transport of pesticides. Ministry of Environment, Danish Environmental Protection Agency, Pesticides Research No. 67.
- Helweg, C., B.B. Mogensen, P.B. Sørensen, T. Madsen, D. Rasmussen & S. Petersen (2002): Fate of pesticides in surface waters, Laboratory and Field Experiments. Ministry of Environment, Danish Environmental Protection Agency, Pesticides Research No. 68.
- Møhlenberg, F., S. Petersen, K. Gustavson, T. Lauridsen & N. Friberg (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., B. Kronvang, K. Vejrup, B.B. Mogensen, A.M. Hansen & L.B. Hansen (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 idea behind the project was 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

The work reported here was performed as part of the project ”Development of an operational and validated model for pesticide transport and fate in surface water” which is also termed Subproject 5. Subproject 5 is a subproject of the main project: ”Model based tool for evaluation of exposure and effects of pesticides in surface water”. The overall goal of the main project was to provide the Danish EPA with a tool that, on the basis of pesticide property data, could be used to evaluate the fate of new pesticides in surface water, within certain scenarios, in relation to registration and regulation. In effect, the heart of the tool is a full catchment fate and transport model for two existing catchments, the Odderbæk and the Lillebæk catchment, that each contains a small stream. Subproject 5 has been concerned with the transport and fate in streams and ponds in these catchments.

This report contains the results of laboratory and field experiments made in Subproject 5. The objectives of the laboratory and field experiments were to gather information on processes critical for fate and transport of pesticides in streams and ponds in order to decide which processes to include in the model, to evaluate the applicability of currently required registration data for modelling and to gather parameter values to be used in the evaluation of the models.

The three pesticides pendimethalin, ioxynil and bentazone were used in the laboratory experiments while the field experiments also included fenpropimorph and glyphosate. The pesticides were chosen to get a wide variety in physico-chemical properties.

The laboratory experiments were set up to investigate sorption and degradation processes. As the streams to be modelled are very small and rather short, the residence time of a pesticide entering the streams will be short. Therefore, both sorption equilibrium and sorption kinetics were investigated. The effects of temperature, pesticide concentration level and sediment properties on the sorption of the selected pesticides were investigated to determine how to set up the model and to get an idea of how well pesticide property data delivered by the registration applicant could be used in the model-based tool.

The sorption processes were investigated in batch experiments where sediment from the catchment streams, the pond used in the field experiments and from a number of lakes were shaken with water and radiolabelled pesticide for different periods of time. Concentrations were measured indirectly by scintillation counting.

The sorption experiments showed that the pesticides sorbed to the sediments according to their hydrophobicity and the sediment organic matter content. Furthermore, as the K_{oc} values measured for stream, pond and lake sediments were in accordance with data for soil as found in the registration material, it seems reasonable to use soil-derived K_{oc} values for the modelling of these types of pesticides. Pendimethalin sorbed rather strongly while ioxynil and bentazon sorbed much less.

The sorption of the strongly sorbing pesticide pendimethalin showed considerable non linearity as sorption was higher at low concentrations than at high, but a Freundlich isotherm expression did not describe data well.

There was no difference between sorption at 4°C and 20°C for the three pesticides and the influence on sorption of temperature variations, which can be expected in the surface water of the catchments is thus considered negligible.

Sorption was fast in all cases. Waterphase concentrations very close to equilibrium were reached within a few hours. However, the rate of sorption is probably not fast enough to be ignored in the stream model. This will be shown by model runs. Variations in initial pesticide concentration did not affect the rate of sorption for a sediment with low organic matter content.

Aerobic degradation processes in stream sediment-surface water suspensions and in surface water were investigated in batch experiments with radiolabelled pesticides. Bulk samples were taken from the water and suspension at regular intervals for approx. 100 days and counted.

The degradation experiments showed that the pesticides degraded quite differently. Seemingly, bentazone did not degrade at all in the experiments, ioxynil degraded slowly but steadily and pendimethalin initially disappeared quite fast but, after a period, no more reduction in activity could be measured. This observation on pendimethalin degradation behaviour could be attributed to a number of reasons of which incorporation into biomass seems to be the most plausible.

The experiments showed that, for the weakly sorbing pesticide ioxynil, degradation rates were higher in the sediment-water suspensions than in water alone, which may be due to the higher biomass concentration in the suspensions.

For the strongly sorbing pesticide pendimethalin, the degradation rates in sediment suspensions and surface water were similar but the level of relative disappearance reached was higher for surface water alone than for surface water-sediment suspensions. This may be attributed to strong sorption of the pesticide to the solids of the suspension, which reduces bioavailability.

A “fate” model including first order sorption, desorption and degradation was successfully fitted to the experimental data and this “fate” model is incorporated in the fate and transport model of the model-based tool. The fitting of the fate model produced a large number of sorption and degradation rates that will be used in the evaluation of the full fate and transport model.

The field experiments were conducted in order to investigate the dissipation time from water for pesticides having different physico-chemical properties and the vertical mixing in more or less stagnant ponds with and without macrophytes, and to get data for evaluation of the effective diffusion coefficient.

The field experiments were conducted in artificial ponds by spraying the pond water surfaces with formulations of the five different pesticides and following the development in concentrations in the water body, at different

depths, and in the sediment. The ponds were well developed with both flora and fauna and thus resembled natural shallow ponds. The pesticide content of water and sediment samples was determined by chemical analysis. In the case of glyphosate, analysis for AMPA, the major degradation product, was also performed.

The two hydrophobic pesticides pendimethalin and fenpropimorph had dissipation half times from the water phase of around one to two days and the dissipation rate for glyphosate was slightly lower. Ioxynil disappeared from the water phase within 20 days while bentazone, being more persistent, could still be measured after 130 days.

There was a large difference between water phase dissipation rates measured in two different years, which demonstrates the importance of variation in conditions. One year, a heavy rain shower in the days before spraying made it necessary to pump water from ponds, which might have caused resuspension of sediment. That year, dissipation rates were markedly higher than the year before when no similar rain event had occurred.

The presence of macrophytes in the ponds did not influence dissipation rates of fenpropimorph and pendimethalin very much and dissipation rates from ponds with macrophytes and ponds without macrophytes were quite similar. However, a statistical analysis showed that the presence of macrophytes initially causes a higher concentration in the water phase whereas, after one day, it causes a lower concentration in the water phase when compared to macrophyte-free ponds. This may be explained by the combined effect of the macrophytes on turbulence and sorption. Macrophytes hinder turbulence and thus initially reduce the movement of pesticides from the surface to the sediment, which results in a higher water concentration. However, after a while the water body is eventually mixed in spite of the macrophytes, and now the macrophytes act as a sorbing compartment that removes pesticide from the water phase and thus reduces concentration.

The experiments showed that two days after spraying, a vertical concentration gradient could still be measured in ponds sprayed with pendimethalin and fenpropimorph. For glyphosate, a gradient was only discernible on the first day after spraying.

The concentrations of pendimethalin and fenpropimorph in sediment 2, 15 and 31 days after spraying were higher in ponds without macrophytes than in ponds with macrophytes. The reason again seems to be the reduction in vertical mixing and thereby reduced transport from surface to bottom, which the macrophytes cause, and the sorption of pesticide to macrophytes.

Sammenfatning

Det arbejde, der rapporteres her, er blevet udført som en del af projektet: "Development of an operational and validated model for pesticide transport and fate in surface water", som også benævnes delprojekt 5. Delprojekt 5 er et delprojekt af hovedprojektet: "Model based tool for evaluation of exposure and effects of pesticides in surface waters". Det overordnede formål med hovedprojektet var at give Miljøstyrelsen i Danmark et værktøj til, på baggrund af nye pesticiders egenskaber, at forudsige og vurdere skæbnen af disse pesticider i overfladevand under visse scenarier, i forhold til registrering og regulering. Grundlaget for værktøjet er en fuld oplands transport- og skæbnemodel, der er sat op for oplandene for åerne Odderbæk og Lillebæk. Delprojekt 5 har omhandlet transport og skæbne i disse åer og i vandhuller beliggende i oplandet.

Denne rapport indeholder resultaterne af laboratorie- og feltforsøg udført i delprojekt 5. Formålene med laboratorie- og feltforsøg har været at samle information om processer, der vurderes at være kritiske for transport og skæbne af pesticider i åer og vandhuller. Denne information blev søgt for at kunne beslutte, hvilke processer modellen skulle kunne beskrive for at kunne vurdere model-anvendeligheden af de data, som leveres i forbindelse med ansøgning om registrering af nye pesticider, og for at skaffe parameterværdier til evaluering af modellerne.

De tre pesticider, pendimethalin, ioxynil og bentazon, blev brugt i laboratorieforsøgene, mens feltforsøgene yderligere omfattede fenpropimorph og glyphosat. Disse pesticider blev valgt for at få et bredt udvalg af fysisk-kemiske egenskaber.

Laboratorieeksperimenterne blev foretaget for at undersøge sorptions- og nedbrydningsprocesser. Da åerne, der modelleres, er meget små og ret korte, kan det forventes at opholdstiden for et pesticid, som kommer i åen, er meget kort. Derfor blev ikke kun ligevægten men også kinetikken i sorptionen undersøgt. Betydningen af temperatur, pesticidkoncentrationsniveau og sedimentegenskaber blev undersøgt for at kunne bestemme, hvordan modellen skulle sættes op og for at få en idé om, hvor godt registreringsdata kan anvendes til modellering.

Sorptionsprocesser blev undersøgt i batchforsøg, hvor sediment fra åerne, fra en række søer og fra vandhullerne brugt i feltforsøgene, blev rystet med vand og ^{14}C-mærket pesticid i perioder af varierende længde. Koncentrationer blev målt indirekte ved scintillationstælling.

Sorptionsforsøgene viste, at pesticiderne sorberede til sedimenterne i overensstemmelse med deres hydrophobicitet og efter sedimenternes indhold af organisk materiale. Herudover var K_{oc}-værdier målt for å-, sø- og vandhulssediment i dette projekt i overensstemmelse med de K_{oc}-data for jord som findes i registreringsmaterialet, og det synes derfor rimeligt at anvende K_{oc}-værdier, målt for jord, til modellering af transport og skæbne af denne type pesticider i overfladevand. Pendimethalin sorberede temmelig kraftigt, mens ioxynil og bentazon sorberede langt mindre.

Sorptionen af det stærkt sorberende pesticid, pendimethalin, udviste betydelig ikke-linearitet, idet sorptionen var stærkere ved lave koncentrationer end ved høje. Et Freundlich udtryk kunne ikke beskrive denne ikke-linearitet.

Der var ingen betydelig forskel mellem sorptionen ved 4°C og 20°C for de tre pesticider, og det vurderes derfor, at der i modelsammenhæng kan ses bort fra betydningen af den temperaturvariation, der kan forventes i åer og vandhuller.

Sorptionen var hurtig i alle tilfælde med vandfasekoncentrationer tæt på umiddelbar ligevægt efter få timer. Sorptionen er dog formodentlig ikke hurtig nok til, at der kan ses bort fra den i å-modellen. Dette vil blive undersøgt i modelkørsler. Variation i pesticidkoncentrationen havde tilsyneladende ingen effekt på hastigheden af sorption til et sediment med lavt indhold af organisk stof.

Aerob nedbrydning i overfladevand og i overfladevand-sediment-suspensioner blev undersøgt i batchforsøg med radioaktivt mærket pesticid. Omsætningen af pesticid blev fulgt ved at udtage bulkprøver med faste intervaller i ca. 100 dage og bestemme aktiviteten ved scintillationstælling.

Nedbrydningsforsøgene viste, at pesticiderne blev nedbrudt forskelligt. Bentazon blev tilsyneladende slet ikke nedbrudt i forsøgene, ioxynil blev nedbrudt løbende men forholdsvis langsomt, og pendimethalin forsvandt til at starte med ret hurtigt, men nåede efter kort tid et niveau, hvor yderligere reduktion i aktiviteten ikke kunne konstateres. Der kan være mange forklaringer på, at der blev observeret et plateau i forbindelse med nedbrydningsforsøgene med pendimethalin, men det mest sandsynlige lader til at være, at der sker en vis indbyggelse af ^{14}C i biomassen.

Forsøgene viste, at nedbrydningsraten for det svagt sorberende pesticid ioxynil var højere i vand-sediment suspensioner end i overfladevand alene, hvilket kan skyldes den større biomasse koncentration i suspensionerne.

For det stærkt sorberende pesticid, pendimethalin, var nedbrydningsraterne i overfladevand og i overfladevand-sediment-suspensioner sammenlignelige, men niveauet af den relative forsvinding, som blev nået, var højere for overfladevand alene end for vand-sediment-suspensioner. Det kan skyldes stærk sorption til sedimentetpartikler i suspensionerne og deraf følgende reduktion af biotilgængeligheden.

En skæbnemodel, som inkluderede første ordens sorption, desorption og nedbrydning, blev succesfuldt fitted til data fra sorptions- og nedbrydningsforsøg, og denne model er indbygget i skæbne- og transportmodellen for overfladevand, som anvendes i Miljøstyrelsens værktøj. Fitningen af skæbnemodellen til eksperimentelle data gav værdier for en række parametre, som vil blive anvendt i evalueringen af skæbne- og transportmodellen.

Feltforsøgene blev udført for at undersøge forsvindingstiden fra vand for pesticider med forskellige fysisk-kemiske egenskaber, den vertikale opblanding i mere eller mindre stillestående vandhuller, med og uden makrofytter og for at tilvejebringe data for den effektive diffusionskoefficient.

Feltforsøgene blev udført i kunstige vandhuller ved at sprøjte formuleringer af de fem pesticider ud over ovefladen af vandhullerne og derefter følge udviklingen i koncentrationen af pesticid i vandsøjlen, i forskellige dybder, og i sedimentet. Vandhullerne var veludviklede og rige på flora og fauna, og lignede således naturlige lavvandede vandhuller i den henseende. Pesticidkoncentrationerne blev bestemt ved kemiske analyser. Udover pesticiderne blev der også analyseret for den vigtigste glyphosatmetabolit AMPA.

De to hydrofobe pesticider, pendimethalin og fenpropimorph, havde forsvindingshalveringstider fra vandfasen omkring en til to dage, og forsvindingsraten for glyphosat var lidt lavere. Ioxynil forsvandt fra vandfasen inden for 20 dage, mens bentazon stadig kunne måles efter 130 dage.

Der var stor forskel på forsvindingsraterne målt i vandfasen to på hinanden følgende år, hvilket illustrerer betydningen af de aktuelle forhold. I det ene år havde der netop inden udsprøjtningen været et kraftigt regnskyl, hvor de havde været nødvendigt at pumpe vand ud af vandhullet. Det kan have medført en resuspension af sediment, og det år var forsvindingsraten betydeligt højere end året før, hvor det ikke regnede tilsvarende inden udsprøjtningen.

Tilstedeværelsen af makrofytter i vandhullerne havde ikke nogen større indflydelse på forsvindingshastigheden, som var forholdsvis ens i vandhuller med og uden makrofytter. Dog viste en statistisk analyse, at tilstedeværelsen af makrofytter til at begynde med medførte en højere koncentration i vandfasen, og at de efter ca. én dag betød en lavere koncentration i vandfasen, når man sammenlignede vandhuller med og uden makrofytter. Dette kan forklares ved den dobbelte rolle, som makrofytter har i forhold til forsvinding. Makrofytterne hindrer ved deres tilstedeværelse turbulens i vandsøjlen og dermed den konvektive transport af pesticid fra overfladen til sedimentet, hvorved pesticidet bliver længere i vandfasen. Efter et stykke tid bliver vandfasen, på trods af planterne, opblandet, og nu er makrofytternes rolle, at de repræsenterer en stor overflade, hvortil pesticidet kan sorbere, og dermed reduceres vandkoncentrationen.

Eksperimenterne viste, at der var en vertikal koncentrationsgradient i vandhullerne i op til to dage efter sprøjtning med pendimethalin og fenpropimorph. For glyphosat kunne en gradient kun registreres den første dag efter udsprøjtning.

Koncentrationerne af pendimethalin og fenpropimorph i sedimentet 2, 15 og 31 dage efter sprøjtning var højere i vandhuller uden makrofytter end i vandhuller med makrofytter. Grunden formodes også her at være den reducerede turbulens og sorption til makrofytterne, der begge vil reducere koncentrationen i sedimentet til en given tid.

1 Introduction

This report describes the findings of subproject 5 (see preface overview) in relation to transport and fate of pesticides in surface water. In the report, the experiments performed to evaluate key processes under relatively controlled conditions are described.

Two approaches, subdivided into more specific tasks, were taken:

1. Laboratory experiments for evaluation of the adsorption and degradation process in relation to:

    - The usefulness of standard registration data in the registration model
    - The applicability of the paradigm of reversible equilibrium/kinetic adsorption
    - The paradigm of bioavailability and degradation (only degradation of dissolved fraction)

2. Full scale experiments in ponds using controlled and known substance input in relation to:

    - Dissipation time from water for substances having different physico-chemical properties
    - Evaluation of the influence from macrophytes including the influence on the mixing conditions in the water column
    - Evaluation of the vertical mixing conditions
    - Generation of data for evaluation of the effective diffusion coefficient

1.1 Laboratory experiments for evaluation of adsorption and degradation processes

The model-based tool (registration model) relies on a suite of predefined scenario runs conducted by the evaluated model(s) (model tools report). The details of the scenarios are given in the "Model tools report". In order to run the scenarios for a new or already registered pesticide, the model must be parameterised with the data supplied to the Danish EPA (Statutory Order) by the manufacturer in compliance with the approval procedure. However, for pesticide properties, such as those related to biodegradation and sorption, the model is not readily parameterised by the data requested by the Danish EPA. This problem can be solved in two ways. Either by using unspecific general parameter values or by estimating the missing parameters from available data. In order to evaluate the feasibility of these two approaches, it was necessary to gather precise data on the processes, which was done in the laboratory.

The adsorption process is very central in the registration model in relation to both retardation and bioavailability. The sorption to solids in the soil system or in the stream sediment causes the pesticide to move slower than the water that transports it. At the same time, sorption in general reduces the bioavailability, which again reduces degradation. For strongly sorbing pesticides, these processes can easily determine pesticide concentration levels

in the streams and special attention was therefore given to the study of sorption processes in the laboratory.

An important question in relation to sorption concerns sorption kinetics. As data on sorption kinetics are not requested by the Danish EPA, and thus not available for modelling, it is important to decide whether the registration model can be made to give realistic results without these data, and whether surrogate data can be derived indirectly from other pesticide properties. The basis for answering these questions is the knowledge on sorption rates and sorption equilibria, which have been studied and reported here, together with knowledge on registration data.

Often data on degradation in stream water and stream-sediment water suspensions have not been made available to the Danish EPA by the registration applicant as is the case with the model pesticides used in this study. As for sorption, it has thus been necessary to obtain experimental data.

The sorption and biodegradation of pesticides are dependent on the conditions of the locality where these processes take place. The sorption and biodegradation experiments were thus conducted with a range of sediments collected at the localities used for calibration of the model and, to some degree, with other sediments. By expanding the data set in this way, relevant catchment-specific data could be derived for evaluation of the model, at the same time as more general conclusions on parameter variability, parameter estimation etc. could be made.

The results from the laboratory experiments are used for a general evaluation of the registration model (Styczen et al., 2002a) and also in a sensitivity analysis of the catchment model, as described elsewhere (Styczen et al., 2002b).

1.2 Full-scale experiments in ponds using controlled and known substance input

The field experiments with ponds were conducted in order to get the knowledge on the processes governing disappearance from the water body of a pond, which is necessary for modelling. In the experiments, the dissipation of different pesticides having different physico-chemical properties was followed.

The depletion of pesticides from the water by adsorption to sediment was studied for three compounds. Influence of macrophytes on the dissipation of pesticides and on hydraulic mixing was studied in directly comparable ponds with and without macrophytes.

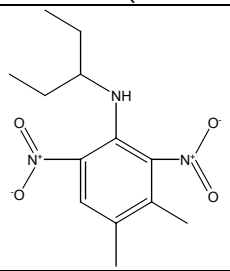
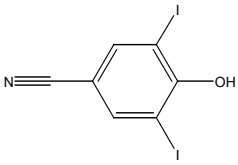
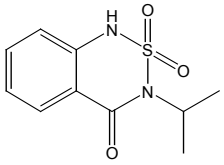
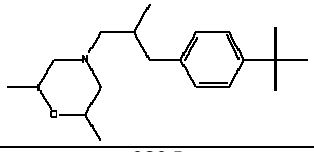
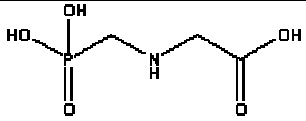
The model system assumes that the water column of surface water is vertically well mixed. Another aim of the ponds experiments was thus to evaluate the validity of this assumption.

A third important purpose of the field experiments was to generate data for the model for evaluation of the effective diffusion coefficients of pesticides into sediment of the ponds since earlier studies have revealed that the effective diffusion coefficient might exceed the molecular diffusion coefficients by several orders of magnitude (Sørensen et al., 2002).

2 Model pesticides

Pesticides used in experiments in this project were selected from a joint list of priority model compounds, which were identified at the start of the overall project. Five compounds were sprayed in the field experiments, three of which were also used in laboratory studies on sorption and degradation. Table 2.1 provides an overview of the structure and physico-chemical properties of the model pesticides.

Table 2.1
Physico-chemical properties of the model pesticides

	Pendimethalin (40487-42-1)	Ioxynil (1689-83-4)	Bentazone (25057-89-0)
Structure			
Molecular weight [g/mole]	281.3	371.8	240.3
Vapour pressure [mPa]	4.0 (25°C)	0.68 (25°C)	0.17 (20°C)
Aqueous solubility [mg/L]	0.3 (Tomlin, 1994)	50 (25°C) (Tomlin, 1994)	570 (20°C, pH 7) (Tomlin, 1994)
K_{ow} [L (water)/L (oct.)]	158489	2691* (Syracuse research corporation, 2000)	219* (Syracuse research corporation, 2000)
K_{oc} [L (water)/ kg (oc)]	13400 (United States department of agriculture, 2001) (pH 6.4)	182-276 (pH 7.3-6.7)	35 (United States department of agriculture, 2001), 42-155 (pH 7.7-6.6)
pKa		3.96 (Tomlin, 1994)	2.92 (Syracuse research corporation, 2000), 3.3 (Tomlin, 1994)
KH [atm·m^3/mole]	$8.56 \cdot 10^{-7}$		$7.11 \cdot 10^{-10}$
KH' [L(water)/L(air)]	$3.56 \cdot 10^{-5}$		
	Fenpropimorph (67306-03-0)	Glyphosate (1071-83-6)	
Structure			
Molecular weight [g/mole]	303.5	169.1	
Vapour pressure [mPa]	2.3 (20°C)	0.04	
Aqueous solubility [mg/L]	4.3 (pH 7)	12000 (25°C)	
K_{ow} [L (water)/L (oct.)]	24475 (pH9) 11441 (pH 7) 395 (pH 5)	0.00000381 (pH 4.3)	
K_{od} [L (water)/kg (soil)] (%OC)	22.6-73.7 (0.51-2.66) (pH 7.0-7.3)	22-205	
pKa	6.98	2.74, 5.63, 10.18	

* Is considered to be for the neutral form although not specified in the source. Unless where specified, data are from Danish EPA (2002).

Pendimethalin is a selective herbicide belonging to the chemical group of dinitroanilines. It has low water solubility and high octanol-water partition coefficient log K_{ow} (5.18 (United States department of agriculture, 2001)). According to the Danish EPA registration database, pKa is 2.8, which, assuming that it is an acid, means that it is a rather strong acid. However, this seems to be an error as no other data indicating acidity have been found.

Bentazone is a selective contact herbicide and a strong acid due to its sulfonamide group, with pKa = 2.92 (Syracuse research corporation, 2000). Bentazone has high water solubility, due to its charge at neutral pH. K_{ow} is quite low even for the neutral form: 219. For different levels of dissociation, K_{ow} has been measured to be 5.84 (pH 5), 0.35 (pH 7) and 0.28 (pH 9) (Tomlin, 1994). Kd values of 0.00 to 0.23 for nine Spanish, German and Italian soils have been reported with no correlation between humic acid content, clay content or pH and Kd (Fomsgaard, 1997).

Ioxynil is also a selective contact herbicide and a relatively strong acid. Ioxynil is available as different salts or as octanoate. The ioxynil octanoate is practically insoluble in water (Tomlin, 1994). In this project, ioxynil salt has been used for experiments.

Fenpropimorph is a systemic fungicide belonging to the morpholine group. K_{ow} is dependent on pH. With pKa about 7, K_{ow} varies three orders of magnitude in the pH range 5-9.

Glyphosate is non-selective herbicide from the phosphonic acid group. It is ionic, water-soluble and adsorbs to soil.

3 Introduction laboratory experiments

As stated in the introduction, the general objective of the laboratory experiments was to investigate the importance of processes and variance of process parameters between different pesticides and between different environmental conditions and to derive suitable parameters for model evaluation.

Various environmental conditions influence sorption. The pH level of the water influences the sorption of pesticides with acidic or basic properties as partitioning of charged species into organic matter, e.g. in the sediment, normally is much lower than that of neutral species. In streams originating from and flowing through calciferous soils, pH can be expected to be between 7.5 and 8.5. For pesticides with acidic properties, this could mean that virtually all of the pesticides is in the charged and more water-soluble form. In this study, however, the effect of pH was not studied as this effect is very pesticide-specific and methods already exist for the correction of pH effect on sorption.

The variation of K_{om} and thereby K_d with temperature is not well investigated but it seems that sorption often diminishes with increase in temperature. The size of the compound is important as it influences dissociation and the influence of temperature on sorption of larger compounds is much more pronounced than on sorption of smaller compounds (Schwarzenbach et al., 1993). The temperature of small streams in Denmark usually varies within approx. 7-25°C.

The concentration of pesticides in the water, in relation to the particle concentration, can be important for sorption rates and sorption equilibria as the sorption may be non-linear. Sorption may also influence biodegradation, due to decreasing bioavailability, and degradation rates in the water column, in water-sediment suspensions and in the sediment can be expected to be different.

Thus, the objective of the laboratory studies was to determine sediment-water partitioning equilibrium constants, sorption and desorption kinetic parameters and degradation rates for the sorption and degradation of selected pesticides in different water-sediment systems, at different temperatures and at different pesticide concentrations:

- Determination of sorption rates
- Determination of desorption rates
- Determination of sorption equilibria
- Determination of variation in sorption rates with concentration
- Determination of variation in sorption equilibria with concentration and temperature
- Determination of biotic degradation rates in surface water and in water-sediment systems

As mentioned in the introduction, the registration model was set up for two catchments, the Lillebæk catchment and the Odderbæk catchment, and thus sorption and degradation in water-sediment systems with sediments from the Lillebæk and the Odderbæk streams were investigated. Additionally, sediments from the four lakes, Vaparanta, Höytiäinen, Kuorinka and Mekrijärvi, were included in the study to broaden the span of sediment properties. As the catchments do not actually contain any suitable ponds, sorption in systems with sediment from the artificial pond at NERI and from four lakes was investigated.

The three pesticides, pendimethalin, ioxynil and bentazone, were chosen as model compounds because they are applied and found in the catchments studied and because they represent diverse physico-chemical properties.

In order to keep the number of experiments within a reasonable number, the processes were only studied with the most relevant combinations of sediment and pesticide. The combinations of pesticide and sediment used for the different studies are shown in Table 3.1.

Table 3.1
Laboratory experiments performed

	Pendimethalin	Ioxynil	Bentazone
Sorption rates	Pond Odderbæk Lillebæk Vaparanta	Odderbæk Lillebæk	
Desorption rates	Pond		
Sorption equilibria	Pond Odderbæk Lillebæk Vaparanta Höytiäinen Kuorinka Mekrijärvi	Pond Odderbæk Lillebæk Vaparanta Höytiäinen Kuorinka Mekrijärvi	Pond Odderbæk Lillebæk Vaparanta Höytiäinen Kuorinka Mekrijärvi
Variation in sorption rates with concentration	Pond Vaparanta	-	-
Variation in sorption equilibria with concentration	Pond Lillebæk Odderbæk Vaparanta	Lillebæk Odderbæk	Lillebæk Odderbæk
Variation in sorption equilibria with temperature	Vaparanta Höytiäinen Kuorinka Mekrijärvi	Vaparanta Höytiäinen Kuorinka Mekrijärvi	Vaparanta Höytiäinen Kuorinka Mekrijärvi
Degradation rates	No sediment Odderbæk Lillebæk	No sediment Odderbæk Lillebæk	No sediment Odderbæk Lillebæk

In order to investigate desorption phenomena, a desorption experiment was conducted in which desorption of recently sorbed pendimethalin from pond sediment was investigated. Two pesticide concentrations were studied in the desorption experiments.

An overview of the performed experiments is given in Tables 4.2 and 4.3 in Section 4.2.

4 Methods and materials, laboratory experiments

4.1 Materials

4.1.1 ^{14}C-labelled pesticides and chemicals

[Benzene(U)-^{14}C]pendimethalin in acetonitrile was obtained free of charge from American Cyanamid. Specific activity was given as 55.42 µCi/mg pendimethalin. Chemical purity > 99% andradiopurity >99.22%. July 1999. Amount supplied was 0.255 mCi in 2.10 mL equivalent to 121 µCi/ml or 2.18 mg/mL.

[Benzene(U)-^{14}C]ioxynil was obtained free of charge from Aventis crop science. Specific activity was given as 72.36 µCi/mg ioxynil. Radiopurity >98.5%. May 2000. Amount supplied was 0.28 mCi as 3.8 mg solid.

[Diazine-ring-^{14}C]bentazone in acetonitrile was obtained from the Institute of Isotopes, Hungary. Specific activity was given as 0.333 µCi/mg bentazone. Chemical purity > 95% and radiopurity >95%. June 2000. Amount supplied was 0.250 mCi or 750 mg in 2.0 mL.

The scintillation liquid, Instagel II plus from Packard bioscience B.V., was used for scintillation.

NaN_3 and $CaCl_2 \cdot 2H_2O$ used were of analytical quality.

4.1.2 Sediments

Sediment from five locations: An artificial pond at NERI Roskilde, a small stream in Jutland (Odderbæk), a small stream on Funen (Lillebæk) and four Finnish lakes, were used for sorption experiments.

Pond sediment
The pond sediment was taken from pond 1 at NERI. The details of this artificial pond are given in Section 7.1. The pond had not, at the time of sampling, been exposed to any pesticides.

The pond sediment was collected in August 1999 using a metal grab. The top sediment was preferred and the approximate maximum depth, to which the sample was taken, was around 5 cm. At the time of sampling, there was an abundance of plants, e.g. reed mace and submerged weed, in the pond and thus, the sample invariably included some of these macrophytes. At the laboratory, the plants were, however, thoroughly rinsed to keep fine particles in the sample and then removed from the sediment. The sediment was sieved to remove particles, leaves and other material larger than 2 mm.

Stream sediments

The Lillebæk catchment is situated east of the town of Oure and the Lillebæk stream reaches the sea at Fredskov on the east coast of Funen. The upper third of the stream is running beneath the ground surface in drain pipes. It is quite a small stream, which has a width of 1-3 metres and is very shallow most of the year, depth 0-30 cm. The catchment is dominated by moraine clay soils.

Sediment from Lillebæk stream was collected in August 2000 by metal grab. The appearance of the sediment was soft muddy/slushy with some larger particles. The sediment was received with a dry weight (D.W.) content of 42.7%.

The Odderbæk catchment is situated in northern Jutland and is dominated by sandy soils. The stream is about 2-3 metres wide and, in March, it was around 75 cm deep. Sediment from Odderbæk was collected by metal grab in August 2000. The sediment appeared sandy with some mud. The sediment was received with a D.W. content of 34.4%.

The sediments were air-dried, sieved to remove particles larger than 2 mm, and stored at 10°C in the dark until use.

Lake sediments

The four lake sediments were collected from four freshwater bodies close to the city of Joensuu in eastern Finland. These sediments were included to expand the ranges of organic carbon and particle distribution. They were chosen because they had already been used in a similar study regarding sorption and degradation. The sediments were unpolluted. The sediments from the lakes Varparanta, Kuorinka and Mekrijärvi were collected by Ekman grab while sediment from the lake Höytiäinen was collected using a pump. The Finnish lake sediments were stored at 5°C prior to shipment. All sediments were homogenized by stirring and wet sieving through a 2-mm sieve.

Measured sediment properties are given in Table 4.1. The organic carbon content of the sediments, f_{oc} or OC, was determined as ignition loss and as non-volatile organic carbon (NVOC). pH was measured in sediment-water slurries with a water to sediment ratio of 2.5. N-contents were only measured for the lake sediments, from 63-37 and 37-20 µm fractions (Elemental Analyzer Model 1106, Carlo Erba Strumentazione, Milano, Italy).

Table 4.1
Sediment properties

	Ignition loss g/kg D.W.	NVOC g/kg D.W.	Slurry pH	N g/kg D.W.
Lillebæk	25	29	7.85	-
Odderbæk	197	100	7.18	-
Pond	82	33	7.57	-
Höitiäinen	86.4	32.0	-	2.3
Kuorinka	31.5	16.4	-	0.7
Mekrijjärvi	413.9	242.8	-	12.6
Varparanta	15.6	5.4	-	0.1

The particle distribution was determined by sieving and weighing. The sediment particle distributions are shown in Figures 4.1-4.2. Raw data are given in Tables B.27-B.28 in Appendix B.

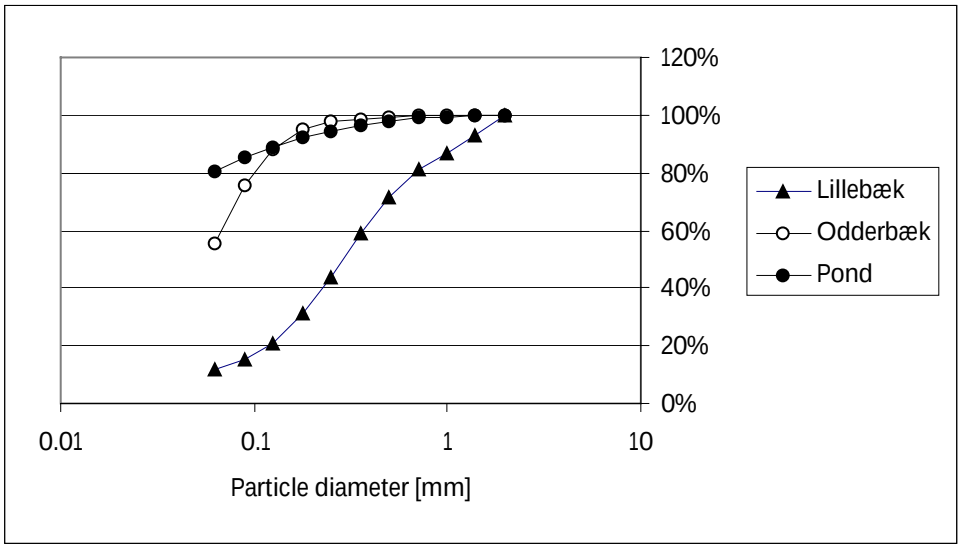


Figure 4.1
Particle size distribution of pond and stream sediments. Only the fraction below 2 mm has been considered.

As Figure 4.1 shows, the Lillebæk sediment has a much more even distribution of particle sizes than the other two sediments, which are composed predominantly of small particles. In the pond sediment, 80% is smaller than 0.063 mm. From Table 4.1, it can be seen that Lillebæk has similar organic matter content as the pond sediment, f_{oc} around 3% while Odderbæk sediment has a somewhat higher organic matter content, f_{oc} of 10%. f_{oc} is the fraction of organic carbon on a weight basis and, when given in %, corresponds to % OC.

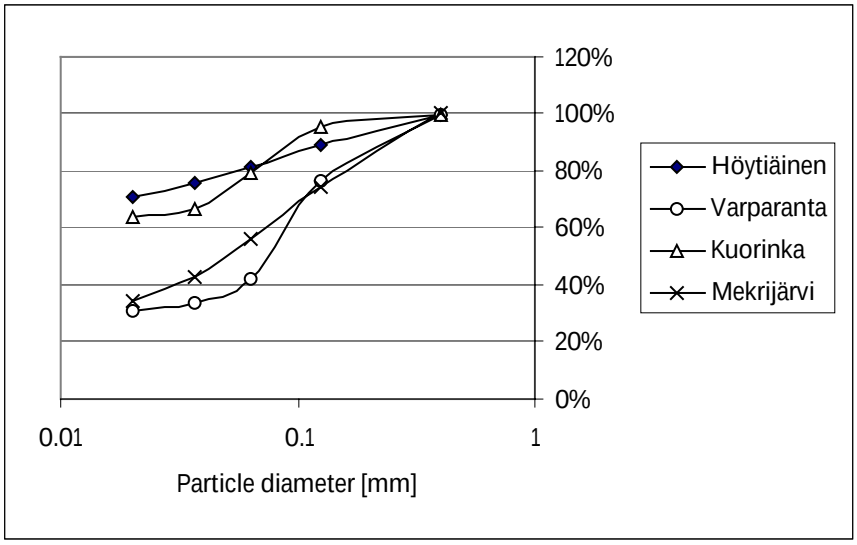


Figure 4.2
Particle size distribution of lake sediments. Only the fraction below 2 mm has been considered.

The lakes Hyötiäinen and Kuorinka have a fine particle size distribution while Lake Mekrijärvi is characterized by very high organic carbon content, f_{oc} of 24%. Lake Varparanta is a sandy, coarse particulate sediment with very low organic carbon content, f_{oc} of 0.5%.

4.1.3 Stream water

For the degradation experiments, water from Mølleåen was used. Mølleåen is a stream running through Lyngby and Søllerød north of Copenhagen and is the connection between the euthrophic lakes Furesøen, Lyngby sø and the sea. It is a slow flowing stream with high biological activity. The water was taken from a slow flowing part downstream of the lakes, approx. one kilometer from where it falls into the sea.

4.2 Set-up overview

Sorption, desorption and degradation experiments were performed. Sorption and desorption were investigated by "kinetic" and "equilibrium" experiments. In the "kinetic" experiments, both kinetics and equilibrium partitioning were investigated while in the "equilibrium" experiments, only the equilibrium distribution was determined. In the degradation experiments, the disappearance from surface water or surfacewater sediment mixtures was investigated.

The kinetics of sorption of the two pesticides, pendimethalin and ioxynil, to the pond, Lillebæk, Odderbæk and Vaparanta sediments was investigated. The kinetics of sorption was not investigated for bentazone as sorption of bentazone is very limited and not considered to be important for its fate in streams and ponds. For the Vaparanta sediment, kinetics of sorption were investigated at five pendimethalin concentration levels and for the pond sediment, at two pendimethalin concentration levels. Otherwise, kinetics was studied at one concentration level only.

Equilibrium partitioning was determined for all combinations of pesticide and sediment except for pond sediment for which equilibrium partitioning was only determined for pendimethalin. Equilibrium partitioning was determined at different pesticide concentration levels and, for the lake sediments, at two different temperatures, 4°C and 20°C.

The kinetics and equilibrium partitioning of desorption was only investigated for pendimethalin and pond sediment.

An overview of the sorption and desorption experiments performed is given in Table 4.2.

Table 4.2
Experimental set-up of sorption and desorption experiments

	Pendimethalin			Ioxynil			Bentazone		
	Exp type	Conc	Phase anal	Exp type	Conc	Phase anal	Exp type	Conc	Phase anal.
Pond	kin. 10 °C	high	w,s all						
	kin. 10 °C	low	w,s all						
	desorp kin. 10 °C	high							
	desorp kin. 10 °C	low							
Lillebæk	kin. 10 °C	high	w, (s final)	eq. 10°C	high	w,s	eq. 10°C	high	w,s
	eq. 10 °C	med	w,s	kin. 10°C	med	w, (s final)	eq. 10°C	med	w,s
	eq. 10°C	low	w,s	eq. 10°C	low	w,s	eq. 10°C	low	w,s
Odderbæk	kin. 10°C	high	w, (s final)	eq. 10°C	high	w,s	eq. 10°C	high	w,s
	eq. 10°C	med	w,s	kin. 10°C	med	w, (s final)	eq. 10°C	med	w,s
	eq. 10°C	low	w,s	eq. 10°C	low	w,s	eq. 10°C	low	w,s
Varparanta	kin. 10°C	v. high	w, (s final)						
	kin. 10°C	high	w, (s final)						
	eq.20°C	med	w	eq. 20°C	med	w	eq. 20°C	med	w
	kin. 10°C	med	w, (s final)						
	eq. 4°C	med	w	eq. 4°C	med	w	eq. 4°C	med	w
	kin. 10°C	low	w, (s final)						
	kin. 10°C	v. low	w, (s final)						
Mekrijärvi	eq. 20°C	med	w	eq. 20°C	med	w	eq. 20°C	med	w
	eq. 4°C	med	w	eq. 4°C	med	w	eq. 4°C	med	w
Kuorinka	eq. 20°C	med	w	eq. 20°C	med	w	eq. 20°C	med	w
	eq. 4°C	med	w	eq. 4°C	med	w	eq. 4°C	med	w
Høytäinen	eq. 20°C	med	w	eq. 20°C	med	w	eq. 20°C	med	w
	eq. 4°C	med	w	eq. 4°C	med	w	eq. 4°C	med	w

"Exp. type" indicates type of experiment (kin. : kinetic or eq. :equilibrium) and temperature, "Conc." indicates concentration level (v. is very) and "Phase anal." indicates the phases (w: water, s: sediment) in which activity was measured at given timepoints (all or final). "All" indicates that activity was measured at all time points.

"Exp. type" angiver eksperimenttypen (kin. : kinetisk eller eq. : ligevægt) og temperatur, "Conc." angiver koncentrationsniveau (v. er meget) og "Phase anal." angiver de forskellige faser (w: vand, s: sediment) hvor aktiviteten blev målt på givne tidspunkter (alle eller slut). "All" angiver, at der blev målt aktivitet på alle tidspunkter.

Degradation was studied in surface water (Mølleåen) at two concentration levels and in mixtures of surface water and stream sediment (Lillebæk and Odderbæk) at one concentration level. The degradation experiments performed are listed in Table 4.3.

Table 4.3
Experimental set-up of degradation experiments with stream and pond sediments

	Pendimethalin		Ioxynil		Bentazone	
	Conc	Phase anal.	Conc	Phase anal.	Conc	Phase anal.
No sediment	high	w, all	high	w, all	high	w, all
	low	w, all	low	w, all	low	w, all
Lillebæk	low	mix, all	low	mix, all	low	mix, all
Odderbæk	low	mix, all	low	mix, all	low	mix, all

"Conc." indicates concentration level and "Phase anal." indicates the phases (w: water, mix: a mixture of water and sediment) in which activity was measured. "All" indicates that activity was measured at all time points.

"Conc." angiver koncentrationsniveau og "Phase anal." angiver de forskellige faser (w: vand, mix: en blanding af vand og sediment) hvor der er målt aktivitet. "All" angiver, at der blev målt aktivitet på alle tidspunkter.

4.3 Experimental procedures

All experiments were performed with radiolabelled compounds.

4.3.1 "Kinetic" sorption experiments

All "kinetic" experiments were conducted as parallel studies with duplicate samples and controls. A large number of microcosms was set up (30-mL pyrex glass tubes with PTFE-lined caps, radiolabelled pesticide, biocide, sediment and water) and terminated individually after equilibration for different periods of time. Controls were similar but without sediment. A sediment to water ratio of 1 g dry weight (air-dried) sediment to 12 mL water was used in all cases. The equilibration was allowed to take place for up to 20 days. After withdrawal, the suspensions were centrifuged at 5400 g, for 2 × 30 min. This should sedimentate particles larger than 0.0001 mm. Concentrations were determined in the aqueous phase, and in selected cases (see Table 4.2), in the solid phase by scintillation counting.

In the "kinetic" experiments, test tubes were terminated at four individual temination times. At all termination times, sets of two test tubes and two control tubes were removed from the shaking bed together, giving duplicate values for all termination times.

Table 4.4
Termination times

Experiment	Time
"Kinetic" experiments, pond sediment	3, 24, 168 and 480 hours
"Kinetic" experiments, stream sediments	2, 6, 24 and 197/198 hours
"Kinetic" experiments, Lake Vaparanta	1, 4, 24 and 48 hours

"Kinetic" sorption experiments with pond and stream sediments
In these experiments, 8 test tubes and 8 controls, giving duplicates at four termination times, were set up for each combination of sediment and pesticide. Each test tube (microcosm) was prepared by adding 1.0 g of air-dried sediment to a 30-mL round-bottomed glass test tube with PFTE-lined screw cap, adding 4 mL of 30 mM NaN_3 solution and shaking for 16 hours at 10°C. This was to pre-wet the sediment and glass surface. After pre-wetting, 8 mL of pesticide solution was added to each tube with a plastic pipette and the shaking was initiated. The tubes were shaken on a shaking table set at 150 rev/min at 10°C in the dark. The control tubes were made in the same way, except that no sediment was added and they were shaken together with the test tubes.

In the experiments with pendimethalin and pond sediment, the content of each of the test tubes was transferred to a pair of 7-mL ultracentrifuge tubes, which were centrifuged twice for 30 min at 5400 g and 4°C. Upon completion of the centrifugation, twice 2 mL of the supernatant from each centrifuge tube were transferred to scintillation vials together with 15 mL scintillation liquid and activity was determined using liquid scintillation counting (LSC). For the test tubes in the other sorption experiments and for all controls, only 5-6 mL was transferred from the test or control tube to one ultracentrifuge tube. Otherwise, the procedure was the same (see Figure 4.4).

The sediment was isolated in the centrifuge tubes by removing as much of the supernatant as possible with a pipette and evaporating the remainder at 60°C in an oven. This was necessary because the solid phase scintillation counter required absolutely dry samples. The centrifuge tubes were weighed before and after drying and the amount of water evaporated from the centrifugate was calculated and used in correction of solid phase analysis results. The dry weight of the sediment was calculated by subtracting the weight of the empty tube from the weight of the tube containing oven-dried centrifugate.

In selected cases (see Table 4.2), the activity in the sediment was determined. This was done by mixing the centrifugates from the pair of centrifuge tubes (originating from the same test tube) thoroughly and withdrawing 0.100 or 0.050 mg to a ceramic sample holder (boat). The boat was placed in an exicator until scintillation counting could be performed. The determination of activity in the dried sediment was made by incineration of the sample in a Carbolite CFM12/1 oven at 600°C, collecting of CO_2 and analysing by LSC. In a few cases, the centrifugate from each centrifuge tube was counted individually to determine variability between centrifuge tubes. When calculating C_s, corrections were made for the activity left in the sediment by evaporating residual water, which could not be removed with pipette before drying.

In order to determine the sorption to glassware for pendimethalin, all glassware, i.e. microcosm bottles and centrifuge tubes used in the experiment with pond sediment, was washed with acetone. Both micrososm bottles and centrifuge tubes were washed with 2 mL of acetone per glass after the content had been removed. The 2 mL of acetone was added to 15 mL scintillation liquid in a scintillation vial and counted using LSC.

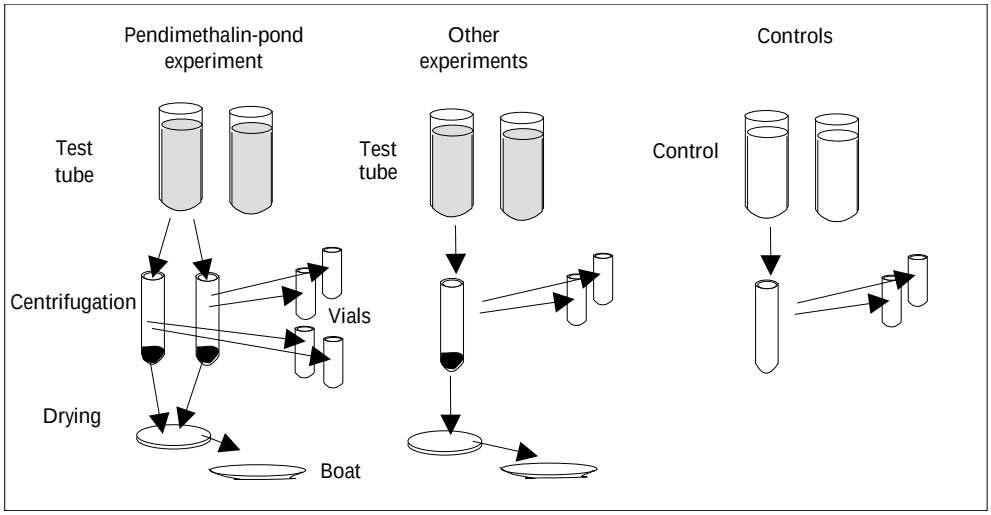


Figure 4.4
Termination procedures followed in sorption experiments

"Kinetic" sorption experiments with pendimethalin and Vaparanta sediment
In this experiment, 8 test tubes and 8 controls, giving duplicates at four temination times, were set up for each of five concentrations of pesticide. Test tubes were set up by weighing 0.5 g air-dried sediment (0.99 g D.W./g sediment) into a 30-mL round-bottomed glass test tube with teflon-lined screw cap and adding azide and $CaCl_2$ solution. After shaking (pre-wetting)

for 24 hours, different amounts of pesticide stock solution were added according to the different concentration levels. The final water volume V_w was 12 mL in all cases giving a solid:liquid ratio of 1:24 [g:mL]. The controls were set up the same way, except that no sediment was added. All tubes were then shaken on a shaking table in the dark, at 10°C, for different periods of time (1, 4, 24 and 48 hours). When a termination time was reached, 2 test tubes and 2 control tubes were withdrawn and subsamples hereof (only test tubes) (approx. 5 mL) were centrifuged for 2 x 30 min at 5400 g. The activity in 2 mL of the supernatant and in the aqueous phase of control tubes was determined using scintillation counting. For the final test tubes, terminated after 48 hours, the activity in the centrifugate was also determined by incineration at 600°C, collection of CO_2 and scintillation counting (see description above).

Amount of stock solution added and nominal total concentration in the test tube is shown in Table 4.5.

Table 4.5
Concentration levels of pendimethalin in kinetic experiments with Vaparanta sediment

Concentration designation	Amount stock sol. added	C_T-nominal concentration in tube	
	mL/tube	dpm/L	mg/L
Very low	0.5	690122	0.0056
Low	1	1380244	0.0112
Medium	2	2760489	0.0224
High	4	5520978	0.0449
Very high	8	11041956	0.0897

4.3.2 "Kinetic" desorption experiments

Initially, a normal sorption experimentwith pendimethalin and pond sediment was conducted exactly as described in Section 4.3.1 for pond and stream sediments: 8 test tubes and 8 controls for each of two concentrations (a total of 32 tubes) were set up. 1 g of air-dried sediment was added to each test tube. In order to pre-wet the sediment, 4 mL of 0.01-M NaN_3 (azide) solution was added and the tubes were shaken for 16 hours. Following the pre-wetting, 8 mL of the relevant pesticide solution was added and the 32 tubes were shaken for 12 days in the dark at 10°C to facilitate sorption. After this period of sorption, the tubes were centrifuged for 21 hours at 870 g. This should sedimentate particles down to 0.0001 mm in diameter. Twice 2-mL samples were withdrawn from the supernatant for determination of activity by LSC and as much as possible of the remaining aqueous phase was removed with a pipette. The amount of residual water was determined by weighing of the test tubes.

The desorption experiment was then initiated by adding 10.5 mL of a 0.01-M azide/0.01-M $CaCl_2$ solution to each test tube. The controls were not altered. Again, the tubes were shaken in the dark at 10°C and sets of two replicate test tubes and two controls with high concentration, and two replicate test tubes and two controls with low concentration, were withdrawn at different termination times (1, 3.5, 24 and 240 hours). The content of the withdrawn test tubes were transferred to pairs of centrifuge tubes, which were

centrifuged twice at 5400 g at 4°C for 30 min with which particles larger than 0.0001 mm should sedimentate. One 2-mL sample from each supernatant was transferred to a vial with 15 mL of scintillation liquid and counted using LSC. The centrifugate was dried at 60°C in the centrifuge tubes. The dry centrifugate was mixed and a sample of approx. 0.100 mg was transferred to a ceramic sample holder (boat) and left in an exicator until activity could be determined. Activity was determined by incineration at 600°C, collection of CO_2 and scintillation counting (see above description). The controls were not centrifugated but two samples of 2 mL from each were withdrawn for determination of activity.

4.3.3 "Equilibrium" sorption experiments

"Equilibrium" experiments with pond and stream sediments
These "equilibrium" experiments were conducted in the same way as the "kinetic" experiments, the only difference being that all samples were terminated at the same time after a 195-hour period of shaking. From the results of the kinetic studies, this period was considered sufficient for equilibration. The concentrations were determined in both phases in these experiments. pH was measured in the supernatant after centrifugation.

"Equilibrium" experiments with lake sediments at different temperatures
"Equilibrium" experiments with lake sediments were performed similar to the other "equilibrium" experiments except that PFTE centrifuge tubes were used and that, for each sediment-pesticide combination, two sets of duplicates were set up and shaken at different temperatures. Each test tube (microcosm) was prepared by adding 1.0 g of air-dried sediment to a 30-mL round-bottomed PFTE test tubes with screw caps, adding 4 mL of 30-mM NaN_3 solution and shaking for 16 hours at 10°C. This was to pre-wet the sediment and inner tube surface. After pre-wetting, 8 mL of pesticide solution was added to each tube with a plastic pipette and the shaking was initiated. Two sets of triplicate control tubes were made in the same way, except that no sediment was added. One set of duplicate test tubes and triplicate controls was shaken on a shaking table at 4°C, in the dark, while another set of test tubes and controls was shaken at 20°C in daylight. After termination at 195 hours, the test tubes were centrifuged for 24 hours at 5000 g. 2 mL of the supernatant was added to 15 mL of scintillation liquid and the activity was determined by LSC. pH was measured in the supernatant.

4.3.4 Degradation experiments

For each pesticide, four types of microcosms were set up in sets of triplicates. Two "pelagic" microcosm sets with stream water and pesticide in different concentrations (low and high) and two "suspension" microcosm sets with the same pesticide concentration (low) but with different sediments (Odderbæk and Lillebæk)(see Table 4.3.). Additionally, one set of four "pelagic" controls with water, biocide and pesticide at low concentration and one recovery set of three pelagic low pesticide concentration bottles were set up. The bioside was added to controls to inhibit biotic degradation. The recovery set was to be used for determination of recovery.

Each microcosm was prepared by adding stock solution according to Table 4.6 to the bottom of a 300-mL serum glass bottle (with PFTE-lined cap) and letting the solvent evaporate. After evaporation, 100 mL of stream water was added and, for the suspension microcosms, additionally 100 mg D.W. of

stream sediment was added. For the "pelagic" controls, water composed of 20 mL of 1 M NaN_3 in 2000 mL of stream water yielding 10 mM NaN_3 was used.

The microcosms were shaken at room temperature (22-25°C) in the dark and samples of 5 mL suspension/water were withdrawn from each test bottle after 1 hour and then every five days. When sampling was performed, the bottles were opened and headspace was passively renewed. In order to get a representative sample from the bottles with suspension, these were shaken well before a sample was withdrawn. Samples were taken from control bottles and recovery bottles after 1 hour and after 103 days. These bottles were kept closed for the duration of the incubation.

In order to remove dissolved radiolabelled CO_2 before LSC, 2 mL of concentrated HCL was added to the withdrawn samples and the mixture was shaken over night. The effectiveness of the stripping was investigated by shaking for 6 hours more and comparing scintillation counts. After stripping, 2 mL of the sample was added to a scintillation vial with 15 mL of scintillation liquid and activity was determined using LSC.

The experiment was finalised by weighing the water/suspension left in the test bottles after the final subsample withdrawal. In the recovery bottles, pH was lowered to 2 by adding HCL, and CO_2 was collected by leading N_2 through the bottle and through an external absorber of 10 mL 1 N NaOH. The activity collected in the absorber was determined by counting a 2-mL subsample using LSC. The residual activity in the recovery bottles was determined from 5-mL subsamples and the residual amount determined by weighing. The activity in the controls was determined in the same way as for the test bottles, by withdrawing and analysing a 5-mL subsample and weighing the residual content.

The amount of stock solution added to the bottles in the degradation experiment and the resulting concentrations are shown in Table 4.6.

Table 4.6
Amounts of stock solution added and resulting nominal and measured concentrations

Test tube	Sediment	Conc level	Stock solution added µL	Nominal conc. in bottle µg/L	Measured conc. µg/L
Pendimethalin pelagic	No sediment	High	250	54.5	54.4
Pendimethalin pelagic	No sediment	Low	125	27.3	27.3
Pendimethalin suspended sediment	Odderbæk	Low	125	27.3	27.3
Pendimethalin suspended sediment	Lillebæk	Low	125	27.3	27.3
Ioxynil pelagic	No sediment	High	500	37.5	43.5
Ioxynil pelagic	No sediment	Low	250	18.75	21.7
Ioxynil suspended sediment	Odderbæk	Low	250	18.75	21.7
Ioxynil suspended sediment	Lillebæk	Low	250	18.75	21.7
Bentazone pelagic	No sediment	High	600	9.0	13.5
Bentazone pelagic	No sediment	Low	300	4.5	6.75
Bentazone suspended sediment	Odderbæk	Low	300	4.5	6.75
Bentazone suspended sediment	Lillebæk	Low	300	4.5	6.75

4.3.5 Pesticide solutions used in experiments

For the experiments, a large number of ^{14}C pesticide solutions were made. Detailed information on the preparation of these solutions is given in Appendix A. In all aqueous solutions, concentration was kept below half of the saturation concentration.

In Table 4.7 below, an overview of the pesticide concentration in the solutions used in the experiments is shown. Before use, the activity of each solution was measured and both nominal and measured concentrations are given.

Table 4.7
Measured and calculated pesticide concentrations in solutions used in the experiments

Experiment	Conc	Nominal		Measured	
		micro Ci/mL	mg/L	micro Ci/mL	mg/L
Pendimethalin					
Degradation	stock	1.21	21.8	1.21	21.8
kinetics pond	low	0.0061	0.11	0.0053	0.096
kinetics pond	high	0.012	0.22	0.011	0.20
equilibrium stream	low	0.0033	0.055	0.0020	0.036
equilibrium stream	medium	0.0061	0.11	0.0052	0.093
kinetics stream	high	0.0097	0.18	0.0066	0.12
temperature, lake	high	0.0097	0.18	0.0072	0.13
Desorption	low	0.0061	0.11	0.0051	0.092
Desorption	high	0.012	0.22	0.011	0.19
Ioxynil					
	stock	0.56	7.6		
equilibrium stream	low	0.0028	0.038	0.0028	0.038
kinetics stream	medium	0.022	0.30	0.023	0.32
equilibrium stream	high	0.028	0.38	0.031	0.43
temperature, lake	medium	0.022	0.30	0.023	0.31
Degradation	Stock 2	0.56	7.6	0.63	8.7
Bentazone					
	stock	0.50	1500	-	-
equilibrium stream	low	0.00020	0.60	0.00023	0.69
equilibrium stream	medium	0.0010	3.0	0.0013	3.9
equilibrium stream	high	0.010	30	0.014	42
temperature, lake	medium	0.0013	3.8	0.0018	5.4
Degradation	stock 2	0.50	1500	0.75	2250

5 Results and discussion, laboratory experiments

The results of the sorption experiments are shown with raw data in Tables B.1-18 in Appendix B.

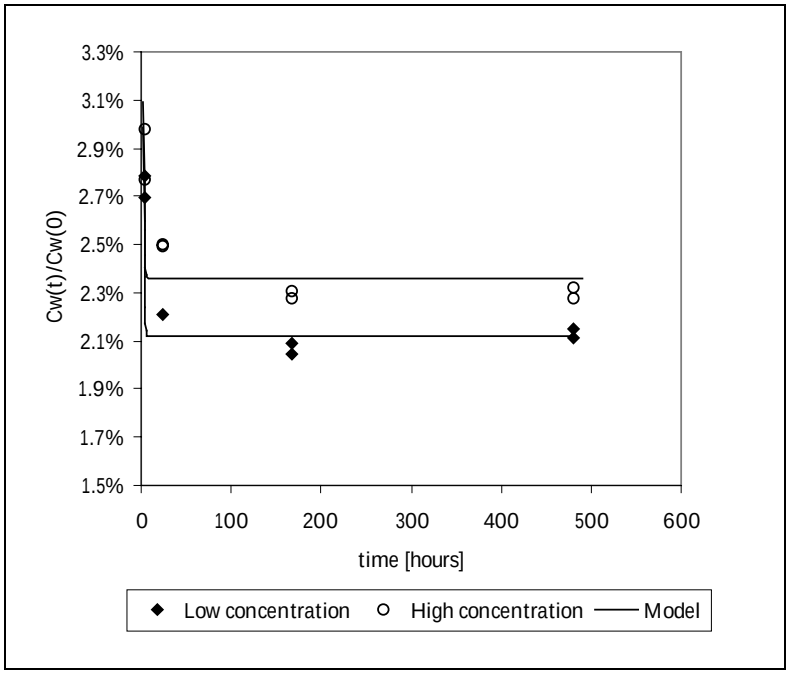
5.1 "Kinetic" sorption experiments

The kinetics of sorption of pendimethalin and ioxynil to pond sediment, two stream sediments and Lake Vaparanta sediment was studied.

5.1.1 Pendimethalin and pond sediment

The kinetics of sorption of pendimethalin, at two concentrations, to pond sediment was investigated and the measured pesticide concentrations in the water phase, at 3, 24, 168 and 480 hours, are shown in Figure 5.1. The raw data are given in Tables B.3 and B.5 in Appendix B. The pesticide concentrations in the water phase were reduced to around 2-3% of the initial value within three hours showing rapid sorption. This is a reduction from 101 to 2.7 µg/L (high concentration) and from 50 to 1.3 µg/L (low concentration). The equilibrium Kd values are given in Table 5.4.

For high and low concentration controls, the deviation between replicates was less than 8.5% and 3.2% in average.



Figures 5.1
Kinetics of sorption of pendimethalin to pond sediment at two concentrations. Measured data were fitted with the model described in Section 5.1.5.

5.1.2 Pendimethalin and stream sediments

Kinetics of sorption of pendimethalin to stream sediments was investigated at one pesticide concentration (high). Measured pesticide concentrations in the water phase, at 3, 24, 168 and 480 hours, are shown in Figure 5.2. Raw data are given in Tables B.5-B.6 in Appendix B. Also in this case, pendimethalin sorbed rapidly. Pesticide concentrations in the water phase were reduced to 2-3% of initial value within 3 hours for the Odderbæk sediment and to 5-6% of initial value for the Lillebæk sediment. This is a reduction in aqueous concentrations from 71 µg/L to 4.1 µg/L and 2.1 µg/L for Lillebæk and Odderbæk, respectively. It is obvious that pendimethalin sorbs more strongly to the Odderbæk sediment than to the Lillebæk sediment. The equilibrium Kd values are given in Table 5.4.

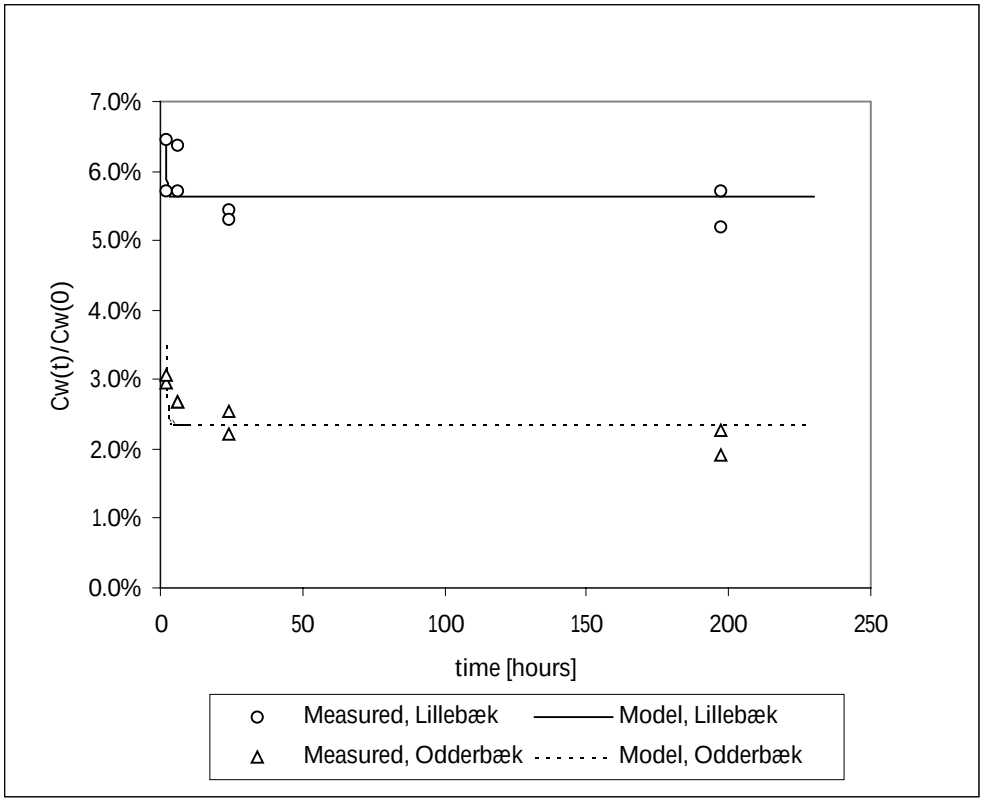


Figure 5.2
Kinetics of sorption of pendimethalin to stream sediments at high concentration. Measured data were fitted with the model described in Section 5.1.5.

5.1.3 Kinetic sorption to Lake Vaparanta sediment

An experiment was performed to evaluate the sorption kinetics at different concentration levels.

Kinetics of the sorption of pendimethalin to Lake Vaparanta sediment were investigated at 5 pesticide concentrations (very low, low, medium, high and very high) with the highest concentration being 20 times higher than the lowest. Measured pesticide concentrations in the water phase, at 1, 4, 24 and

48 hours, are shown in Figure 5.3. The raw data are given in Tables B.9-B.13 in Appendix B. The equilibrium Kd values are given in Table 5.4. Sorption seems to be fast at all concentrations with no discernible difference in sorption rates. It can be noted that there seemed to be a slight continuous decline in aqueous concentration, for the “med”, “high” and “very high” concentrations, even at 48 h when the experiment was terminated. The reason for such a decline could be intraparticle diffusion: After an initial sorption to available surfaces, the pesticide starts to diffuse slowly into the particles making room for additional sorption. However, the results from the other sorption studies, which were continued for a much longer period, did not in general indicate a second phase of slow sorption and no attempts were made to investigate this further. The decline is small and thus at least not important for the streams, in which retention time is short.

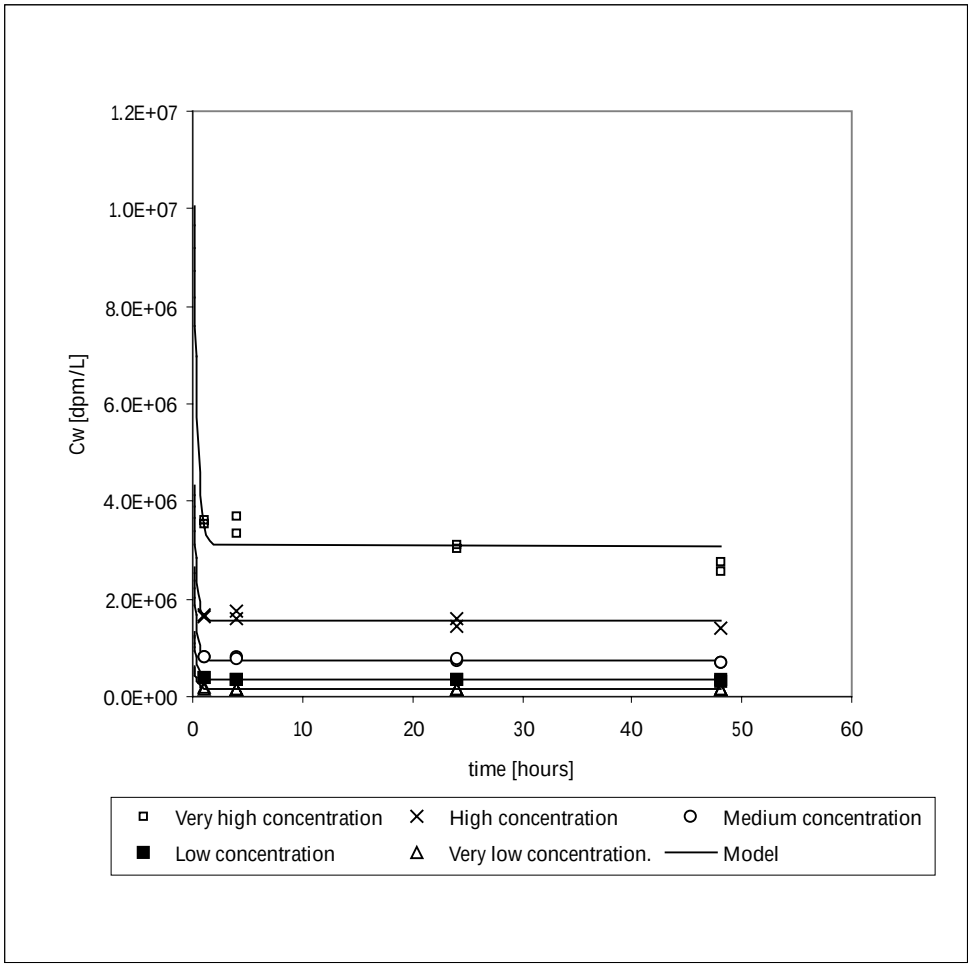


Figure 5.3
Sorption of pendimethalin to Lake Vaparanta sediment at different pendimethalin concentrations. Measured data were fitted with the model described in Section 5.1.5.

5.1.4 Ioxynil and stream sediments

In the kinetic experiment with ioxynil sorption to stream sediments, C_s was measured at all termination times: 2, 6, 24 and 198 hours. The sorption of ioxynil to the Odderbæk and Lillebæk sediments, at one concentration (medium), was investigated. Ioxynil did not sorb as much as pendimethalin

but the sorption was rapid, with a reduction in ioxynil aqueous concentration to 70% and 40% of initial values, within two hours, for Lillebæk and Odderbæk, respectively. This was a reduction from 210 µg/L to 150 µg/L and 90 µg/L, for Lillebæk and Odderbæk, respectively. The results are presented in Figure 5.4. Kd values are given in Table 5.4. The results indicate that the same kinetic sorption parameters can be used more or less regardless of pesticide concentration. This is in correspondance with the sorption model used, see Section 5.1.5.

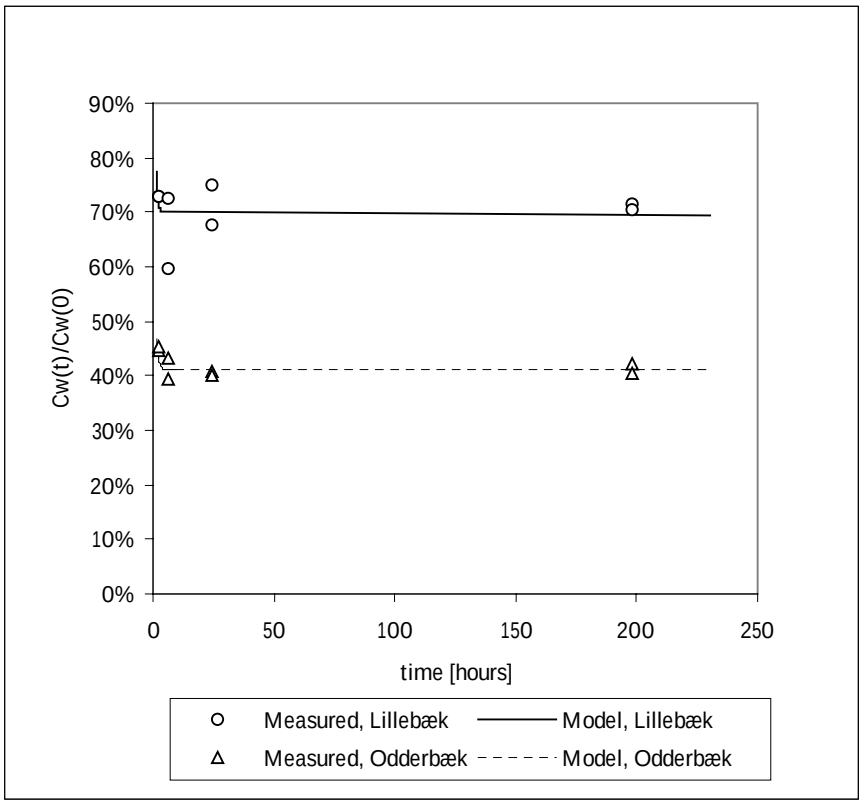


Figure 5.4
Kinetics of sorption of ioxynil to stream sediments at medium concentration. Measured data were fitted with the model described in Section 5.1.5.

5.1.5 Fitting of model to experimental sorption data

Many attempts to model the sorption/desorption kinetics have been described in literature. Often, the sorption process is observed to be biphasic: A rapid first phase accounting for 20-50% of the total sorption followed by a slower sorption, and the slower part of the sorption is often explained by diffusion of the solutes into the particles. The first phase is primarily considered to be a sorption process to the surface of the particles. In the majority of studies reported in literature, focus has been on the slower part of the sorption process, which is relevant when the contact time between sediment and chemical is long. Here, however, the first process has been focussed as the residence time is quite low in the flowing water systems considered.

It is assumed that the fast initial sorption can be regarded as a second order process according to:

Solute + Sorbent $\leftrightarrow$ Solute-Sorbent

If the kinetics are assumed to be linear, adsorption and desorption of solute on solids are expressed by the two-rate model (Thomann et al., 1987; Nyffeler et al., 1984) given by the differential equations:

$$\frac{dC_w}{dt} = -k_{sorp} \cdot C_w + k_{desorp} \cdot C_s$$
$$\frac{dC_s}{dt} = k_{sorp} \cdot C_w - k_{desorp} \cdot C_s$$

Equation 1

where C_w [mass/volume] is concentration of pesticide in water, C_s [mass/volume] is concentration of pesticide in sediment and k_{sorp} and k_{desorp} [time^{-1}] are first order sorption and desorption rate constants.

This sorption and desorption model is employed in the stream fate model incorporated in the registration model.

In order to fit this model to the experimental data and derive estimates of k_{sorp} and k_{desorp}, the differential equations have been solved algebraically (see Appendix G) yielding the expression:

$$C_w = C_T \cdot \frac{k_{sorp} \cdot e^{-(k_{sorp}+k_{desorp})\cdot t} + k_{desorp}}{k_{sorp} + k_{desorp}}$$

where C_T [mass/volume] is total concentration.

Using this expression, the model has been fitted to the data from the "kinetic" sorption experiments with non-linear least squares regression and the results are shown on Figures 5.1-5.4. Equal variation around the curve was assumed in all cases. The pesticide concentration in water C_w is measured in the experiments as dpm/L while C_T is derived from $C_{control}$ or, in the case of pond sediment, from an average of measured C_s and C_w, for all termination times, $C_T = C_w + C_s$. In the latter case, C_s[dpm/L water] was calculated as C_s[dpm/kg sed D.W.] $\cdot$ CP[kd sed D.W./L water] where CP is sediment concentration. The added amount of sediment, corrected to dry weight, was used in all cases for determining CP. $C_{control}$ was used for C_T in most fitting because C_s was considered unreliable and was not measured at all termination times.

The fitted values of k_{sorp} and k_{desorp} together with standard deviations are given in Table 5.1.

Table 5.1
Summary of sorption kinetics fitted model parameters

Pesticide	Sediment	Conc	Nominal C_T		C_T model		Kd values	k_{sorp} ± S.D.	k_{desorp} ± S.D.
			dpm/L	mg/L	dpm/L	origin	L/kg DW	h^{-1}	h^{-1}
Pendimethalin	Pond	Low	7848222	0.064	5742228	C_w+C_s	615	1.65 ± 0.03	0.036 ± 0.00093
Pendimethalin	Pond	High	16189889	0.132	11340599	C_w+C_s	551	1.71 ± 0.06	0. 041 ± 0.0020
Pendimethalin desorp	Pond	Low	7503452	0.061	5732893	$C_{control}$	832	7.0 ± 0.80	0.10 ± 0.013
Pendimethalin desorp	Pond	High	15517620	0.13	11541314	$C_{control}$	811	6.9 ± 0.92	0.10 ± 0.015
Pendimethalin	Lillebæk	High	9757167	0.079	8756531	$C_{control}$	224	2.50 ± 0.36	0.15 ± 0.024
Pendimethalin	Odderbæk	High	9757167	0.079	8756531	$C_{control}$	545	2.47 ± 0.18	0.060 ± 0.0063
Pendimethalin	Vaparanta	V. low	845184	0.0056	845184	$C_{control}$	50.5	3.12 ± 0.25	0.75 ± 0.07
Pendimethalin	Vaparanta	Low	1380244	0.011	1770744	$C_{control}$	49.2	2.93 ± 0.2	0.72 ± 0.06
Pendimethalin	Vaparanta	Med	2760489	0.022	3475806	$C_{control}$	44.5	2.83 ± 0.32	0.77 ± 0.1
Pendimethalin	Vaparanta	High	5520978	0.045	5638947	$C_{control}$	31.5	2.8 ± 0.88	1.08 ± 0.37
Pendimethalin	Vaparanta	V. high	11041956	0.090	12440113	$C_{control}$	36.7	2.21 ± 0.44	0.73 ± 0.17
Ioxynil	Lillebæk	Med	33708833	0.210	33624889	$C_{control}$	5.9	0.34 ± 0.17	0.77 ± 0.42
Ioxynil	Odderbæk	Med	33708833	0.210	33624889	$C_{control}$	19.2	0.79 ± 0.08	0.55 ± 0.059

Nominal C_{total} is nominal total concentration in the test tube based on activity determined in working solutions (given in Table 4.7).
Kd was calculated from Kd = Kd'/CP where Kd' = k_{sorp}/k_{desorp}.
C_T-model is the C_T used in fitting.

Nominal C_{total} er den nominelle, totale koncentration i reagensglassene beregnet ud fra den aktivitet, som er bestemt i arbejdsopløsningerne (se Table 4.7).
Kd blev beregnet ud fra Kd = Kd'/CP hvor Kd' = k_{sorp}/k_{desorp}.
C_T-model er den C_T, som er brugt ved tilpasningen (fitting).

It must be noted that, in all cases, sorption was very fast and that the experimental procedure did not allow measurements with very short intervals. The fitted rates reflect this and they may be underestimations of the actual rate but hardly overestimations. However, the shaking of pesticide, water and sediment is of course an ideal situation, in which optimal conditions for sorption is created, and sorption rates in systems, in which diffusion is important can be expected to be smaller. This would for example be the case in pond sediment, and here diffusion is taken into account in the model. From Table 5.1, it can be seen that fitted sorption rates for pendimethalin are between 1.65 and 3.12 h^{-1} while desorption rates are between 0.03 and 0.88 h^{-1}. The fitted sorption rate from the desorption experiment with pendimethalin is higher than that determined from the sorption experiment with the same pesticide and concentration. Fitted sorption rates for ioxynil are slightly lower than for pendimethalin while fitted desorption rates are larger, corresponding to the lesser sorption tendency.

Besides the fitting with least squares regression, another approach has been taken. For a large number of combinations of k_{sorp} and k_{desorp} (around the values giving the least sum of squares), the likelihood of model-C_ws belonging to a normal distribution around measured values, has been calculated. In this case, the different variations at different time points were taken into consideration. The results, shown as contour plots, confirm the values determined by sum of squares minimization given in Table 5.1. An example of such a contour plot is given in Figure 5.5.

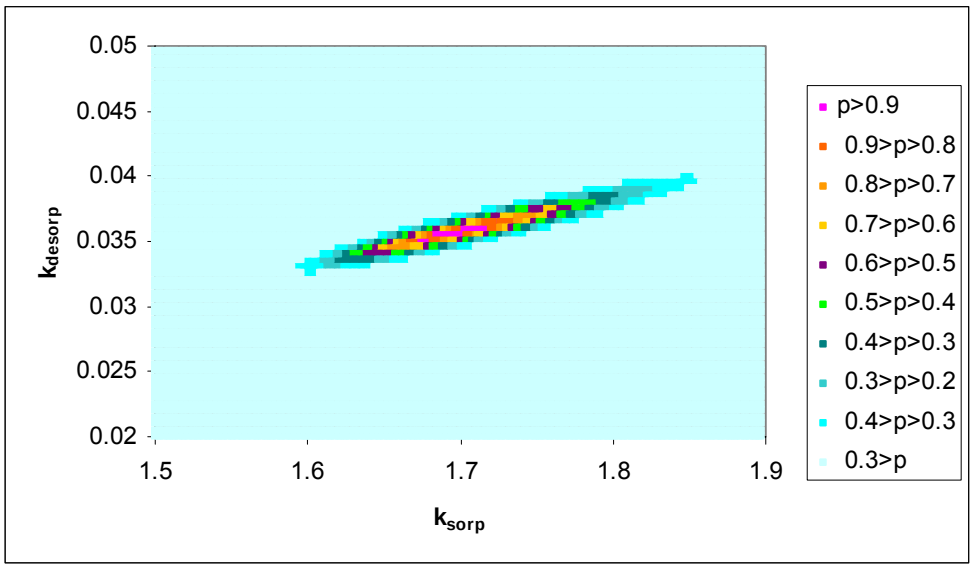


Figure 5.5
likelihood of model-C_w belonging to a normal distribution around measured C_w for sorption of pendimethalin to pond sediment

In order to give an idea of the time scale of sorption, a collection of fitted models are shown together in Figure 5.6 below.

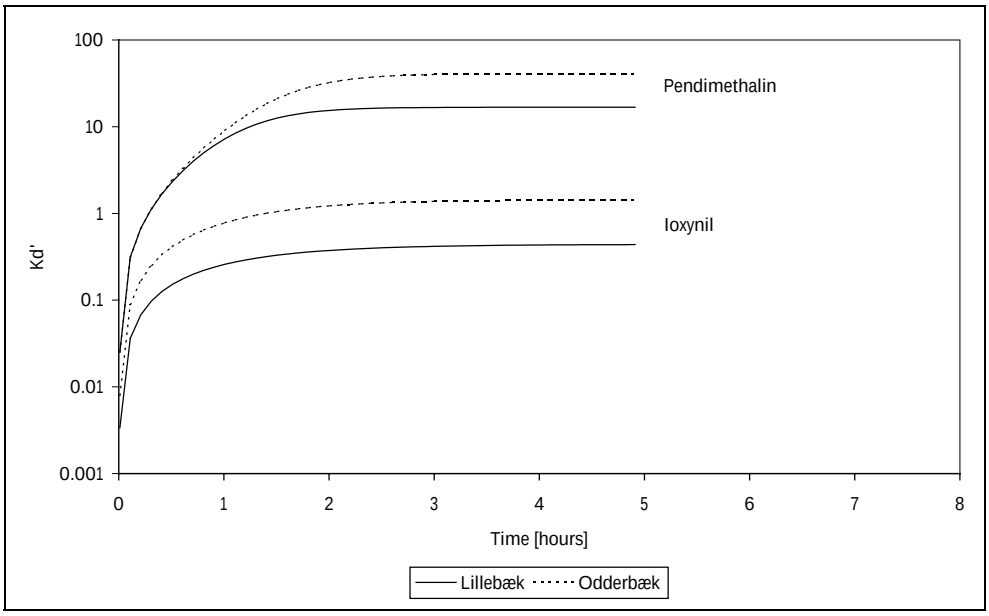


Figure 5.6
Fitted model for sorption to stream sediments shown as partition coefficient Kd'(t) = $C_s(t)/C_w(t)$

From Figure 5.6, it can be seen that the sorption of pendimethalin and ioxynil to the Odderbæk sediment was slightly stronger than to the Lillebæk sediment and that pendimethalin sorbed quite a lot more strongly than ioxynil.

In general, the sorption to pond, stream and lake sediments in the laboratory experiments was rather fast. The fitted model predicted that $C_w(t) = \beta \cdot C_w(\infty)$ would be reached within the time t given by

$$t = \frac{\ln\left(\frac{(\beta - 1)k_{desorp}}{k_{sorp}}\right)}{-(k_{sorp} + k_{desorp})}$$

Equation 2

Applying this expression for different βs and with fitted model parameters gave the results shown in Table 5.2.

Table 5.2
The time t [hours] to reach $C_w(t) = \beta \cdot C_w(\infty)$ in the experiments according to fitted model. Model parameters given in Table 5.1.

Experiment	β				
	2.00	1.50	1.10	1.01	1.001
Pendimethalin, Pond Low	2.3	2.7	3.6	5.0	6.4
Pendimethalin, Pond High	2.1	2.5	3.4	4.8	6.1
Pendimethalin, Lillebæk High	1.1	1.3	1.9	2.8	3.7
Pendimethalin, Odderbæk High	1.5	1.7	2.4	3.3	4.2
Ioxynil, Lillebæk Med	-0.7	-0.1	1.3	3.4	5.5
Ioxynil, Odderbæk Med	0.3	0.8	2.0	3.7	5.4

From Table 5.2, it can be seen that for pendimethalin shaken with pond sediment, the pesticide concentration in the water is twice the equilibrium concentration after two hours. After 5 hours, the pesticide concentration in the water is only 1% higher than at equilibrium. The sorption to stream sediment was slightly faster with the pesticide concentration reaching within 1% of the equilibrium concentration in three hours. For ioxynil, the sorption to stream sediments is slightly slower. No literature data on the kinetics of sorption of these pesticides have been found for comparison.

5.2 Desorption experiments

From the analysis of the supernatants removed after sorption for 12 days, average partition coefficients could be calculated assuming that $C_s = C_T - C_w$ where C_T is nominal total concentration. For the low concentration, the partition coefficient was Kd = 985 ± 21 and, for the high concentration, it was Kd = 912 ± 62. This is comparable to the Kds determined in the sorption studies (low conc. Kd = 615 and high conc. Kd = 551) although slightly higher due to the use of nominal total concentrations. After replacement of the aqueous phase and desorption, C_w and C_s were measured at the times: 1, 3.5, 24 and 240 hours. These values are given in Tables B.14-B.15 in Appendix B and the measured values of C_w are shown in Figure 5.7.

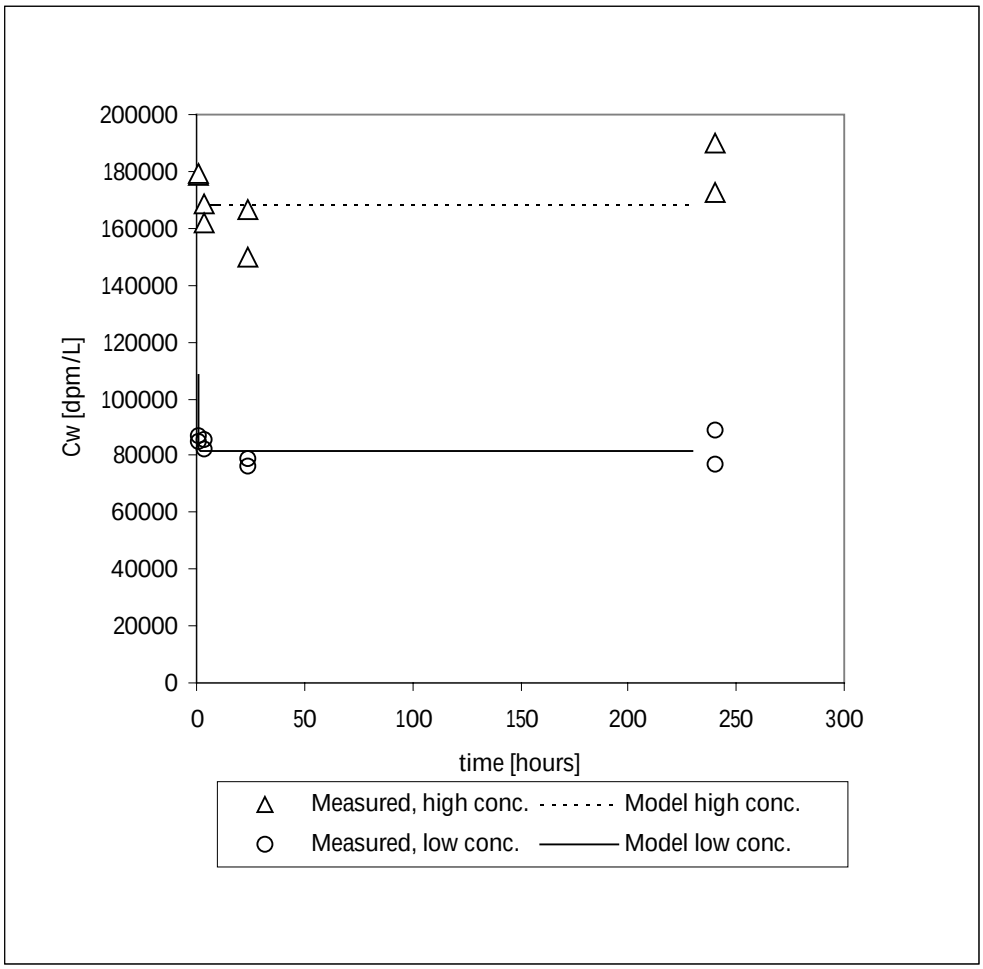


Figure 5.7
Desorption of pendimethalin from pond sediment

The desorption experiment shows that, after 12 days of sorption, desorption is fast. The new equilibrium created by desorption was close to equilibrium after sorption with similar, slightly higher, Kd values.

The kinetic parameters determined for desorption are quite different from the parameters determined for sorption, with both k_{sorp} and k_{desorp} being larger for desorption indicating faster rates of desorption than of sorption. Fitted values of k_{sorp} and k_{desorp} are given in Table 5.1.

The results from the desorption parameters confirm the assumption that sorption is reversible, even after a long period of sorption. Although this is only shown for one pesticide, it is expected to be the case for most pesticides in streams when the pesticide enters the stream within a short timeframe, as after e.g. a spraying. Here, after an initial increase in the pesticide water concentration and sorption, the pesticide water concentration will soon decrease causing a desorption a short time after the sorption took place.

5.3 "Equilibrium" sorption experiments

A large number of "equilibrium" experiments were performed. The majority, performed at 10°C, were made at varying concentrations in order to investigate sorption linearity while the rest, performed at 4°C and 20°C, were

made in order to investigate the influence of the temperature on equilibrium partitioning. The raw data from the equilibrium experiments are given in Tables B.16-B.24 in Appendix B. In these experiments, C_s was measured in all cases except for the lake sediments. However, when measured, the values were often unrealistically high, presumably due to the analysis of un-representative subsamples. In these cases, the measured solid phase concentrations were disregarded and values calculated from the difference between aqueous concentration in the controls and in the microcosms were used instead. The calculated Kd values are given in Tables 5.3-5.4 together with Kd values derived from the "kinetic" experiments.

The difference in equilibrium partitioning of pendimethalin, ioxynil and bentazone between lake sediment and water is shown in Figures 5.8-5.10. It seems that there is no particular difference between Kd values determined at 4°C and at 20°C.

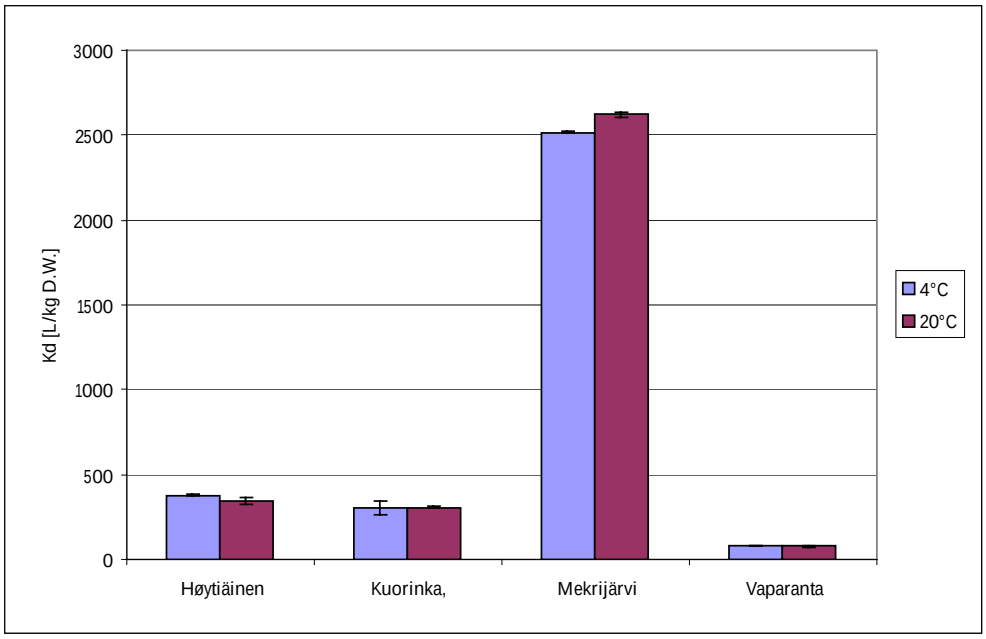


Figure 5.8
The influence of temperature on the sorption of pendimethalin to lake sediments

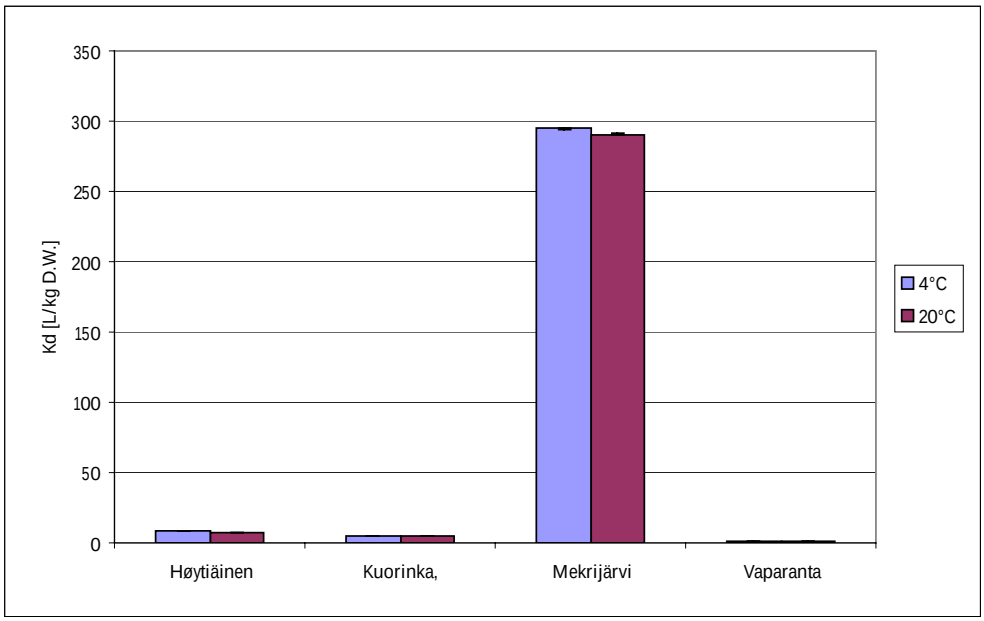


Figure 5.9
The influence of temperature on the sorption of ioxynil to lake sediments

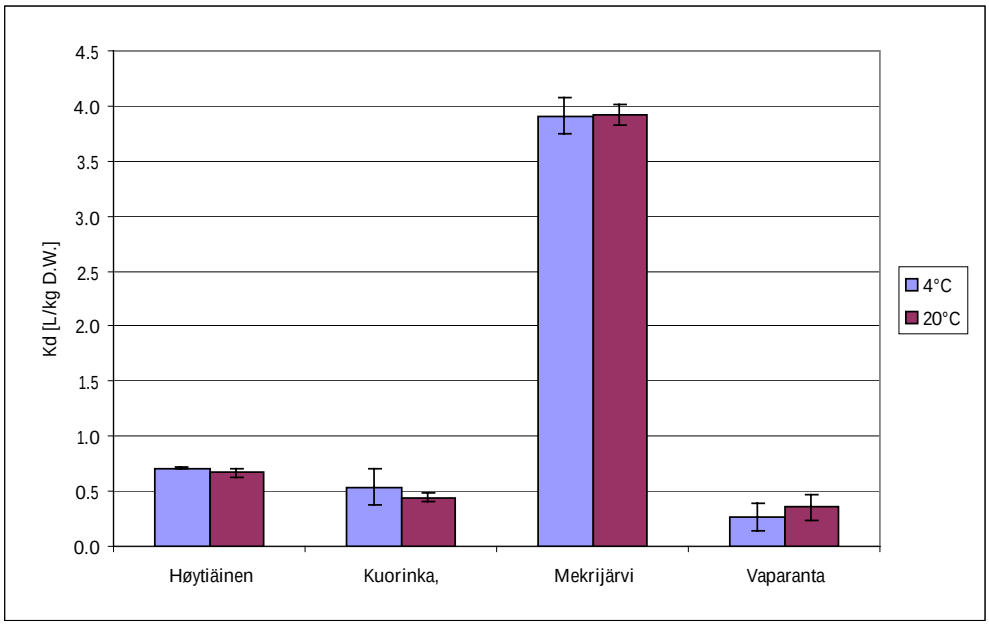


Figure 5.10
The influence of temperature on the sorption of bentazone to lake sediments

In Tables 5.3-5.4, all determined Kd values have been shown together. The partition coefficients given for the kinetic experiments are calculated from Kd' = k_{sorp}/k_{desorp} and Kd = Kd'/CP while partition coefficients given for the equilibrium experiments are calculated from an average of measured C_w and C-control. pH in the controls were similar, i.e. 6.9-7.1 for all three pesticides. This is close to the pH of 7.18-7.85 measured in sediment slurries without pesticide, azide and $CaCl_2$ and thus indicates that no change in pH was

caused by the pesticides themselves in these experiments. The pH of the experiments can thus be considered realistic.

Table 5.3
Equilibrium partition coefficients (Kd) for pendimethalin

Pesticide	Sediment	Conc	Nominal C_T		Exp. type	Kd ± S.D.	K_{oc}	pH
			dpm/L	mg/L		L/kg D.W.	L/kg oc	
Pendimethalin	Pond	Low	7848222	0.064	Kinetic	615	18647	-
Pendimethalin	Pond	High	16189889	0.132	Kinetic	551	16700	-
Pendimethalin	Pond	Low	7503452	0.061	Kinetic desorp	832	25218	-
Pendimethalin	Pond	High	15517620	0.126	Kinetic desorp	811	24579	-
Pendimethalin	Lillebæk	Low	2952667	0.024	Equilibrium	610 ± 51	21050	7.3
Pendimethalin	Lillebæk	Med	7656389	0.062	Equilibrium	432 ± 14	14914	7.3
Pendimethalin	Lillebæk	High	9757167	0.079	Kinetic	224	7712	-
Pendimethalin	Odderbæk	Low	2952667	0.024	Equilibrium	2074 ± 98.1	20739	7.1
Pendimethalin	Odderbæk	Med	7656389	0.062	Equilibrium	1183 ± 26.8	11831	7.1
Pendimethalin	Odderbæk	High	9757167	0.079	Kinetic	544	5446	-
Pendimethalin	Vaparanta	v. low	845184	0.0056	Kinetic	50.5	9351	-
Pendimethalin	Vaparanta	Low	1380244	0.011	Kinetic	49.2	9108	-
Pendimethalin	Vaparanta	Med	2760489	0.022	Kinetic	44.5	8238	-
Pendimethalin	Vaparanta	High	5520978	0.045	Kinetic	31.5	5840	-
Pendimethalin	Vaparanta	v. high	11041956	0.090	Kinetic	36.7	6788	-
Pendimethalin	Höytiäinen 4°C		10189444	0.083	Equilibrium	379 ± 6.7	11841	5.4
Pendimethalin	Kuorinka 4°C		10189444	0.083	Equilibrium	302 ± 37.5	18436	5.8
Pendimethalin	Mekrijärvi 4°C		10189444	0.083	Equilibrium	2518 ± 6	10371	5.0
Pendimethalin	Vaparanta 4°C		10189444	0.083	Equilibrium	77 ± 0.8	14267	6.2
Pendimethalin	Höytiäinen 20°C		11016389	0.090	Equilibrium	344 ± 18.4	10741	5.8
Pendimethalin	Kuorinka 20°C		11016389	0.090	Equilibrium	306 ± 5.3	18638	6.0
Pendimethalin	Mekrijärvi 20°C		11016389	0.090	Equilibrium	2621 ± 18.1	10795	5.2
Pendimethalin	Vaparanta 20°C		11016389	0.090	Equilibrium	78 ± 3.6	14487	6.4

Kd from kinetic experiments is calculated from fitted sorption and desorption rates while Kd for equilibrium experiments is an average of Kds calculated for replicates.
K_{oc} values have been calculated as Kd/f_{oc}.
pHs given are in the test glasses after equilibration.

Kd fra de kinetiske forsøg er udregnet ud fra "fittede" sorptions- og desorptionshastigheder, mens Kd for ligevægtsforsøg er et gennemsnit af Kd værdier udregnet for replikater.
K_{oc} værdier er udregnet som Kd/f_{oc}.
pH værdierne er fra testglassene efter ligevægt.

Table 5.4
Equilibrium partition coefficients (Kd) for ioxynil and bentazone

Pesticide	Sediment	Conc	Nominal C_T		Exp. type	Kd ± S.D.	K_{oc}	pH
			dpm/L	mg/L		L/kg D.W.	L/kg oc	
Ioxynil	Lillebæk	Low	4090667	0.025	Equilibrium	5.8 ± 0.81	201	7.3
Ioxynil	Lillebæk	Med	33708833	0.210	Kinetic	5.9	202	-
Ioxynil	Lillebæk	High	45705500	0.285	Equilibrium	0.0 ± 0.05	0	7.3
Ioxynil	Odderbæk	Low	4090667	0.025	Equilibrium	19.2 ± 2.27	192	7.0
Ioxynil	Odderbæk	Med	33708833	0.210	Kinetic	19.2	192	-
Ioxynil	Odderbæk	High	45705500	0.285	Equilibrium	7 ± 1.76	67	7.1
Ioxynil	Höytiäinen 4°C		34043611	0.212	Equilibrium	8.8 ± 0.24	276	5.6
Ioxynil	Kuorinka 4°C		34043611	0.212	Equilibrium	4.8 ± 0.38	291	6.0
Ioxynil	Mekrijärvi 4°C		34043611	0.212	Equilibrium	294.6 ± 0.78	1213	5.1
Ioxynil	Vaparanta 4°C		34043611	0.212	Equilibrium	1 ± 0.02	186	6.3
Ioxynil	Höytiäinen 20°C		32752222	0.204	Equilibrium	7.5 ± 0.18	233	5.9
Ioxynil	Kuorinka 20°C		32752222	0.204	Equilibrium	4.7 ± 0.16	289	6.1
Ioxynil	Mekrijärvi 20°C		32752222	0.204	Equilibrium	290.7 ± 0.37	1197	5.3
Ioxynil	Vaparanta 20°C		32752222	0.204	Equilibrium	0.9 ± 0.01	160	6.5
Bentazone	Lillebæk	Low	339667	0.46	Equilibrium	0.5 ± 0.00	18	7.3
Bentazone	Lillebæk	Med	1937333	2.62	Equilibrium	0.5 ± 0.09	17	7.3
Bentazone	Lillebæk	High	20717000	28.02	Equilibrium	0.5 ± 0.15	17	7.3
Bentazone	Odderbæk	Low	339667	0.46	Equilibrium	0.9 ± 0.07	9	7.1
Bentazone	Odderbæk	Med	1937333	2.62	Equilibrium	0.8 ± 0.03	8	7.1
Bentazone	Odderbæk	High	20717000	28.02	Equilibrium	0.7 ± 0.10	7	7.1
Bentazone	Höytiäinen 4°C		2652500	3.588	Equilibrium	0.7 ± 0.01	22	5.7
Bentazone	Kuorinka 4°C		2652500	3.588	Equilibrium	0.5 ± 0.16	33	5.9
Bentazone	Mekrijärvi 4°C		2652500	3.588	Equilibrium	3.9 ± 0.17	16	5.2
Bentazone	Vaparanta 4°C		2652500	3.588	Equilibrium	0.3 ± 0.13	50	6.4
Bentazone	Höytiäinen 20°C		2717861	3.676	Equilibrium	0.7 ± 0.04	21	6.0
Bentazone	Kuorinka 20°C		2717861	3.676	Equilibrium	0.4 ± 0.04	27	6.1
Bentazone	Mekrijärvi 20°C		2717861	3.676	Equilibrium	3.9 ± 0.09	16	5.3
Bentazone	Vaparanta 20°C		2717861	3.676	Equilibrium	0.4 ± 0.12	65	6.9

Kd from kinetic experiments is calculated from fitted sorption and desorption rates while Kd for equilibrium experiments is an average of Kds calculated for replicates.
K_{oc} values have been calculated as Kd/f_{oc}.
pHs given are in the test glasses after equilibration.

Kd fra de kinetiske forsøg er udregnet ud fra "fittede" sorptions- og desorptionshastigheder, mens Kd for ligevægtsforsøg er et gennemsnit af Kd værdier udregnet for replikater.
K_{oc} værdier er udregnet som Kd/f_{oc}.
pH værdierne er fra testglassene efter ligevægt.

The partition coefficients determined are in accordance with the expectations based on the octanol-water partition coefficients and the organic content of the sediment. The sorption to the Mekrijärvi sediment gave the highest Kd values, followed by the Odderbæk sediment. Kd values for the Lillebæk and pond sediments were comparable.

It should be noted that the weak sorption of bentazon only causes minor reductions in aqueous phase concentration and thus the determination of sorption coefficients for bentazon is uncertain.

The data generated in this study have been compared with K_{oc} data from registration material in Table 5.5, and it can be seen that the K_{oc} values generated in this study are in good accordance with these values. The

literature K_{oc} values in the registration data were not reported with concentration levels and, consequently, a direct comparison is difficult.

Table 5.5
Comparison of experimental $K_{oc} = Kd/f_{oc}$ data with registration K_{oc} from Table 2.1.

	Sediment particulate structure	pH	Organic matter content (NVOC) [g/kg]	K_{oc} [L/kg oc]		
				Pendimethalin	Ioxynil	Bentazone
Registration data		6-7		13400	182-276	42-156
Pond sediment	very fine	7.6	33	16700-18647	-	-
Lillebæk	coarse	7.8	29	7712-21289	117-203	17-18
Odderbæk	fine	7.2	100	5446-21704	126-201	7-10
Vaparanta	medium		5.4	5782-14487	160-186	124-132
Höytiäinen	very fine		32	10741-11841	233-276	14-17
Kuorinka	very fine		16	18436-18638	289-291	239-239
Mekrijärvi	medium		243	10371-10795	1197-1213	1.1-1.5

In general, it seems that K_{oc} is slightly higher for the very finest sediment, which could be due to an increase in the fine particle inorganic sorption capacity but it is not a clear trend when all sediments are considered.

Kd values for pendimethalin in seven different soils have been determined at one concentration (initial water concentration 0.15 mg/L, CP=0.2 kg/L) by Pedersen et al. (1995) using OECD guideline 106.

Table 5.6
Kd values for pendimethalin (Pedersen et al., 1995). K_{oc} calculated here.

Organic carbon %	Clay (<0.002 mm) %	Kd (no unit given)	K_{oc}
0.01	0.6	2.23	22300
0.59	12.4	99.8	16915
1.6	11.3	284	17750
1.6	5.1	331	20687
2.3	4.4	314	13662
8.0	42.9	1360	17000
16.9	17.6	1638	9692

For soil, these values are quite similar to those obtained in this study for stream, pond and lake sediments (see Table 5.5). Both experiments show that not only organic material, measured as organic carbon, determines sorption of pendimethalin. Especially at very low organic matter concentrations, sorption to inorganic particles may become more important, causing a faulty increase in K_{oc} when calculated from Kd.

The relationship between Kd and organic matter content in the sediment for pendimethalin has been illustrated in Figure 5.11. Here, data have been grouped according to pesticide concentration level but with some variation in

concentration within each group. This variation is clearly important as it causes considerable scatter.

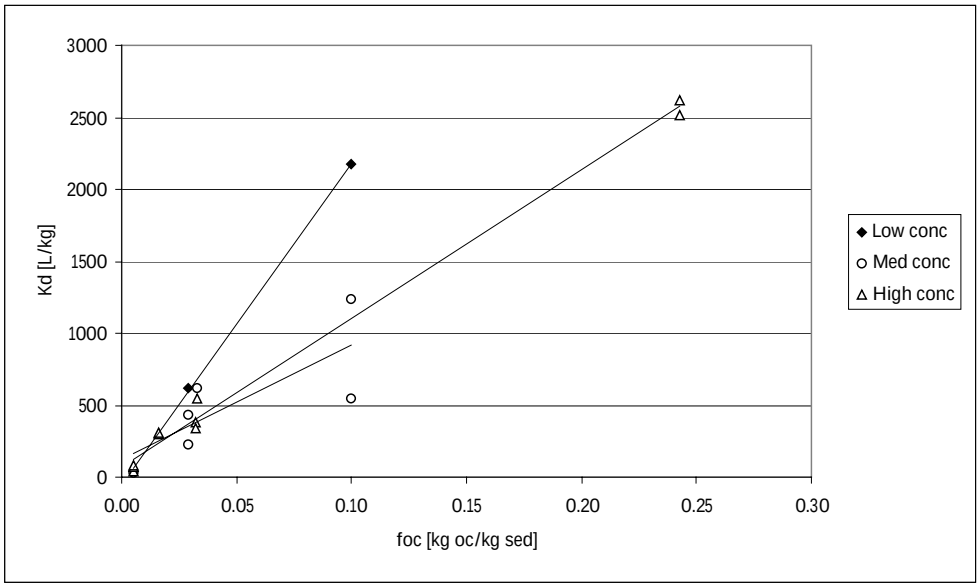


Figure 5.11
Relationship between Kd and organic carbon content (f_{oc}) for pendimethalin. Lines represent linear models.

It is obvious that the relationships between f_{oc} and Kd are different for different concentration levels.

Fomsgaard has reported Kd values for the sorption of bentazone to different European soils determined by OECD guideline 106, which is similar to the approach used here. CP=0.2 kg/L, initial pesticide concentration 5 µg/g soil D.W. or 1 mg/L (Fomsgaard, 1997).

Table 5.7
Kd values for bentazone (Fomsgaard, 1997). K_{humus} was calculated in this study.

Humus [%]	Clay [%]	Kd [kg/L]	K_{humus}
3.6	16.6	0.23	6.4
0.6	20.9	0.04	6.7
0.6	21.1	0.00	0
3.5	30.5	0.04	1.1
3.7	30.1	0.04	1.1
2.1	7.9	0.17	8.1
0.2	9.7	0.14	70
0.1	6.9	0.00	0

These results reported for soils are similar to the ones determined in this study, for stream, pond and lake sediments.

The variation of Kd with K_{oc} for ioxynil and bentazone is showed in Figures 5.12-5.13.

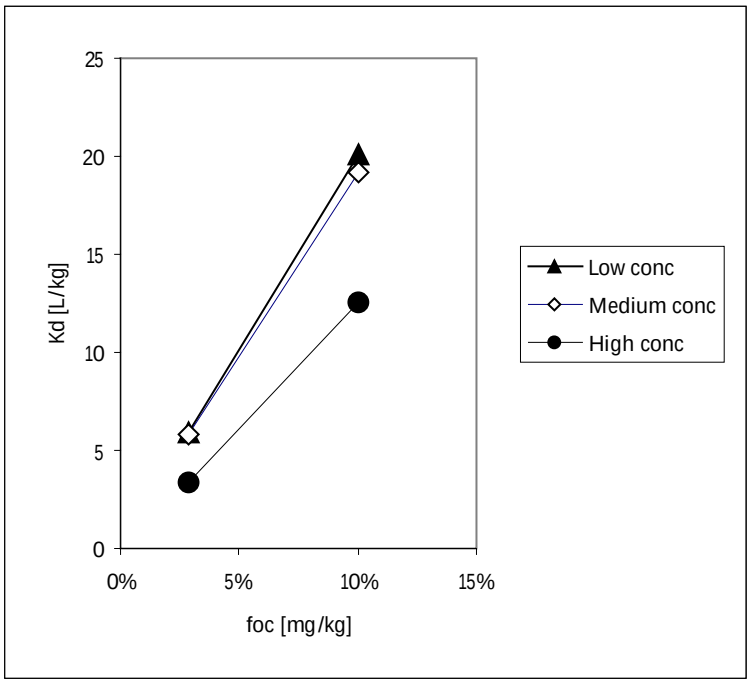


Figure 5.12
Relationship between Kd and organic carbon content (f_{oc}) for ioxynil

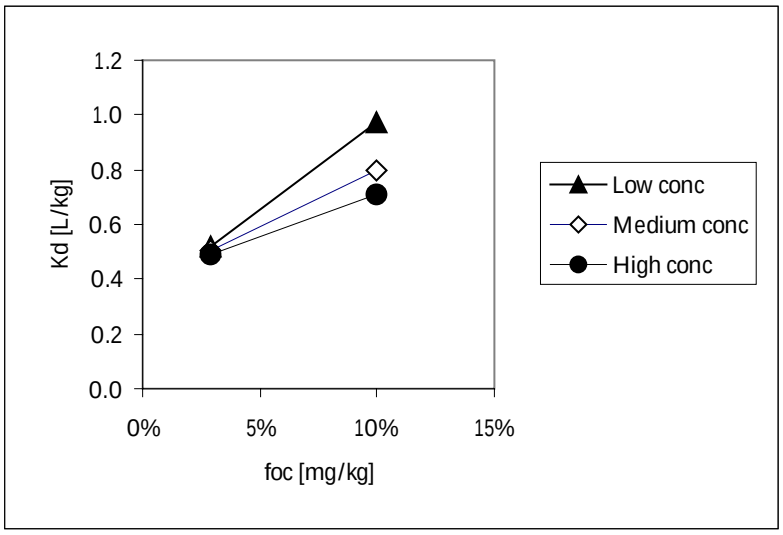


Figure 5.13
Relationship between Kd and organic carbon content (f_{oc}) for bentazone

Romero et al. have found a good relationship between organic matter content and Kd (equilibrium concentration 200 mg/L) for bentazone (r=0.88) for nine Spanish soils (Romero et al., 1996).

It is obvious that, for all three pesticides, there is a positive correlation between f_{oc} and Kd, although determined Kds of bentazon are uncertain, but also that the relationship is different at different pesticide concentrations. This seems to be due to non-linearity of Kd.

If equilibrium partition coefficients are considered at different total concentrations of pesticide, it can be seen that the sorption to stream sediment was non-linear for pendimethalin. For ioxynil and bentazone, the sorption was weak and there is some indication of non-linearity, but again, for bentazone the uncertainty of sorption coefficients makes accurate conclusions difficult for this pesticide.

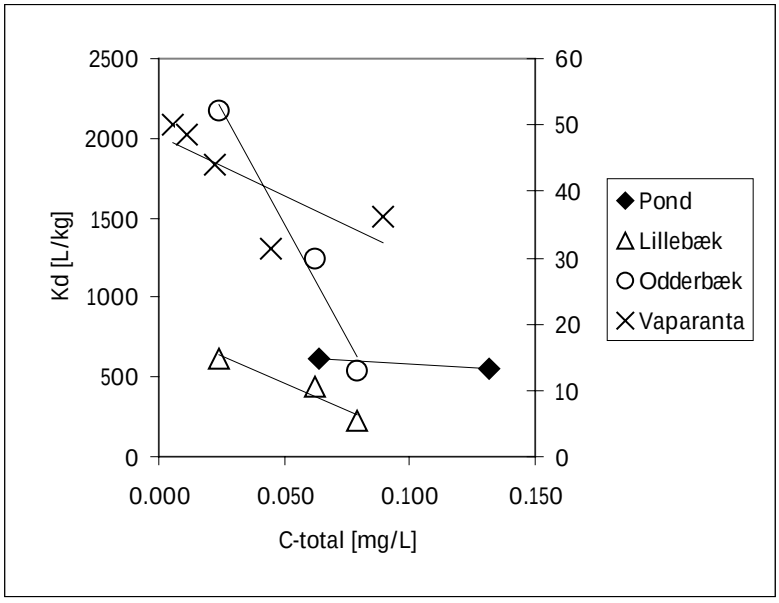


Figure 5.14
Non-linearity of Kd for pendimethalin

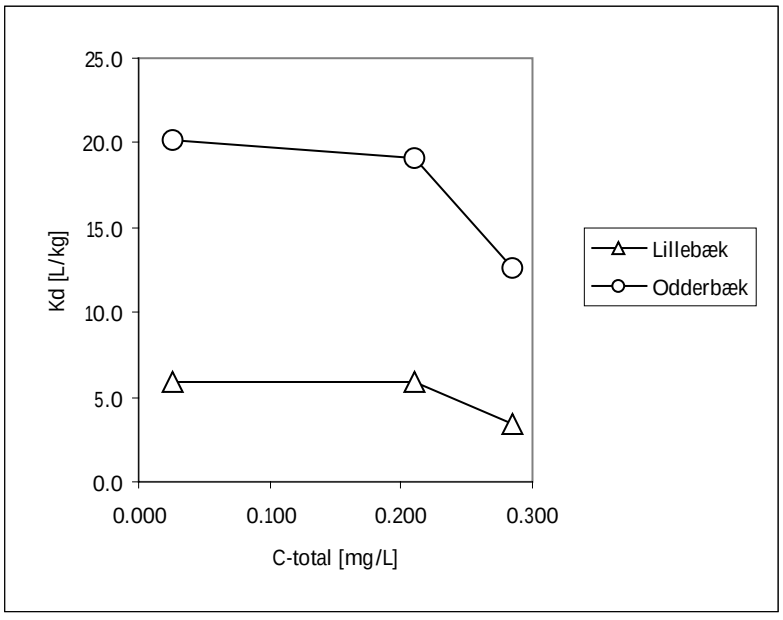


Figure 5.15
Non-linearity of Kd for ioxynil

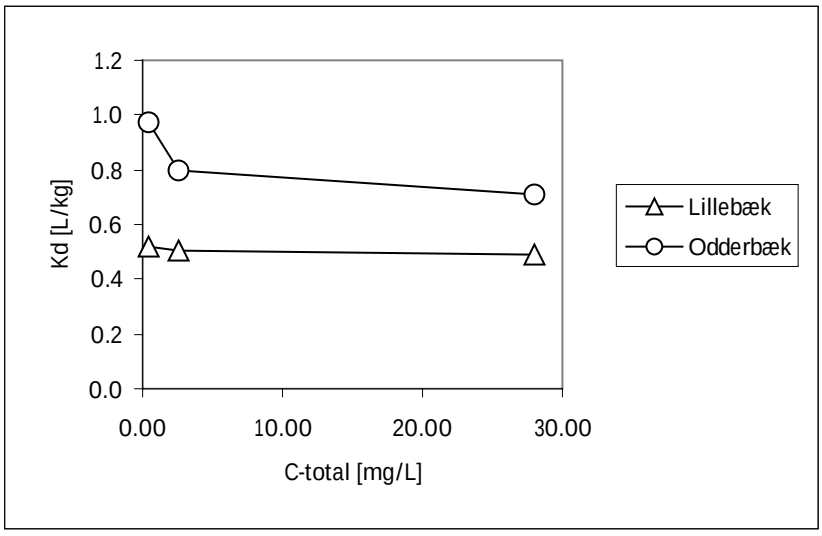


Figure 5.16
Non-linearity of Kd for bentazone

Romero et al. have demonstrated non-linear Freundlich relationships for bentazone for 8 out of 10 Spanish soils (Romero et al., 1996).

If a Freundlich isoterm expression ($C_s = Kd_f \cdot C_w^n$) is fitted to pendimethalin equilibrium data for C_s and C_w (Tables B.5-B.6 and Table B.16), the following results can be obtained.

Table 5.8
Fitted values of Freundlich Kd_f and n for pendimethalin

Sediment	Kd_f [L/kg]	n
Lillebæk	53717 ± 74498	0.587 ± 0.109
Odderbæk	167622 ± 161919	0.542 ± 0.082
Vaparanta	449 ± 961	0.871 ± 0.147

As it can be seen, the standard deviation on predicted Kd_f is quite large (96-138%) while it is relatively smaller on n (15-19%). The $n < 1$ case, as observed here, is usually explained by limited availability of sorption sites on the sediment. As pesticide concentration increases, it becomes increasingly rare that the pesticide comes in contact with a vacant sorption site and thus partitioning into sediment is diminished. Non-linearity is normally not caused by the sorption to organic bulk material but rather to surfaces (Schwarzenbach et al., 1993). The fitted Freundlich model is shown together with measured data in Figure 5.17 below.

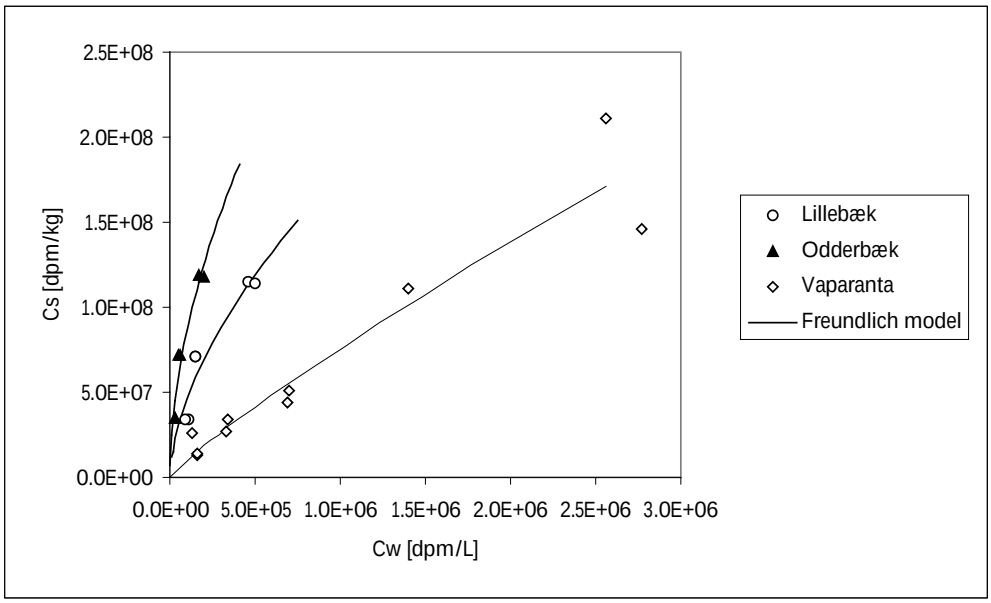


Figure 5.17
Freundlich isotherm for sorption of pendimethalin to sediment from Lillebæk and Odderbæk

Freundlich isotherms do not describe the non-linearity of Kd observed in these experiments very well as shown by the large uncertainty on the fitted parameters. It should be noted that extrapolation of a Freundlich isotherm to very low pesticide concentrations may be problematic (Styczen et al., 2002a). Here, the Freundlich expression has only been fitted to pendimethalin data and these are on quite low concentrations.

For the two ionizable pesticides, bentazone and ioxynil, a correction for the influence of pH on Kd was calculated as shown in Appendix F. The calculations show that the effective Kd will change drastically at low pH while at pH above 7, it is more or less independent of pH. This means that an increase in pH as may be caused by photosynthesis will have no effect on the partitioning of these pesticides. A decrease below pH of 6 will, however, lead to a stronger sorption. An increase of up to 700 to 900 times of the sorption can be expected in extreme cases.

5.4 Relationship between Kd and sorption rate constants

From the results generated here, it seems that sorption rate constants are necessary in the description of pesticide fate in streams. For small streams, as those used in the scenarios of the registration model, the retention time can be as low as 1 hour and sorption can take 6 hours to reach equilibrium. However, sorption rate constants are usually not available to the Danish EPA. It has thus been investigated whether predetermined universal sorption rate constants could be used with desorption rates determined from Kd of the pesticide in question.

In shaking sorption experiments, the sorption is not believed to be limited by diffusion as optimal contact between pesticide and sorbent is ensured by shaking. The probability of a pesticide molecule reaching a sorption site on sediment within a given time could thus be expected to depend mainly on the sediment concentration and on the initial pesticide concentration (total

concentration). The attractions between pesticide and sediment and the hydrophobicity of the pesticide are not expected to be important for the sorption rate as they only work at short distances and as formation of complexes is fast.

The desorption rate on the other hand could be expected to be rather independent of sediment concentration while hydrophobicity and attractions (Kd) are important factors.

If this conceptual model is accepted, it may be reasonable to determine a common sorption rate constant for pesticides, at a given particle concentration, and to let the desorption rate constant depend on Kd by the relationship stated in Appendix G.

In order to test this approach and to determine a common sorption rate constant, analytical expressions for C_w were fitted to pendimethalin and ioxynil sorption data together. Two identical analytical expressions for C_w were set with up, one for pendimethalin and one for ioxynil, with different k_{desorp} but same k_{sorp}. The sum of squared differences between model and data for all datapoints (both pendimethalin and ioxynil) were then minimised by adjusting k_{sorp} and $k_{desorp\text{-}pendimethalin}$ and $k_{desorp\text{-}ioxynil}$.

The data, to which the analytical expressions were fitted, were the data on the sorption to the stream sediments, Lillebæk and Odderbæk (Tables B.5-B.8).

In these experiments, the nominal start concentrations were $4.23 \cdot 10^{-7}$ [mole/L] and $8.61 \cdot 10^{-7}$ [mole/L] for pendimethalin and ioxynil, respectively, which are quite similar, and the same sediment concentration was used (1 g/12 mL). Unfortunately, there are no measurements before two hours (not possible with separation by the centrifuge available) and, after two hours, the concentration did not further decrease. This meant that apparent equilibrium was reached within two hours and that any combination of parameters, which could describe this, was equally good from a statistical point of view. The relationships between k_{sorp} and $k_{desorp\text{-}pendimethalin}$ and k_{sorp} and $k_{desorp\text{-}ioxynil}$ are given by the equilibrium constants.

The fitting was thus made in such a way that the slowest possible kinetics fitting the data was manually chosen. The resulting parameters are shown in Table 5.9.

Table 5.9
Commonly fitted kinetic sorption parameters

	Lillebæk	Odderbæk
k_{sorp} (common)	1.25	2.50
k_{desorp} (pendimethalin)	0.075	0.061
k_{desorp} (ioxynil)	2.96	1.81

In Figures 5.18-5.19, the fitting shows that it was possible to obtain a reasonable fit to these experimental data on two pesticides with a common sorption rate and individual desorption rates.

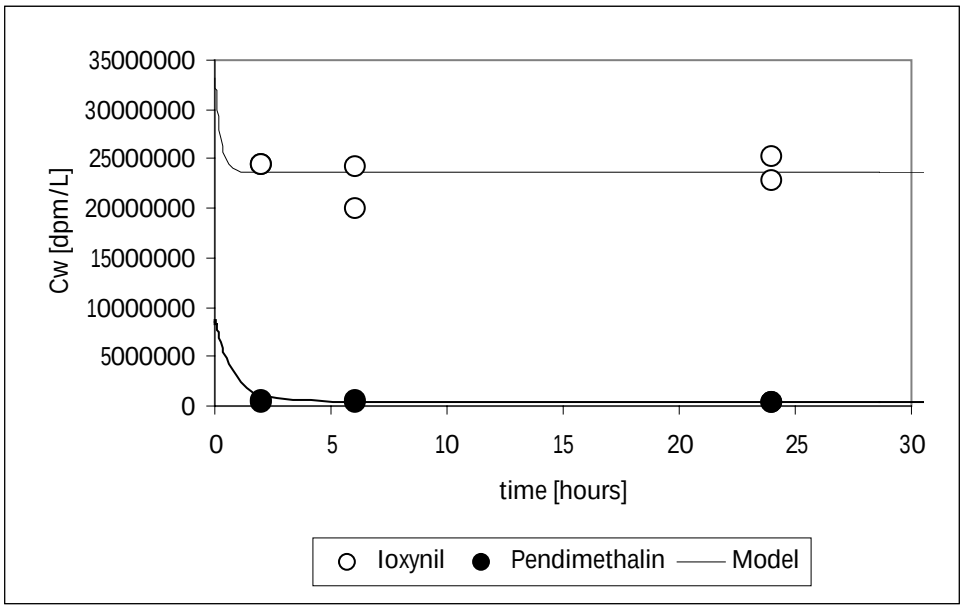


Figure 5.18
Sorption of pendimethalin and ioxynil to the Lillebæk stream sediment and simultaneously fitted sorption-models with co-ordinated parameters. First 30 hours shown.

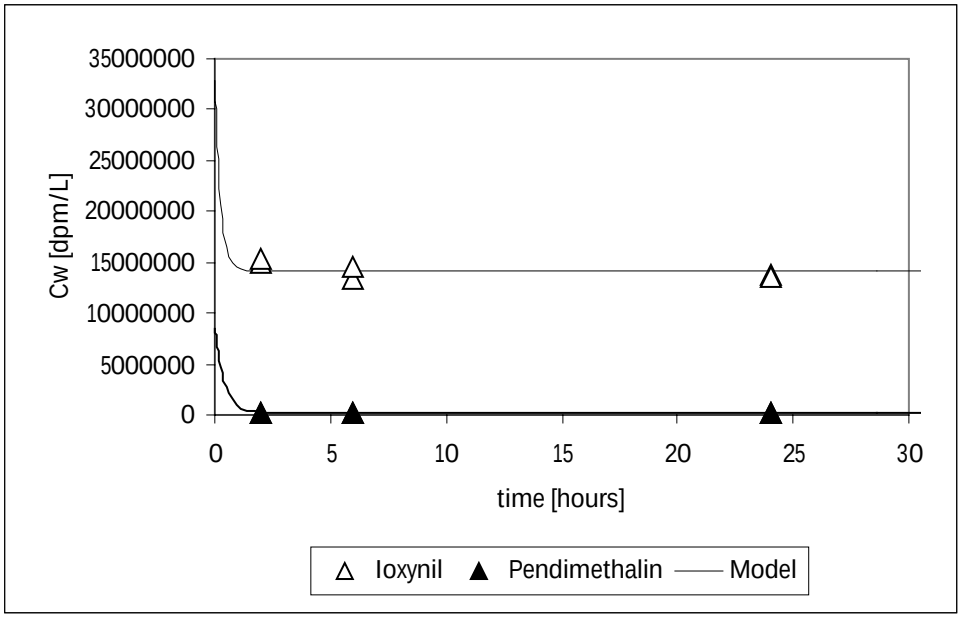


Figure 5.19
Sorption of pendimethalin and ioxynil to the Odderbæk stream sediment and simultaneously fitted sorption-models with co-ordinated parameters. First 30 hours shown.

The variation between the individually determined sorption parameters was not large either.

Ramos et al. (2000) have found sorption rate constants for four different pesticides (atrazin, chlorpyrifos, bromophos-ethyl, diazinon) of 12.7, 4.0, 5.0 and 14.8 hr^{-1}, respectively, at a suspended matter concentration of 0.0068

kg/L. These four sorption rates are quite similar even though the more hydrophobic pesticides have a sligthly lower sorption rate than the more hydrophillic. It should, however, be noted that the sorption rates presented by Ramos et al. are slightly higher than the sorption rates determined in the present study.

Even though the assumption of a uniform sorption rate is crude and the data available for evaluation is scarce, it is considered a reasonable way of making a rough estimate of the sorption rate constant. It would be preferable to have more kinetic data on the fast sorption in order to make a better estimate of the common sorption rate constant.

5.5 Recovery and accuracy of sorption and desorption experiments

For the experiment with sorption of pendimethalin to pond sediment, detailed mass balances based on radioactivity were made. After emptying of test tubes and centrifuge tubes, these were washed in 2 mL of acetone and the activity was determined using LSC. The results are presented in Tables B.2 and B.4 in Appendix B. The total activity measured (sum of activity in sediment, water and on glass surfaces) was compared to both a theoretical total, calculated from added activity, and to the activity in the relevant controls.

The radioactive residue on test tubes and centrifuge tubes was in average only 0.06% and 0.04% of the total activity, respectively. The highest amount found by washing test and centrifuge tubes with acetone was 0.20% of the total radioactivity. The residue on glassware did thus not contribute significantly to the mass balance. This is confirmed by experiments with sorption of pendimethalin to new and worn glass surfaces (see Appendix C). By applying the results in a three-compartment model (see Appendix G.2), it can be calculated that 0.4% of the total amount of pendimethalin, in experiments with pond sediment, would be found on the glassware.

The variability in the measured C_w, C_s and calculated Kd is due to natural variation, especially in sediment composition, and due to errors introduced in the experimental and analytical procedures. The variability between measured C_ws and C_ss from replicate test tubes are given in Table B.25 in Appendix B. The variability in C_w includes the variability arising from sediment composition differences between test tubes and errors arising from centrifugation, transfer of samples and analysis. As it can be seen from Table B.25, the standard deviation between C_ws from replicate test tubes is, however, relatively small, less than 10% and 3% in average. This is comparable to the variability between controls, which was less than 13% and also 3% in average. This suggests that the variation between properties of 1-g samples, caused by differences in composition, is small and that 1-g samples thus are reasonably representative of the sieved sediment as such. The variabilities between C_s include variability arising from differences between sediment composition of test tubes and errors arising from centrifugation and transfer of samples. However, the most important cause of variance, especially for the stream sediments, seems to be that the subsamples analysed were non-representative. The stream sediments, and especially the Lillebæk sediment, are much less homogenic than the pond sediment (see Figure 4.1), which may explain the problems with the determination of stream sediment concentration. The concentrations believed to be non-representative, giving calculated recoveries far exceeding 100%, were not used in the calculation of Kd.

The variability between measured C_ws from pairs of centrifuge tubes was small for pond sediment with standard deviation of less than 2.6% (average 1.35%) and, consequently, a subsample of the test tube content was transferred to only one centrifuge tube in the subsequent experiments with stream sediment. As described above, this procedure seems, however, to have introduced a systematic error as it is likely that mainly the smaller particles of the stream sediment were transferred to centrifuge tubes and analysed. This seems to be the explanation of the unrealistically high recoveries calculated in some experiments, especially in the sorption of pendimethalin to stream sediments. This effect is less important for less sorbing chemicals.

The variance between determined activity in vials from the same centrifuge tube was 0.89% (2.67%), n=128 in the experiment with pendimethalin and pond sediment whereas it was 1.24% (7.43%), n = 89 in the remaining experiments.

5.6 Degradation experiments

Degradation experiments were conducted with stream water from Mølleåen and with the Odderbæk and Lillebæk sediments.

From the initial activity $C_T(t=0)$ (calculated from amount added) and $C_T(t)$, the relative decrease in activity is calculated as $(C_T(t=0)-C_T(t))/C_T(t=0)$. The cause of a decrease in activity is believed mainly to be the escape of $^{14}CO_2$ mineralised from the labelled pesticide. However, sorption to glass and evaporation will also cause a decrease in activity. Thus, the term "relative disappearance" is used throughout this section. The average relative disappearance from degradation experiments with ^{14}C-labelled pendimethalin is shown with standard deviation in Figure 5.20 below. The raw data are given in Table B.26 in Appendix B.

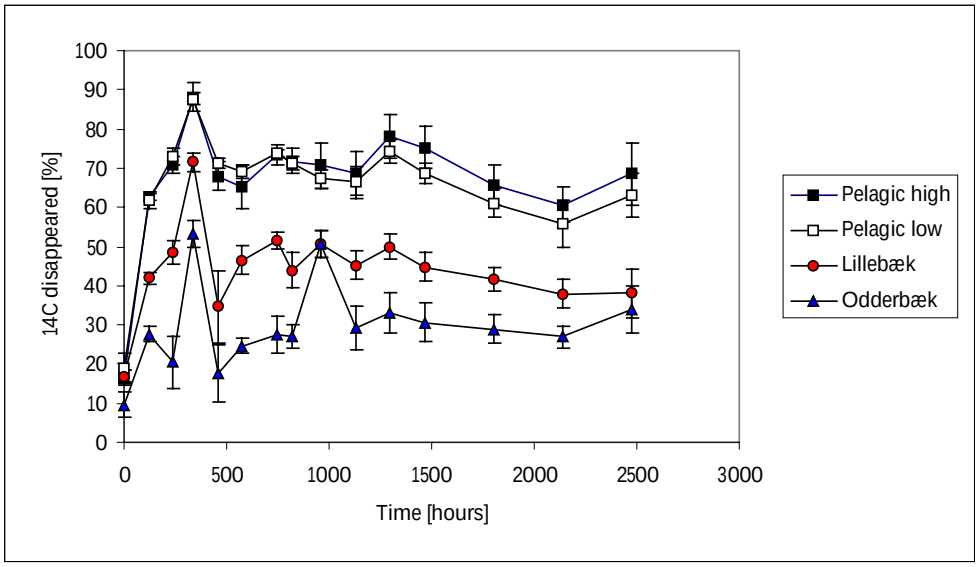


Figure 5.20
Relative disappearance of pendimethalin

Unfortunately, the results of the determinations seem quite uncertain over time. As it can be seen, there is more or less a downward trend of disappearance, which must be attributed to uncertainties. The error seems to

be systematic as the deviation between replicates is small and the development in test bottles with and without sediment is parallel. It seems as if a final level, or a period of very slow disappearance, is attained after approx. 250-500 hours. The disappearance level at high concentrations is a bit higher than at low concentrations in the pelagic experiments and the disappearance level is higher for the Lillebæk sediment than for the Odderbæk sediment. The reason for the ceasing of disappearance, or drastically lowering of disappearance rate, after 250-500 hours could be the formation of persistent metabolites, toxic effects of the pesticide, build-up of toxic metabolites, assimilation of ^{14}C in living biomass, incorporation of ^{14}C in organic material, exhaustion of co-substrate or sorption. According to Vestergaard (2002), no formation of persistant metabolites is known so this seems not to be the explanation. Sorption is also unlikely to be the main cause as levelling also occurs in pelagic test bottles. Furthermore, only very fast degradation rates combined with fast sorption and very slow desorption could fit the full sorption degradation model, developed in Section 5.6.1, to the data shown in Figure 5.20. It is thus considered most likely that the levelling is caused by the incorporation of ^{14}C in biomass and organic material but the actual reason is not known.

It may be noted that an initial disappearance of 9.5 to 18.5% occurs in one hour. Most likely, this is not due to biotic degradation and is attributed to the experimental procedure. It might be due to fast sorption to the glass walls of the bottle. However, sorption to glass walls has been investigated (see Appendix C) and the partition coefficient was around 0.3 L/m^2. The glass walls of the bottles (r=2.75, h=11.5cm) have an inner area of approx. 230 cm^2, which together with the water volume of 100 mL yields a $Kd'=0.3[L/m^2] \cdot 230 \cdot 10^{-4} m^2/0.1$ L = 0.07. This means that 7% of the total amount will be sorbed to the glass walls in the pelagic experiments (at equilibrium) whereas much less will be sorbed to the glass walls in the bottles with sediment. This can thus only explain part of the initial disappearance. The fact that the disappearance is smallest for the bottles with the Odderbæk sediment, the strongest sorbing sediment, supports, however, the idea that glass sorption is part of the explanation.

Available studies on degradation of pendimethalin are few. Singh & Kulshrestha (1991) found that fungi could dealkylate pendimethalin and reduce the nitro-groups to amines. They did not pursue the degradation pathway further. Nitrobenzenes such as pendimethalin can be reduced by Fe(II) present in soil and sediments and produced by bacteria (Klausen et al., 1995). The disappearance of ioxynil is shown in Figure 5.21.

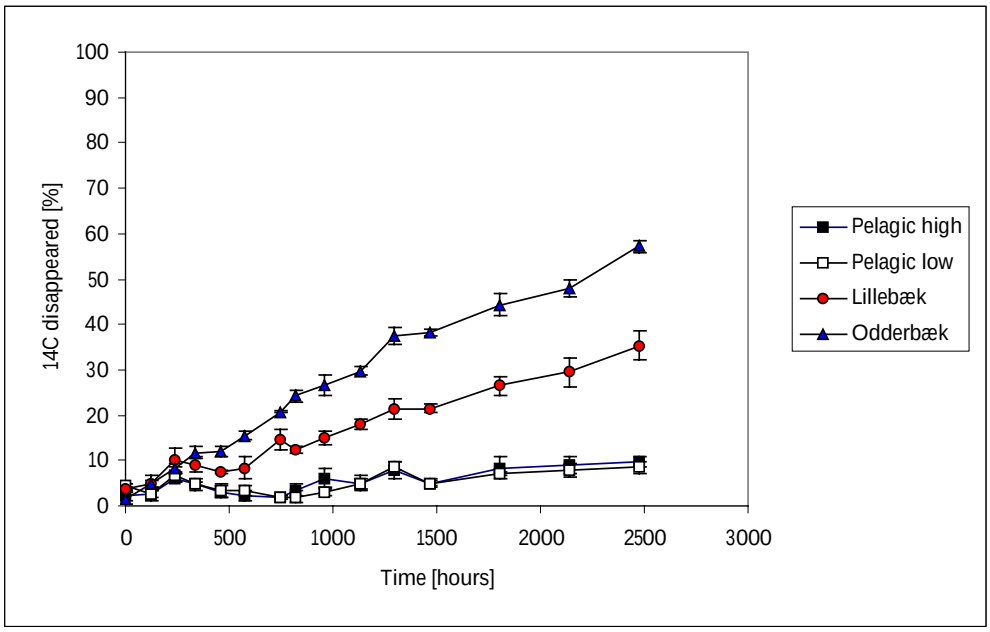


Figure 5.21
Relative disappearance of ioxynil

The disappearance of ioxynil is slow for "pelagic" test bottles, similar for high and low concentrations while it is higher for test bottles with sediment. The disappearance is faster for the Odderbæk sediment than for the Lillebæk sediment.

The disappearance of bentazone is shown in Figure 5.22 below.

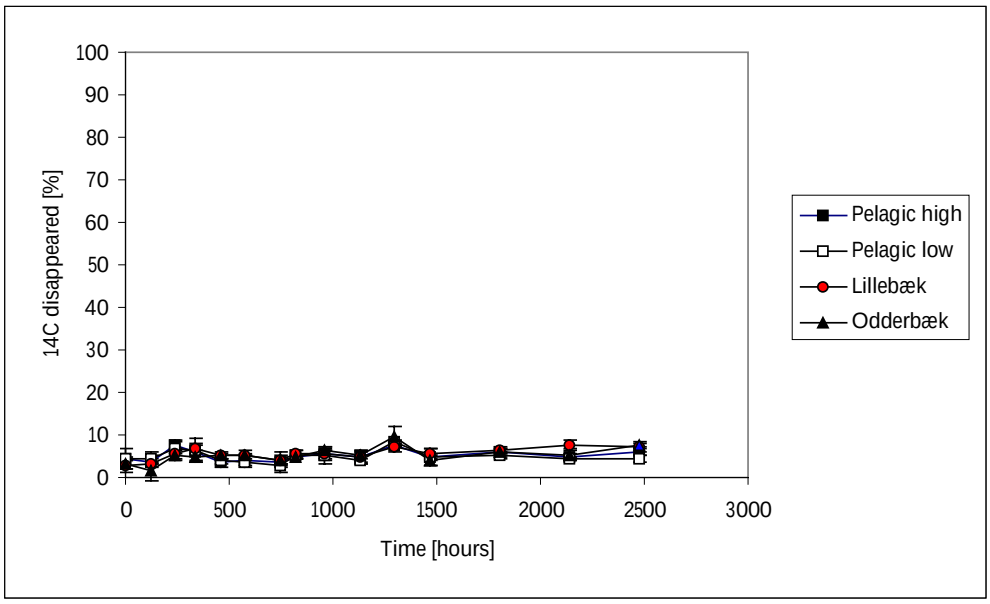


Figure 5.22
Relative disappearance of bentazone

The transformation of bentazone to CO_2 during the 103 days of aerobic incubation was very limited. In all experiments with bentazone, less than 10% of the initial amount was transformed. There is no discernible difference

between disappearance in bottles with and without sediment or high and low concentrations. Romero et al. (1996) have found that there was very little disappearance of bentazone in two Spanish soils, less than 20% in 40 days. In a thorough study by Knauber et al. (2000), it was found that 12-15% of added bentazone was mineralised immediately, 5% was methylated and afterwards demethylated, and 65-85% was hydrolylated to 8-OH-bentazone that could bind directly to soil humic substances or be dimerized and then be bound to humic substances. The residues that bind covalently with organic matter transform slowly. The rate of the transformation of residues to CO_2 was three times slower than for the parent compound (Knauber et al., 2000).

The degradation behaviour of the three pesticides is very different, seemingly due to the combination of sorption and degradation properties. When sediment is introduced to the water, two things occur: A sorbent becomes available for sorption, which limits the water concentration available for degradation and thus the degradation rate, and the biomass concentration is increased, which, in itself, leads to faster degradation. For the strongly sorbing pendimethalin, the addition of sediment leads to faster initial degradation rates according to modelling (Table 5.11) but also leads to a lower level of transformation. This could be due to a sorbed fraction resisting degradation. For ioxynil, which does not sorb strongly, the degradation rate increases much more with the addition of sediment and thereby biomass (Table 5.12) and no levelling occurs, indicating that sorption is less important. For bentazone, the degradation rate is very small and similar with and without sediment.

Recovery

The recovery was determined only for the recovery bottles. The recovery was determined as the activity at day 103 in water and stripped CO_2 compared with the activity determined in the water at 1 hour.

Table 5.10
Activities and recoveries for pelagic bottles (triplicates) with low pesticide concentrations

Activity [dpm/bottle]	Pendimethalin	Ioxynil	Bentazone
1 hour, water	267320 ± 9679	348633 ± 2378	477406 ± 5657
103 days, water	113293 ± 65184	313600 ± 7499	469786 ± 7465
103 days, CO_2	3691 ± 2375	9577 ± 2995	3678 ± 143
103 days total	116985 ± 67511	323177 ± 4603	473465 ± 7540
Recovery [%]	43.3 ± 24.4	92.7 ± 0.8	99.2 ± 1.4

For pendimethalin, the recovery is remarkably low. If the final activity is compared with the initial activity based on added amount and not on the 1-hour measurement, it is even lower. For ioxynil and bentazone, the recovery is high. The property distinguishing pendimethalin from the two other pesticides is the sorption tendency but as there is no sorbent in these bottles, this seems unimportant.

The air of the recovery bottles was not renewed during the incubation period of 103 days.

5.6.1 Fitting of model to degradation data

For the degradation experiments involving simultaneous sorption and degradation, the sorption model must be expanded to include degradation. This is done by adding a simple first-order degradation term.

$$\frac{dC_w}{dt} = -k_{sorp} \cdot C_w + k_{desorp} \cdot C_s - k_{deg} \cdot C_w$$
$$\frac{dC_s}{dt} = k_{sorp} \cdot C_w - k_{desorp} \cdot C_s$$

Equation 3

With this formulation, it is assumed that degradation only takes place in the aqueous phase. This assumption has been supported by the findings of many experimenters (Guerin et al., 1997; Robinson et al., 1990; Ogram et al., 1984; Zhao et al., 1999) although it has also been shown that e.g. bacteria may influence desorption (Park et al., 2001), indicating that a more complex model would be suitable. However, no complex model has been shown to be universally applicable and the more complex models usually require more parameters, which may not be available from the registration material. Therefore, the simple approach expressed in Equation 3 has been chosen for the registration model.

This set of equations (Equation 3) can be solved analytically (see Appendix G) and yields a solution that, as shown in the appendix, leads to an expression for the total concentration

$$C_T = -k_{deg}\left(\frac{c_1}{R_1} \cdot e^{R_1 t} + \frac{c_2}{R_2} \cdot e^{R_2 t}\right)$$

Equation 4

This model (named the full degradation sorption model) describes the sorption and degradation of the mother pesticide. But the activity measured in the degradation experiment includes activity from both labelled mother pesticide, ^{14}C containing metabolites and ^{14}C taken up by organisms or incorporated in organic material. Therefore, the model was modified for the pupose of deriving first-order degradation rates from the degradation experiments. The model was modified by assuming that a certain fraction of the transformed pesticide ends up in forms that remain in the suspension (metabolites, assimilated C in microorganisms, etc.) while the remaining fraction leaves the suspension as CO_2. The fraction that is transformed into something other than CO_2 is here named α, and α is fitted together with the other parameters. As an example, an α of 0.3 indicates that 70% of the transformed pesticide has been mineralised to CO_2 while 30% of the transformed pesticide molecules has been transformed into some form still in suspension. This model, given in Equation 5, is named the partial degradation-sorption model.

$$C_{T,measured} = C_{T,pesticide} + C_{T,other} =$$
$$C_{T,pesticide} + \alpha \cdot (C_T(0) - C_{T,pesticide}) =$$
$$(1-\alpha) \cdot C_{T,pesticide} + \alpha \cdot C_T(0)$$
$$C_{T,measured} = -(1-\alpha) \cdot k_{deg} \left(\frac{c_1}{R_1} \cdot e^{R_1 t} + \frac{c_2}{R_2} \cdot e^{R_2 t} \right) + \alpha \cdot C_T(0)$$

Equation 5

The model was fitted to the data from the degradation studies with suspended stream sediment by two approaches. In the first approach, sorption parameters derived from the sorption experiments under reasonably similar conditions were applied leaving only the degradation rate constant k_{deg} to be determined. The second approach was to determine both sorption and degradation rate constants from the degradation data. In both cases, the fitting was done by minimisation of residual sum of squares.

In order to be able to use the sorption and desorption rates determined in the sorption studies, in the degradation experiment (first approach), the sorption rate constant was recalculated to take account of the difference in particle concentration. $k_{sorp,model} = k_{sorp,exp} \cdot CP_{model}/CP_{exp}$ while the desorption rate constant was used directly: $k_{desorp,model} = k_{desorp,exp}$. This recalculation does, however, not take into account any actual difference in Kd or in the rates. The particle concentration (CP) in the degradation studies were much lower than in the sorption studies (0.001 kg/L versus 0.0833 kg/L) and the results generated in this study show that Kd varied with pesticide concentration versus sediment concentration. Partition coefficients increase with decreasing concentration and it could thus be expected that the pesticides had sorbed more strongly to sediment in the degradation experiments than in the sorption experiments. However, experiments with sorption of pendimethalin to Lake Vaparanta sediment showed that, within the concentration range tested (factor 20 from highest to lowest concentration), k_{sorp} and k_{desorp} did not vary much. The k_{desorp} and recalculated k_{sorp} parameter values from sorption experiments, showed below, were thus used without further correction.

Table 5.11
Original and recalcualted k_{sorp} values together with initial concentrations in test bottles

	From sorption experiments			Used in degradation exp.	
	Concentration	k_{sorp}	k_{desorp}	Concentration	k_{sorp}
	[mg/L]	[h^{-1}]	[h^{-1}]	[mg/L]	[h^{-1}]
Pendimethalin, Lillebæk	0.079	2.50	0.15	0.027	0.030
Pendimethalin, Odderbæk	0.079	2.47	0.060	0.027	0.030
Ioxynil, Lillebæk	0.21	0.34	0.77	0.022	0.0041
Ioxynil, Odderbæk	0.21	0.79	0.55	0.022	0.0095

5.6.2 Fitting of model to pendimethalin degradation data

The model was fitted to data from experiments with water and the two stream sediments. As the C_T measured after one hour was somewhat lower (9.5-18.8%) than what could be calculated from added amount and concentration, and as this was most likely not due to degradation, the value measured after one hour was used as $C_T(0)$ in the model.

With a slight increase in C_T over time and levelling out of degradation rate, the variation in data made automatic fitting difficult. Also, the few available data in the critical first hours make the fitting uncertain. If the k_{sorp} and k_{desorp} values determined from sorption experiments (Table 5.11) are considered, desorption rate is larger than sorption rate for both sediments, and as desorption never becomes limiting for degradation, no levelling will occur according to the full degradation-sorption model (α=0). Therefore, the full sorption model cannot be fitted reasonably to the data when sorption parameters determined in the sorption experiments are applied. When the full degradation-sorption model was fitted to data without restrictions on k_{sorp}, k_{desorp} and k_{deg}, a minimum of residual sums of squares was found for k_{sorp}=0.0137, k_{desorp}=0.0000101 and k_{deg}=0.0118. The k_{sorp} is in the same order of magnitude as that determined in sorption studies but the k_{desorp} is much lower indicating a slow desorption rate and high equilibrium sorption. The parameters equal a sorption coefficient Kd' of 1367 or a Kd of $1.37 \cdot 10^6$ [L/kg], which is about 600 times higher than that determined in the sorption experiments. This is not realistic, considering the sorption experiment results, and it indicates that the levelling of the pendimethalin curves is not due to sorption of the type that is described by the model.

As the levelling of the curve is thus likely to be caused by partial mineralisation (including incorporation in biomass etc.), the partial degradation-sorption model, given in Equation 5, was fitted to data.

The application of sorption parameters determined from the sorption experiments (Table 5.11) led to the results given in Table 5.12.

For the "pelagic" bottles, a simplification (k_{sorp} = k_{desorp} = 0) of the partial degradation-sorption model, corresponding to a situation with no sorption, was fitted to data as the particulate matter content of the filtered natural water was believed to be low.

$$C_{T,measured} = (1-\alpha) \cdot C_T(0) \cdot e^{-k_{deg}t} + \alpha \cdot C_T(0)$$

Table 5.12
Fitted parameters of the partial degradation-sorption model for pendimethalin, Sorption parameters are from the sorption experiments, Low concentration

Parameter		Sediment suspension		Pelagic	
		Lillebæk	Odderbæk	High conc.	Low conc.
k_{sorp}	h^{-1}	0.030	0.0296		
k_{desorp}	h^{-1}	0.150	0.0600		
k_{deg}	h^{-1}	0.023	0.0280	0.0150	0.0182
α		0.644	0.7817	0.322	0.377
Kd'		0.202	0.494		

It should be noted that considerable variation of k_{sorp} and k_{desorp} gave very little change in residuals squared as the measured data are very scarce in the critical first hours. The parameters determined by fitting are thus quite uncertain.

As it can be seen, the α is somewhat smaller for the pelagic experiment reflecting the higher level of the curves. An immediate explanation of this

difference could be that the sorption is only very slowly reversible so that once sorbed, the water concentration remains low and so does the degradation rate. However, initial sorption takes place within a few hours and despite this, the degradation proceeded at a high rate until 500 hours. The high particle concentration of the suspensions may increase the possibility of incorporation of ^{14}C in organic matter leading to less mineralisation.

Another plausible explanation can be found in the experimental procedure. When samples are taken from the bottles with suspended sediment, the sample will most likely contain less than average sediment. As much pesticide is sorbed to the sediment (around 20% as regards Lillebæk, 40% as regards Odderbæk), this may lead to an underestimation of the concentration and amount in the bottle and may thus explain the difference in α.

It seems that the difference in α may well be caused by the experimental procedure and by the use of ^{14}C pesticides and therefore it does not lead to any alterations of the model formulation.

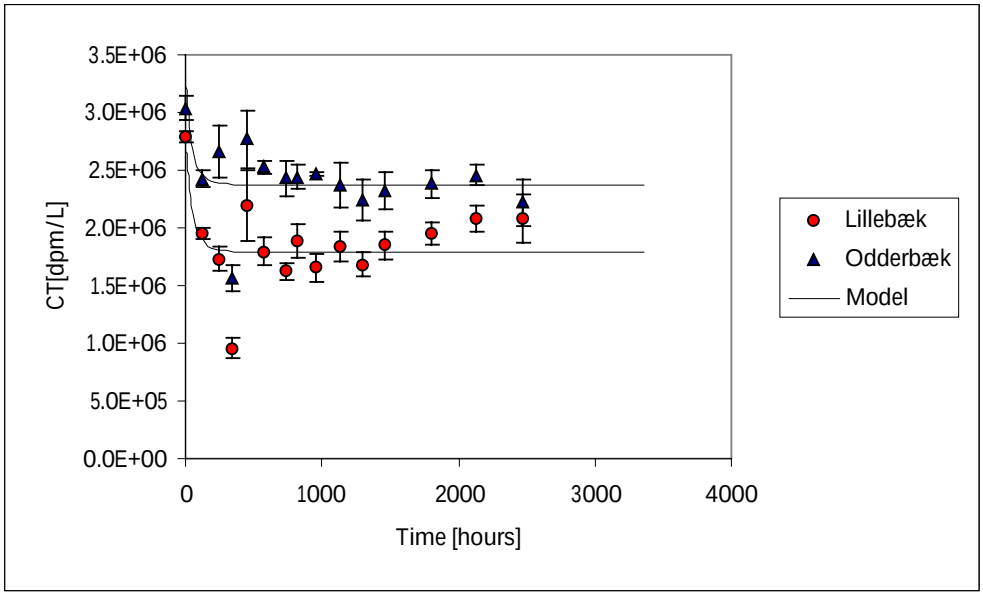


Figure 5.23
Degradation of pendimethalin in Lillebæk and Odderbæk sediment-water suspensions. Average of three bottles ± st.dev. Partial degradation-sorption model was used for fitting, parameter values are given in Table 5.12.

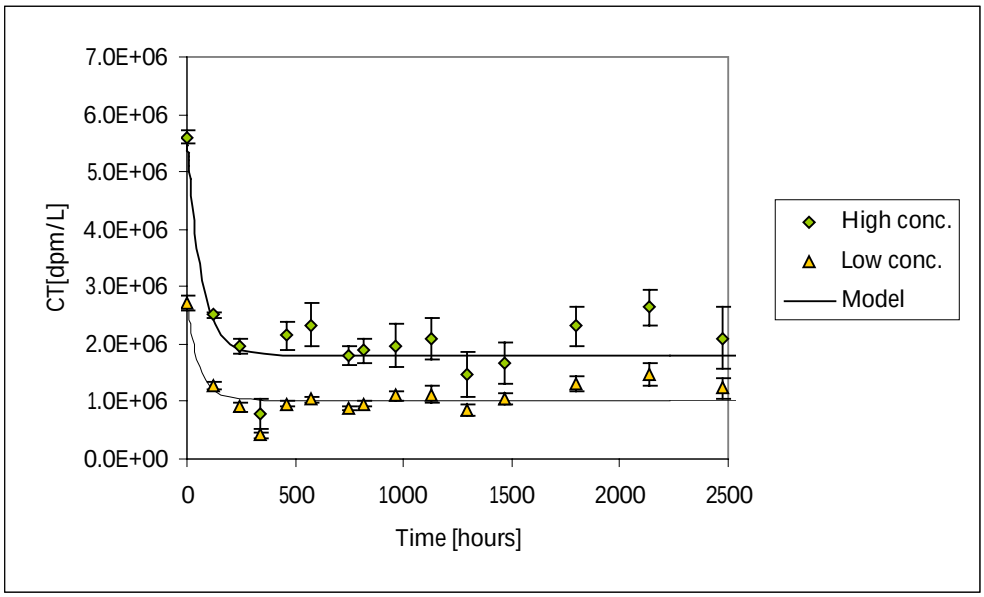


Figure 5.24
Degradation of pendimethalin in stream water at two concentrations. Partial degradation-sorption model was used for fitting, parameter values are given in Table 5.12.

5.6.3 Fitting of model to ioxynil degradation data

As for pendimethalin, the degradation-sorption model was fitted to ioxynil data. The raw data are given in Table B.26. For ioxynil, no apparent levelling occurs and α was thus set to zero. The data obtained on ioxynil is more suitable for fitting than those obtained on pendimethalin. The measured activity decreased evenly with time and the standard deviation between test bottles was small. When sorption parameters from the sorption experiments were employed (see Table 5.11), the degradation rate constant could be fitted.

Table 5.13
Fitted parameters of the partial degradation-sorption model for ioxynil, sorption parameters are from the sorption experiments

Parameter		Sediment suspensions		Pelagic	
		Lillebæk	Odderbæk	High	Low
k_{sorp}	h^{-1}	0.0041	0.0095		
k_{desorp}	h^{-1}	0.770	0.550		
k_{deg}	h^{-1}	0.000149	0.000318	0.000025	0.000012
Kd'		0.0053	0.017		

For ioxynil, the degradation rate is higher in sediment-water suspensions than in water alone, presumably due to the higher concentration of biomass. The degradation rate constant is higher for the Odderbæk than for the Lillebæk sediments, which may be attributed to differences in microbial activity. Ioxynil sorbs stronger to the Odderbæk sediment than the Lillebæk sediment but this is seemingly overshadowed by a higher microbial activity.

The fitted model is shown together with measured data for sediment suspensions in Figure 5.25.

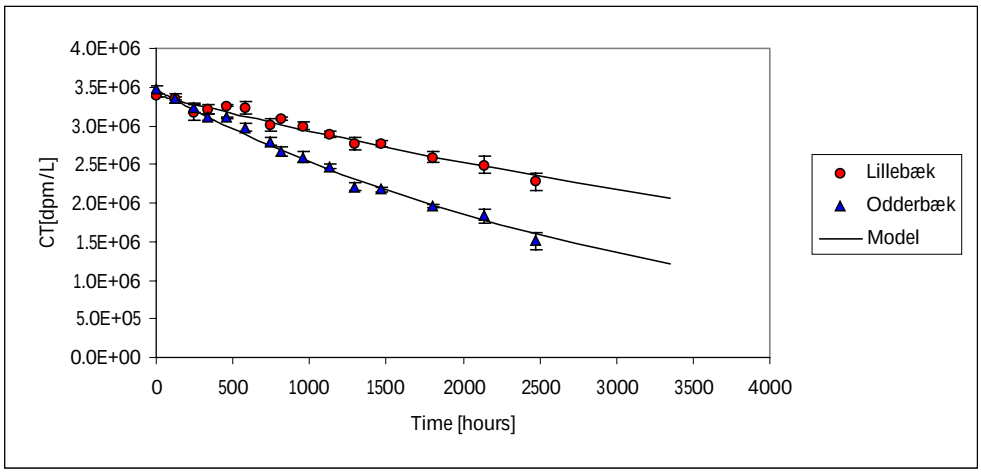


Figure 5.25
Sorption and degradation of ioxynil in the Lillebæk and the Odderbæk sediment-water suspensions. Average of three bottles ± st.dev. Degradation-sorption model was used for fitting, parameter values are given in Table 5.13.

The fitted degradation in stream water without sediment is shown in Figure 5.26 below.

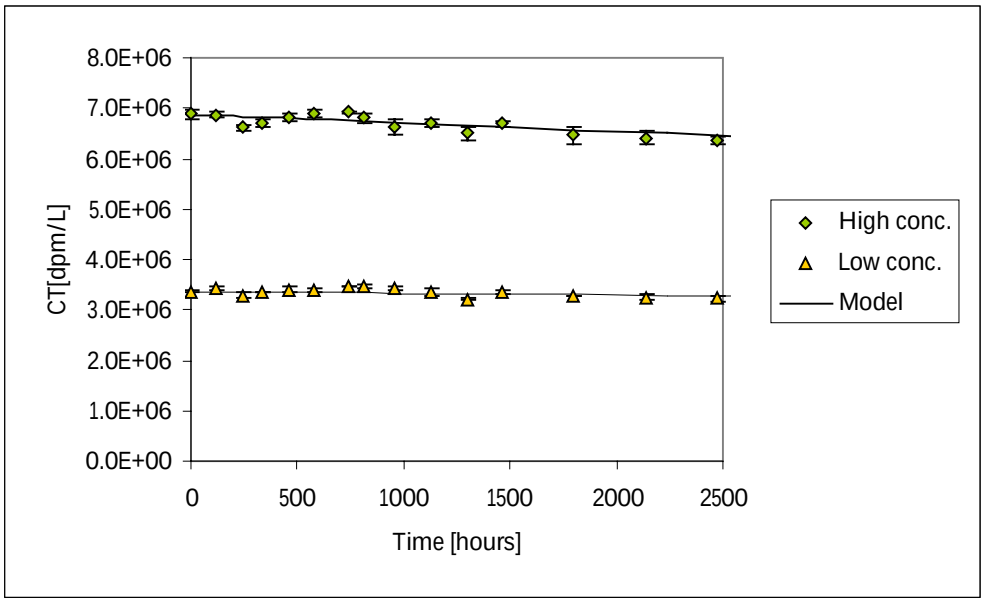


Figure 5.26
Degradation of ioxynil in stream water. Average of three bottles ± st.dev. Degradation model was used for fitting, parameter values are given in Table 5.12.

5.7 Particle concentration and biodegradation

When biodegradation data from suspension experiments are to be used in modelling, one is confronted with the problem that in these experiments, sorption and degradation occur simultaneously. Therefore, the derivation of

degradation rates must be made with care. Here, an approach taking both mechanisms into account has been described.

The concentrations of particles can affect the biodegradation of pesticides in two ways, which may have opposite effects on the degradation of pesticides. Many bacteria live in close association with particles and the concentration of bacteria and particles may therefore be positively correlated. On the other hand, the pesticides can sorb to the particles with which the bioavailability of the pesticides is reduced at high particle concentrations. In order to take these opposite effects of particles into account the following model was developed and applied to the biodegradation and sorption experiments.

The model is implemented in the user interface of the registration model, with which the dichotomy of particles and biodegradation is taken into account.

5.7.1 Model set-up

The rationale behind the model is:

From the user interface, a degradation rate (h^{-1}) and the particle concentration of the experiment are available. The degradation of the total concentration of pesticide is described by the following differential equation:

$$(1) \quad \left.\frac{dC_{tot}}{dt}\right|_{degradation} = C_{tot} \cdot k_{tot}$$

where C_{tot} denotes the total pesticide concentration and k_{tot} a first-order degradation rate.

According to the model, the pesticides may either be dissolved or sorbed to particles. The sorption is assumed to be linear, reversible and instantaneous yielding the expression:

$$(2) \quad \frac{C_s}{C_w} = K_d$$

where C_s is the concentration (in relation to the dry mass of sorption medium) of sorbed substance (kg/kg), C_w is dissolved substance concentration (kg/L) and K_d is the sorption coefficient (L/kg). A mass balance for the substance is:

$$(3) \quad C_{tot} = \theta \cdot C_w + \rho \cdot C_s$$

where θ is the volume fraction of water, ρ is the dry bulk density of the sorption medium (kg/L). A combination of (2) and (3) yields:

$$(4) \quad C_{tot} = R \cdot C_w, R \equiv (\theta + \rho \cdot K_d),$$

where R is defined as a retention factor.

It is further assumed that bacteria are only able to assimilate dissolved pesticides and not pesticide sorbed to particles. The degradation of dissolved pesticide is then given be the following differential equation:

(5) $$\frac{dC_w}{dt} = C_w \cdot k_{dis}$$

Where k_{dis} denotes a first-order degradation rate for the dissolved pesticide.

Combining equations (4) and (5) yields:

(6) $$\frac{dC_w}{dt} = C_{tot} \cdot \frac{k_{dis}}{R}$$

Combining equations (1) and (6) yields:

(7) $$k_{tot} = \frac{k_{dis}}{R}$$

Assuming that the bacterial activity per volume of particles is constant and that the activity of pelagic bacteria is constant, k_{dis} can also be written as:

(8) $$k_{dis} = K_3 \cdot (K_1 + K_2 \cdot \frac{(1-\theta)}{\theta})$$

Where K_1 denotes a relative activity of the free-living "pelagic" bacteria and K_2 is a particle volume-specific activity of the bacteria associated with particles. K_3 denotes a pesticide-specific degradation rate per bacterial activity.

Combining (7) and (8) yields:

(9) $$k_{tot} = \frac{K_3 \cdot (K_1 + K_2 \cdot \frac{(1-\theta)}{\theta})}{R}$$

For the experiments without particles (pelagic), equation (9) is reduced to:

(10) $$k_{tot} = K_3 \cdot K_1$$

For ioxynil, K_3 is set to 1 and K_1 is then equal to the first-order degradation rate measured in the experiment without particles. Subsequently, K_3 for pendimethalin can be calculated as the ratio of the first-order degradation rates of pendimethalin to ioxynil measured for the experiments without particles. When K_1 and K_3 are known, K_2 can be calculated. Applying the above equations and rationale to the results of Tables 5.12-5.13, the following results are obtained (Table 5.14).

Table 5.14
Calculated values of the constants K_1, K_2 and K_3 for the biodegradation experiments with pendimethalin and ioxynil conducted with and without particles

Pesticide	Unit	Ioxynil	Pendimethalin	Ioxynil	Pendimethalin
Locality		Lillebæk		Odderbæk	
k_{tot}	hr^{-1}	0.00015	0.023	0.00032	0.028
Water volume	L	0.1	0.1	0.1	0.1
Particle mass	kg	0.0001	0.0001	0.0001	0.0001
Particle density	kg/L	2.4	2.4	2.4	2.4
Particle volume	L	$4.2 \cdot 10^{-5}$	$4.2 \cdot 10^{-5}$	$4.2 \cdot 10^{-5}$	$4.2 \cdot 10^{-5}$
Porosity	L/L	0.9996	0.9996	0.9996	0.9996
Dry bulk density	kg/L	0.001	0.001	0.001	0.001
K_d	L/kg	5.9	224	19.2	2074
Retention		1.01	1.22	1.02	3.07
K_3	hr-1	1	897	1	897
K_2	hr-1	0.0000185	1.85E-05	0.0000185	1.85E-05
K_3	hr-1	0.315	0.0309	0.733	0.185721

On the basis of the constants of Table 5.14, an extrapolation to a natural aerobic sediment with a porosity of 0.75 was conducted. If a median value of 0.25 for K_2 is used, the degradation rates, shown in Table 5.15, are obtained.

Table 5.15
First-order degradation rates (h^{-1}) for sediments in Odderbæk and Lillebæk with a porosity of 0.75 calculated on the basis of the constants of Table 5.14.

Pesticide	Location	k_{tot} [hr^{-1}]
Ioxynil	Lillebæk	0.019
Ioxynil	Odderbæk	0.0068
Pendimethalin	Lillebæk	0.55
Pendimethalin	Odderbæk	0.060

6 Conclusions from laboratory experiments

A large number of sorption and desorption rates for the three model pesticides with different sediments have been produced together with a large number of equilibrium partitioning constants.

Pendimethalin sorbed strongly to sediments while ioxynil and bentazone sorbed much less.

For all pesticides, the degree of sorption was depending on sediment organic matter. Thus, K_{oc} values must be used when predicting sorption. For pendimethalin, differences in pesticide concentration influenced equilibrium partioning markedly, and sorption was higher at low concentrations.

A temperature difference of 16°C did not influence equilibrium sorption, indicating that the influence of temperature on sorption rates may be omitted in the stream and pond pesticide fate models.

Sorption was very fast in all experiments with most of the sorption happening within the first couple of hours. The sorption rate did not seem to depend on pesticide concentration level for a weakly sorbing sediment. Although the sorption was fast, it is probably too slow to be disregarded in systems with short residence times such as the small streams of Odderbæk and Lillebæk. This will be shown by model runs with the parameters generated here.

The changes in aqueous pesticide concentrations could be modelled well with the suggested sorption model.

A number of degradation rates for stream water and stream-sediment suspensions have been produced.

It was shown that for a moderately sorbing pesticide such as ioxynil, the degradation rate in water-sediment suspensions was higher than in water alone, probably due to higher degrading biomass.

For a strongly sorbing pesticide such as pendimethalin, it was shown that the presence of sediment caused a smaller degradation, probably due to reduced bioavailability caused by sorption.

7 Materials and methods, field experiments

Four experiments were carried out in the mesocosm facilities of NERI (National Environmental Research Institute). The five pesticides used in these experiments are given in Table 2.1. The pesticides were selected to cover a range of physico-chemical properties in order to strengthen the generalisation value of the model**.** It was expected that the more hydrophilic compounds (bentazone and ioxynil) would readily be mixed into the water column while the more hydrophobic compounds might show a vertical concentration gradient (Mogensen et al., 2002; Sørensen et al., 2002). Sorption of pesticides to sediment was studied in experiments with highly sorbing compounds (fenpropimorph, pendimethalin and glyphosate). The impact of macrophytes on the dissipation of pesticides from the water phase was studied in one experiment (fenpropimorph and pendimethalin).

7.1 Experimental ponds

The mesocosm facilities at NERI consist of four ponds with a bottom area of about 90 m^2 and a depth of about 1 m. The mesocosm facilities were established in November-December 1994. NERI is situated at the peninsula of Risø at Roskilde Fjord 8 km north of Roskilde, Sealand, Denmark. The mesocosms are established in an area with heavy clay making it possible to retain water in the ponds without assistance of an artificial membrane. Figure 7.1 provides an overview of the experimental area. For further information about the establishment of the ponds, see Mogensen et al. (2002). For the current experiment, two ponds, ponds 3 and 4, were sprayed with pesticides and one pond, pond 2, was used as a control. The ponds are mature with a variety of plant and animal species.

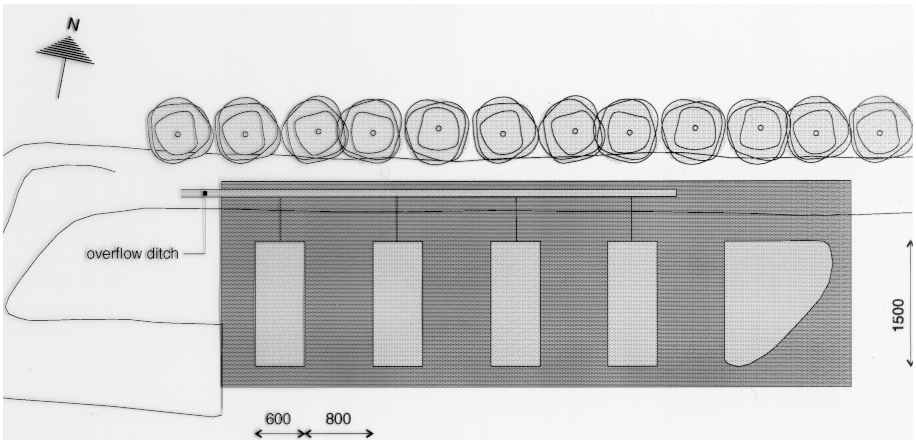


Figure 7.1
Overview of the experimental site at NERI, including 4 ponds and a reservoir. All measures are in cm. The ponds are numbered from 1 to 4, number 1 being next to the reservoir.

In one experiment, a screen made of polyethylene fast lock plates was mounted to divide one pond into two separate ponds with identical conditions. A gap in the partition wall was left open until two days before spraying in order to allow mixing of water from the two separate parts. In one part, all macrophytes were removed or cut down to a few cm about two weeks before spraying. The removed macrophytes were dried and weighed. Average amount of removed macrophytes was 713 g dry matter per square meter.

The actual depth of the ponds changes according to climatic conditions. Table 7.1 includes measured depth of the ponds during the experiments.

Table 7.1
Date of pesticide application and measured depths of experimental ponds during the experiments

Date of spraying	Pond #	Depth (m)						
		day 0	day 6	day 14	day 31	day 39	day 40	day 83
090699	3	0.95					0.75	0.57
070999	4	0.80		0.64				
090500	4	1.05				0.75		
050900	3	0.55	0.59	0.55	0.56			

7.2 Spraying of pesticides

Pesticides were sprayed onto the surface of the ponds using an 8-m hand-carried spraying boom. Pesticides were mixed with 10 L of tap water in a steel bottle and all of the mixture was applied uniformly onto the surface of the pond. All pesticide solutions were prepared from formulated products: Basagran (bentazone) from BASF, Totril (ioxynil) from Rhône-Polenc, Corbel (fenpropimorph) from Novartis, Stomp SC (pendimethalin) from Cyanamid, Roundup Bio (glyphosate) from Monsanto. Table 7.2 provides an overview of the amount of active ingredient applied in each of the four experiments and the initial nominal concentration of pesticide in the water. The nominal concentration assumes even distribution of pesticide within the water body.

Table 7.2
Spraying dates, applied amount of each active substance and calculated initial concentrations

Date of spraying	Pond #	Sprayed Substance	Total sprayed mass (mg)	Calculated initial concentration Co (µg/L)
090699	3	Ioxynil	113	1.40
090699	3	Bentazone	120	1.49
070999	4	Pendimethalin	100	1.48
070999	4	Fenpropimorph	100	1.48
090500	4	Glyphosate	857	9.64
050900	3	Pendimethalin[1]	100	2.15
050900	3	Fenpropimorph[1]	100	2.15

[1]: In this experiment, the pond was divided into two separate parts by a partition wall. In one part the macrophytes were removed while they were kept in the other part.

[1]: I dette forsøg blev vandhullet delt op i to adskilte dele med en skillevæg. I den ene halvdel blev vandplanterne fjernet, mens de blev bevaret i den anden.

7.3 Sampling techniques

7.3.1 Water samples

Water samples were collected from the bank. A Duran red cap bottle was equipped with two silicone tubes, a short one for letting water into the bottle and a long one for letting air out of the bottle. The bottle was attached to a long fishing rod by adjustable lines allowing the sampling bottle to be lowered into the pond and samples to be collected at a desired depth. Water samples were combined from different positions and depths for average concentration measurements. Gradient samples were collected from two or three depths.

7.3.2 Sediment samples

Top sediment from the control pond was sieved through a 2-mm mesh and mixed into a homogeneous mixture. Sediment was placed in trays made of perforated stainless steel lined with nylon tissue. The sediment layer was two cm deep. The sediment trays were placed in a big stainless steel tray and lowered to the bottom of the ponds prior to spraying. The sediment trays were collected one by one as indicated in the sediment graphs.

7.4 Methods of analysis

7.4.1 Water samples

Ioxynil, ***bentazone***, ***fenpropimorph*** and ***pendimethalin*** were analysed by the same method of analysis. Water samples were extracted by solid phase extraction using Porapak RDX cartridges 500 mg. Samples were eluted using 2 x 5 mL dichloromethan/methanol (80:20) for bentazone and ioxynil analyses and with 2 x 5 mL 100% dichloromethane for pendimethalin and fenpropimorph analyses. The extracts were reduced under a stream of nitrogen.

A detailed description of the method of analysis is available in the report from subproject 8.

Glyphosate. All samples were analysed by Danish Institute of Agricultural Sciences (Spliid, 2002). The analytical principles are outlined below. Water samples: The amino group in the glyphosate and AMPA molecules was derivatised under basic conditions followed by extraction with a mixture of dichloromethane and methanol. The solvent was discarded, the water phase was acidified and extraction was repeated. The organic phase was evaporated to dryness and the bottle rinsed with dichloromethane. The derivatives were released from the glass surface with methanol/water. Separation and detection of the derivatives were carried out by HPLC followed by electrospray (ESI) ionisation and mass-spectrometry.

Detection limits (DL) for AMPA and glyphosate were 0.01-0.02 µg/L in lysimeter water. It is assumed that the same detection limits apply for pond water. Day-to-day method uncertainty was about 20%.

7.4.2 Sediment samples

Fenpropimorph and ***pendimethalin***. Sediment samples were freeze-dried and homogenised. 5.0 g of dry sediment was weighed into a teflon tube adding

100 µL of 1000 ng/L isodrin as a recovery standard. The acetone solvent was evaporated. 20 mL of acetone was added as extraction solvent. The tube was closed and the extraction procedure carried out in a microwave oven. After extraction, the samples were allowed to settle for 45-60 min before they were removed from the oven. The extract was transferred to a 1000-mL round-bottom flask using a pasteur pipette. Volume of the extract was reduced by rotor evaporation and transferred to a 16-mL dram glass and further reduced to about 75 µL with a flow of nitrogen using 1000 µL of isooctane as a keeper. 5 mL of hexane was added to the remaining extract. This extract was cleaned up on a florisil column. Columns were conditioned with 10 mL of 10% ethylacetate in hexane followed by 10 mL of hexane. The extract was added to the column, which was eluted with 10 mL of 5% ethylacetate in hexane. Run through and eluate were combined and the volume reduced to about 75 µL using isoctane as a keeper. Hexachlorobenzene was added as an internal standard and volume adjusted to 1 mL. Analysis was performed using GC-MS.

Detection limits (DL) for fenproprimorph were 5.2 µg/kg dry matter and for pendimethalin 1.6 µg/kg dry matter. Standard deviations within batch/between batches were 4.3/12.2% for fenpropimorph and 5.4/5.8% for pendimethalin.

Glyphosate. Sediment samples were initially extracted by basic extraction. After extraction, the analysis followed the method described for water samples. Detection limits (DL) for AMPA and glyphosate were 0.5-1.0 µg/kg in soil. It is assumed that the same detection limits apply for sediment. Day-to-day method uncertainty was about 20%.

8 Results and discussion, field experiments

8.1 Bentazone and ioxynil

Bentazone and ioxynil were sprayed simultaneously. Average water concentration is shown in Figure 8.1 as a function of time.

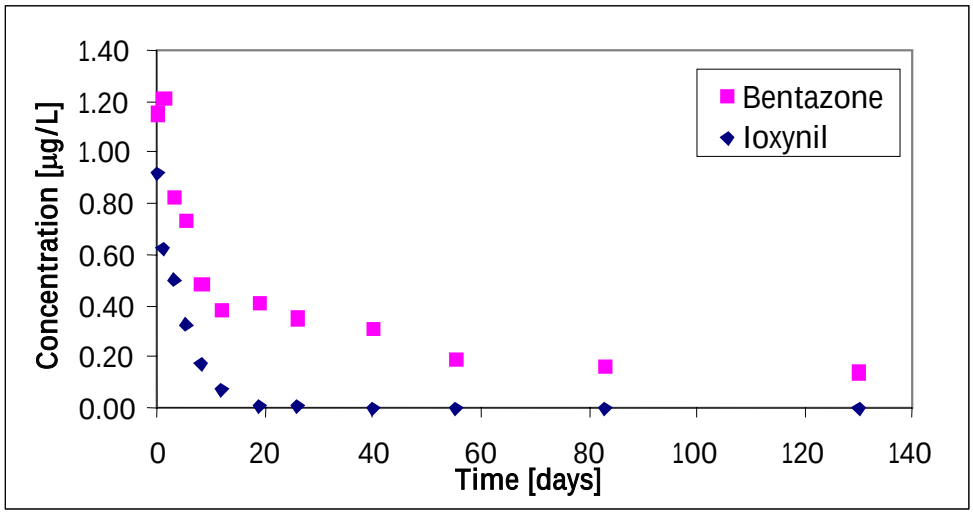


Figure 8.1
The time trend of bentazone and ioxynil

Ioxynil is seen to disappear within the first 20 days while bentazone seems more persistent. The long tailing of the bentazone concentration level is in contrast to the relatively rapid drop in the bentazone concentration level during the first few days when the bentazone concentration seems to drop at the same rapid rate as ioxynil. The high initial dissipation rate is probably due to photolysis of the compound in the upper part of the water column where most of the compound is located (Vestergaard, 2002).

8.2 Pendimethalin and fenpropimorph

8.2.1 Water phase

Pendimethalin and fenpropimorph show low water solubility and high K_{ow} compared to bentazone and ioxynil. Two experiments were carried out with mixtures of these two compounds. In the first experiment, the vertical concentration gradient and the sediment uptake were studied along with dissipation from the water column. In the second experiment, the impact of macrophytes on the dissipation and hydraulic mixing was studied in addition to the other processes. The average water concentration of the pesticides is shown in Figure 8.2. The application rate of pesticides was the same for both

experiments. Dissipation of pesticides of fen 1 and pendi 1 (1999) was therefore expected to be similar to that of fen 2 (incl. macro) and pendi 2 (incl. macro)(2000). It is thus surprising to see the relatively large difference between the two years. The calculated initial concentration in Table 7.2 was higher for year 2000 compared to year 1999, however, that difference cannot explain the large difference in dissipation rates shown in Figure 8.2. One explanation may be that there are some extra sorption sites in the water phase in 2000 compared to 1999. Removal of macrophytes from the pond was mainly performed 3 weeks prior to spraying of the pond with extra cutting 1 week before spraying. This caused resuspension of the sediment, which had, however, settled again. Two days before spraying, there was a heavy rainfall, which caused flooding of the partition wall and it was necessary to pump the excess water into pond 1. The rainfall and the pumping may have caused resuspension of sediment, which may explain the extra sorption. Sorption of pesticides to suspended matter would hinder the transfer from the water column to solid surfaces due to sorption because the free dissolved part of the substance in the water column was reduced. The chemical analysis of pesticides in the water phase includes dissolved compound as well as compound sorbed to suspended matter. Measurements of turbidity did not show any differences between the two years. However, the turbidity measurement may not suffice to detect the difference in water content of any possible medium for sorption. Such a sorption medium could be either suspended solids or dissolved organic matter.

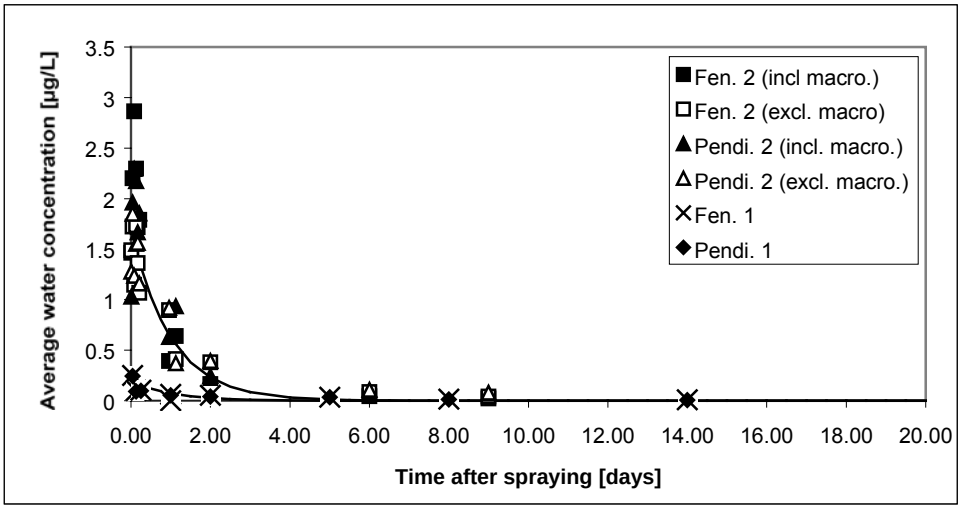


Figure 8.2
Average concentration of pendimethalin and fenpropimorph as a function of time. The curves are fit to the experimental data. The lower curve includes data for 1999 (Fen. 1 and Pendi. 1). The upper curve includes data from 2000 (Fen. 2 incl. and excl. macro. and Pendi. 2 incl. and excl. macro).

While there is significant difference in concentration and dissipation rate between years, there is only little difference within the same year in experiments with and without macrophytes. It may surprise that the water concentration of pesticides is not highly affected by the removal of macrophytes remembering that 713 g dry matter per m^2 had been removed

from one part of the pond. In this experiment, macrophytes seem to have little significance as sorption medium.

Macrophytes do, however, affect the fate of pesticides in the ponds. Figures 8.3-8.4 compare concentrations of fenpropimorph and pendimethalin in the water phase in ponds with and without macrophytes at different times after spraying. Figure 8.3 includes data points before 1.13 days while Figure 8.4 includes data points after 1.13 days. For the first 1.13 days, the macrophytes result in a higher water concentration while, after 1.13 days, they result in a lower water concentration. The significance of this observation was tested statistically using a binomial test on pairs of observations (bigger than/smaller than). Significance level for data in Figure 8.3 is 0.999 and for data in Figure 8.4 it is 0.965.

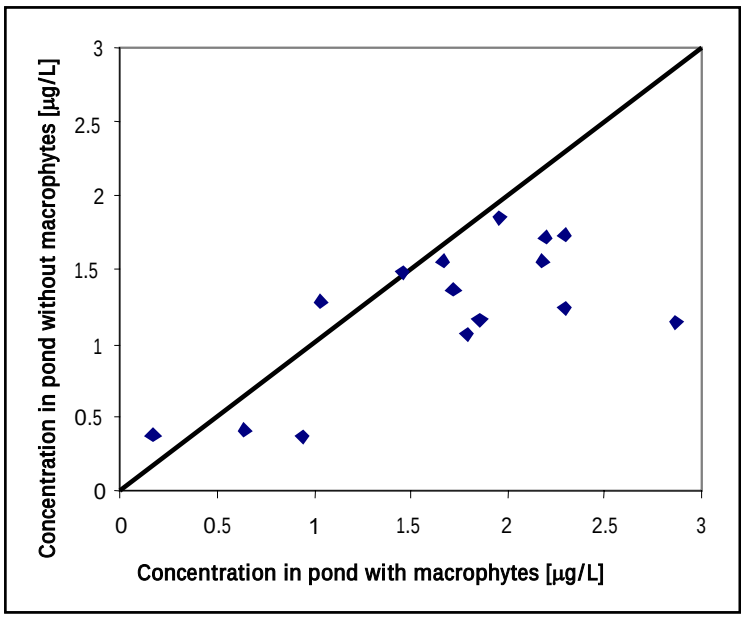


Figure 8.3
Concentration of fenpropimorph and pendimethalin in water column from pond without macrophytes, at different times, versus concentration from pond with macrophytes at the same times. Only times before 1.13 days are included.

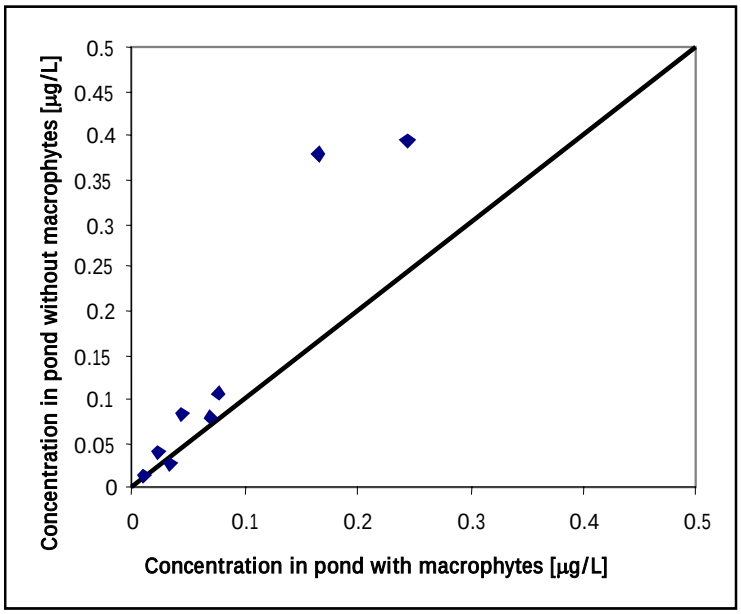


Figure 8.4
Concentration of fenpropimorph and pendimethalin in water column from pond without macrophytes, at different times, versus concentration from pond with macrophytes at the same times. Only times after 1.13 days are included.

The explanation of the observed differences may be that the macrophytes hinder the turbulence in the water column and thus the initial high rate of removal from the water column caused by transport and sorption to sediment. After about one day, the increased surface for sorption related to macrophytes results in a lower concentration level in the water.

The model used for prediction of environmental fate of pesticides assumes momentarily mixing of pesticide into the waterbody. If that is the case, the concentration of pesticide should be the same in the upper and lower parts of the water column. The assumption was investigated by analysing water samples from different depths of the pond. Figure 8.5 compares concentrations of pendimethalin and fenpropimorph in the upper part of the pond with concentrations at the same time about 35 cm from the bottom. A distinct concentration increase can be observed in upward direction. The sampling method introduced some turbulence in the water and thus the actual concentration differences may be larger than the measurements indicate. The observation is in accordance with previous observations of concentration gradients in ponds sprayed with pyrethoid insecticides (Mogensen et al., 2002).

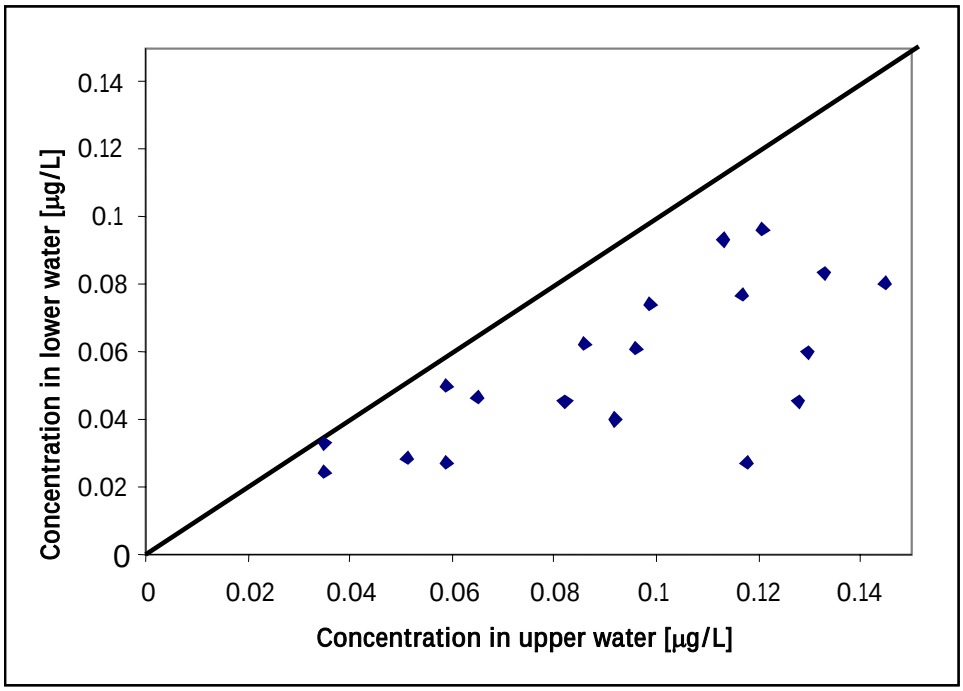


Figure 8.5
Concentration of fenpropimorph and pendimethalin in upper part of the pond compared to that in the bottom part on the first two days after application. September 1999.

8.2.2 Sediment

In the pond with macrophytes, there were only traces of the two pesticides in the sediment. In the pond without macrophytes, the concentrations of both compounds were measurable. The difference in concentrations was most pronounced for pendimethalin, which is the more hydrophobic of the two pesticides (Figure 8.6).

There was an open connection between the two parts of the pond until the day before spraying when the last fragment of the partition wall was installed. The composition of the water in the two parts should therefore be almost identical.

The concentration of pesticide in the sediment reflects the concentration of pesticide in the water layer immediately above the sediment. Since there is a higher concentration of pesticides in the sediment in the macrophyte-poor part of the pond, the concentration in the water close to the bottom must have been higher as well.

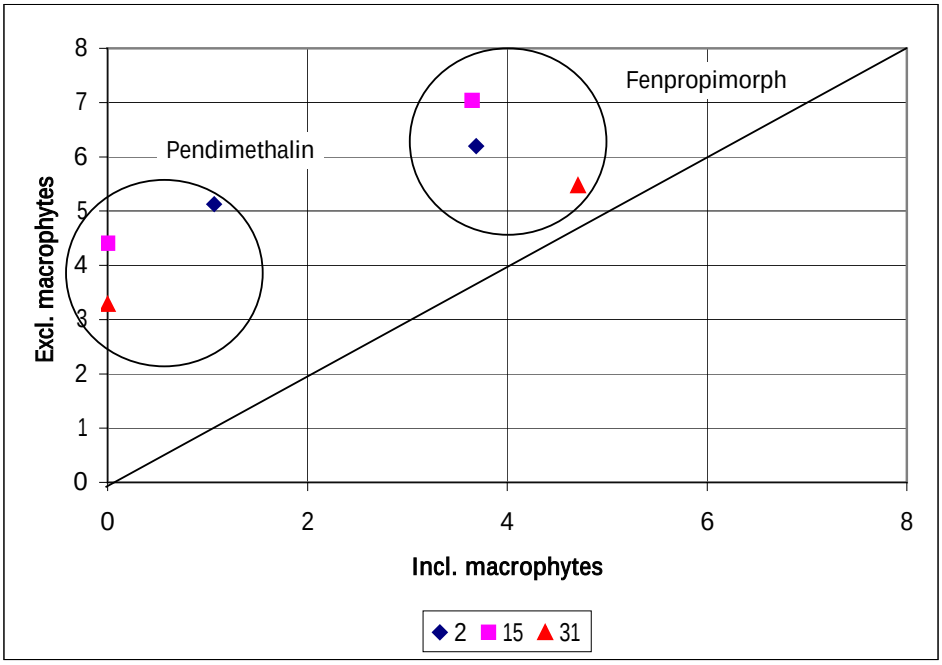


Figure 8.6
Concentration of fenpropimorph and pendimethalin in sediment from sediment trays 2, 15 and 31 days after spraying. Sediment in pond with macrophytes versus pond without macrophytes.

A higher concentration of pesticide in the bottom water may be caused by a less pronouced concentration gradient in the pond without macrophytes. The gradient in the macrophyte pond may result from slow mixing or from sorption of pesticides to the macrophytes. If sorption to macrophytes was the main controlling factor, a lower concentration of pesticides in the bulk water samples would be expectable. This does not seem to be the case. Alternatively, the higher concentration in the sediment in the non-macrophyte pond may be due to faster vertical transport caused by faster mixing. This theory is supported by the above observations of pesticide concentrations in the water phase.

8.3 Glyphosate and AMPA

8.3.1 Water phase

Glyphosate is a small ionic compound. It is water-soluble and sorbs to soil and sediment, especially to clay particles. It was selected for this experiment because of its special physico-chemical properties and its widespread use in Danish agriculture. Glyphosate was applied once in the spring of 2000. Both glyphosate and the degradation product AMPA were analysed. Figure 8.7 shows the water concentration of glyphosate during the first one and a half days after spraying. Sampling took place in three different depths, top, middle and bottom. A gradient is identified during the first day when the concentration increases from bottom towards the surface. The result is similar to that observed with fenpropimorph and pendimethalin. After about one day, the gradient has levelled out.

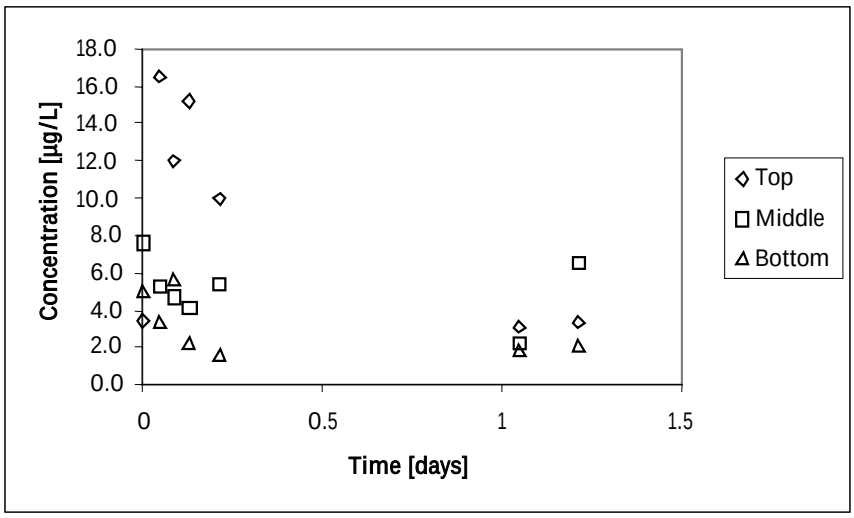


Figure 8.7
Concentration of glyphosate in water samples in three different depths (top, middle and bottom)

Figure 8.8 displays the average concentration of glyphosate in the water phase during the first two weeks after application. Most of the substance dissipated during the first week after spraying.

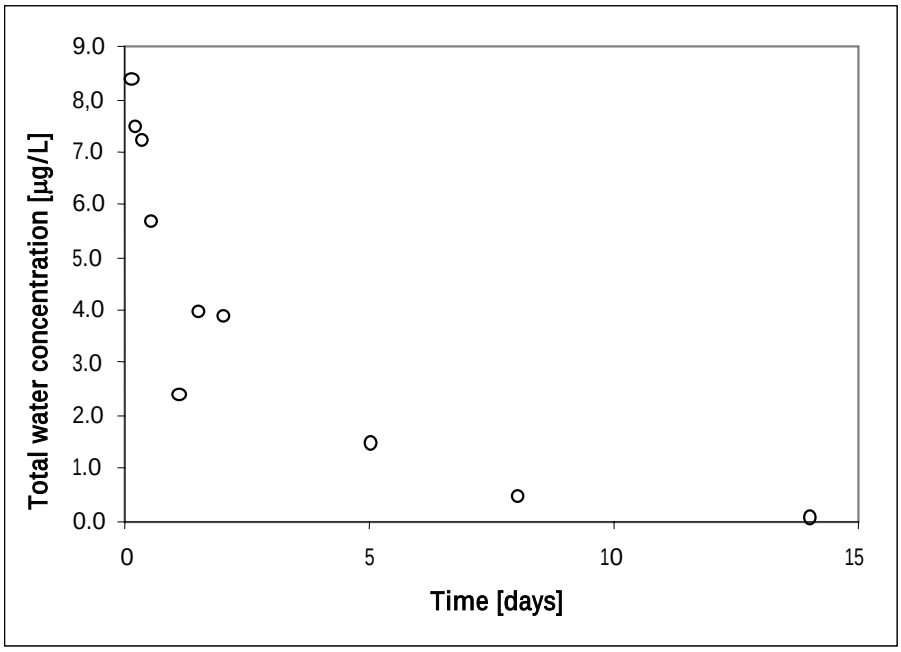


Figure 8. 8
Average concentration of glyphosate in the water phase during the first two weeks after application

Degradation of glyphosate into AMPA was slow in the water phase, the concentration of AMPA not exceeding 0.14 µg/L compared to 16 µg/L of glyphosate. As for glyphosate, there was a concentration gradient with highest concentrations in the top samples (Figure 8.9).

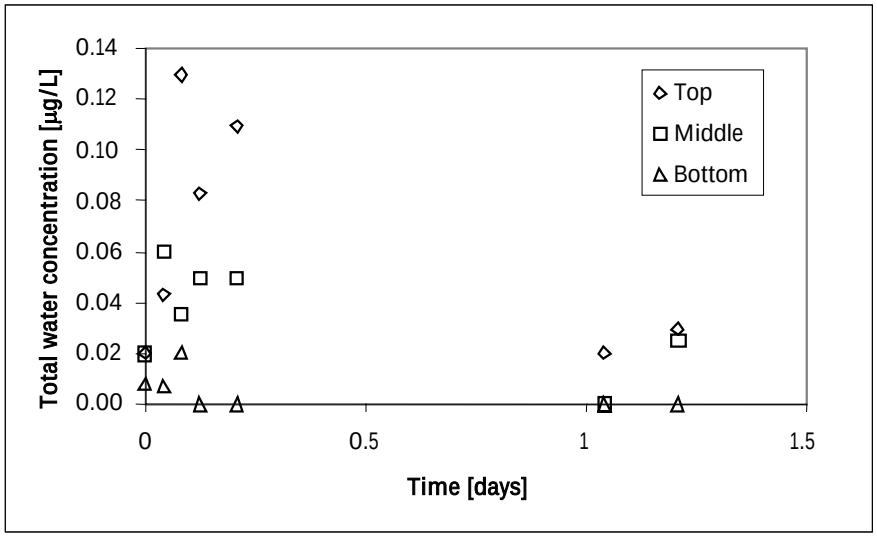


Figure 8.9
Concentration of AMPA in water samples in three different depths (top, middle and bottom)

8.3.2 Sediment

In the sediment measurement, AMPA was dominant compared to glyphosate (Figure 8.10). Glyphosate sorbed to the sediment where it was transformed into AMPA.

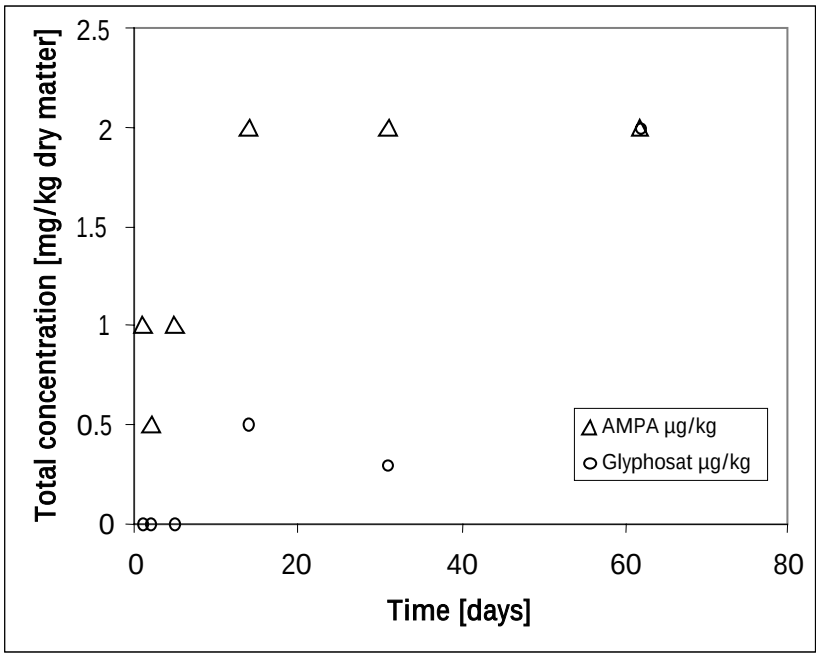


Figure 8.10
Concentration of AMPA and glyphosate respectively, in the sediment as a function of time

8.4 Comparison with effect studies in mesocosm systems

A comprehensive review of effect studies of pesticides conducted with mesoscosms experiments was performed by Møhlenberg et al. (2001). The review included more than 100 original studies, which were selected among many more studies from literature according to objective quality criteria. Furthermore, the analysis of the collected literature included overall statistical analysis of the data material extracted from the literature and detailed analysis of selected studies. The majority of the mescosm experiments reviewed by Møhlenberg et al. were conducted in ponds of similar dimensions and specifications as the ponds used in the present studies. Especially the effect studies including macroinvertebrates were conducted in ponds similar to the ponds used in the present exposure study. In order to facilitate the linkage between the exposure and effect studies, a comparison between the main results of Møhlenberg et al. and the exposure studies of the present report was made.

An important result of the statistical analysis of Møhlenberg et al. was that the size of the K_{ow} values or the ability to sorb was more important for the toxic response of the macroinvertebrates in the ponds than the inherent single species toxicity of the compound. The single species toxicity was measured by standardised toxicity tests, in which the test organisms were exposed to the pesticide through the water phase. In the ponds, the main exposure route for the invertebrate may, however, be through ingested particles, to which the pesticides sorb. The statistical analysis of Møhlenberg et al. might therefore reflect that macroinvertebrates in the ponds are mainly exposed to pesticide sorbed to ingested particles rather than to pesticides dissolved in the water phase. Indirect evidence for this hypothesis is provided by the exposure studies of the present report, in which the rapid disappearance of, in particular, hydrophobic pesticides from the water column can be explained by sorption to particles in the sediment (Styczen et al., 2002a; Sørensen et al., 2002).

9 Conclusions from field experiments

Distinct time trends of decreasing water concentration levels were recorded for all the pesticides sprayed in the artificial ponds. A nearly complete removal was seen within the first two weeks. Bentazone, however, showed a rapid decrease during the first few days followed by a more stable water concentration during the next 130 days or more (the experiment lasted 130 days). The more hydrophobic substances such as pendimethalin and fenpropimorph dissipated rapidly from the water column during the first few days. The year-to-year variation for pendimethalin and fenpropimorph greatly exceeded the variation within the same year for ponds with and without macrophytes. One explanation may be the presence of sorption sites in suspension either as suspended solids or as organic matter. This indicates that the modelling of exposure levels in real systems needs to be done with care and, even for relatively simple systems, in which the spraying is well controlled, large variability in the results may occur.

The most rapid recorded decrease in water concentration indicates that a diffusion process takes place as this specific transfer process can introduce an initially infinitely high concentration decrease rate.

The field experiments have generated fate data for calibration and validation of the registration model for pesticides with a range of physico-chemical properties. The use of these data for calibration and validtion will improve the field of validity of the model.

It may take 1-2 days after pesticide application until the concentration of pesticide is evenly distributed in the ponds. This is contrary to the assumption of the model that there is instantly complete mixing.

Presence of macrophytes influence dissipation of pesticides from the water phase by reducing the hydraulic mixing and thereby delaying transport of pesticides to the sediment. Furthermore, pesticides may sorb to macrophytes thereby reducing the concentration in the water phase.

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Appendix A.
Preparation of pesticide solutions

For each pesticide concentration to be investigated, a pesticide solution of suitable concentration was made. In this way, the same volume of pesticide solution could be added to all flasks. In order to improve sedimentation during centrifugation (OECD 106), a solution of $CaCl_2$ was used as the aqueous phase in the test tubes and thus also in the fabrication of pesticide solutions.

The following terms are used in the description of the preparation of pesticide solutions.

- Original solution: The solution provided by supplier
- Basic solution: A solution made by increasing the volume of the original solution with solvent or a solution made by dissolving solid pesticide with solvent
- Stock solution: The solution from which the working solutions typically were made.
- Working solutions: The solutions of different concentrations added to test tubes

The concentrations of the pesticide working solutions were determined by liquid scintillation counting (LSC) before use.

Pendimethalin

Stock solution
A stock solution was prepared by adding acetone to 0.1 mL of the original solution (C = 121 µCi/mL) in a 10-mL measuring flask, resulting in a concentration of 1.21 µCi/mL or 21.8 mg/L. Three 10-µL samples were analysed and the average concentration was 2682700 ± 48900 dpm/mL or 1.21 µCi/mL

Kinetic experiments with pond sediment
A low concentration working solution was prepared by adding 1 mL of the stock solution (C = 1.21 µCi/mL) to a-200 mL measuring flask and adjusting volume to 200 mL with a 0.01-M $CaCl_2$ millipore water solution. This made a nominal concentration of 0.00606 µCi/mL or 0.109 mg/L. Three samples of this solution were analysed (counted) and the concentration was 11772 ± 367 dpm/mL, which equals 0.00530 µCi/mL or 0.0960 mg/L (S.D. 1.56%).

A high concentration working solution was prepared by adding 2 mL of the stock solution (C = 1.2127 µCi/mL) to a 200-mL measuring flask and adjusting volume to 200 mL with a 0.01-M $CaCl_2$ millipore water solution. This made a nominal concentration of 0.0121 µCi/mL or 0.219 mg/L. Three samples of this solution were analysed (counted) and the concentration was 24285 ± 1354 dpm/mL, which equals 0.0109 µCi/mL or 0.197 mg/L (S.D. 2.79%).

Kinetic and equilibrium experiments with stream sediment
A high concentration working solution was prepared by adding 2 mL of the stock solution (C = 1.21 mCi/mL) to a 250-mL measuring flask and adjusting volume to 250 mL with a 0.01-M $CaCl_2$ millipore water solution. This made a nominal concentration of 0.00970 μCi/mL or 0.175 mg/L. Three samples of this solution were analysed (counted) and the concentration was 14636 ± 273 dpm/mL, which equals 0.00659 μCi/mL or 0.119 mg/L (S.D. 0.93%).

A medium concentration working solution was prepared by adding 0.5 mL of the stock solution (C = 1.21 mCi/mL) to a 100-mL measuring flask and adjusting volume to 100 mL with a 0.01-M $CaCl_2$ millipore water solution. This made a nominal concentration of 0.00606 μCi/mL or 0.109 mg/L. Three samples of this solution were analysed (counted) and the concentration was 11485 ± 468 dpm/mL, which equals 0.00517 μCi/mL or 0.0933 mg/L (S.D. 1.0%).

A low concentration working solution was prepared by adding 25 mL of the medium concentration solution (C = 0.00606 mCi/mL) to a 50-mL measuring flask and adjusting volume to 50 mL with a 0.01-M $CaCl_2$ millipore water solution. This made a nominal concentration of 0.00303 μCi/mL or 0.0547 mg/L. Two samples of this solution were analysed (counted) and the concentration was 4429 ± 9.19 dpm/mL, which equals 0.00200 μCi/mL or 0.0361 mg/L (S.D. 0.4%).

Kinetic experiments with Lake Vaparanta sediment
The above stock solution was used.

Experiments with temperature variation, lake sediments
A high concentration working solution was prepared by adding 2 mL of the stock solution (C = 1.21 mCi/mL) to a 250-mL measuring flask and adjusting volume to 250 mL with a 0.01-M $CaCl_2$ millipore water solution. This made a nominal concentration of 0.00970 μCi/mL or 0.175 mg/L. Three samples of this solution were analysed (counted) just before use and the concentration was 15904 ± 930 dpm/mL, which equals 0.0072 μCi/mL or 0.129 mg/L (S.D. 5.8%).

Desorption experiments
A low concentration working solution was prepared by adding 1 mL of the stock solution (C = 1.2127 μCi/mL) to a 200-mL measuring flask and adjusting volume to 200 mL with a 0.01-M $CaCl_2$ millipore water solution. This made a nominal concentration of 0.00606 μCi/mL or 0.109 mg/L. Three samples of this solution were analysed (counted) and the concentration was 11255 ± 68 dpm/mL, which equals 0.0051 μCi/mL or 0.092 mg/L (S.D. 0.60%).

A high concentration working solution was prepared by adding 2 mL of the stock solution (C = 1.2127 mCi/mL) to a 200-mL measuring flask and adjusting volume to 200 mL with a 0.01-M $CaCl_2$ millipore water solution. This made a nominal concentration of 0.0121 μCi/mL or 0.219 mg/L. Three samples of this solution were analysed (counted) and the concentration was 23276 ± 457 dpm/mL, which equals 0.0105 μCi/mL or 0.189 mg/L (S.D. 1.97%).

Degradation experiments
The above stock solution was used.

Ioxynil

Basic solution
A basic solution was prepared by dissolving 3.8 mg of ioxynil/0.28 mCi in 100 mL of acetone making a concentration of 2.8µCi/mL or 38 mg/L.

Stock solution
From the basic solution, a stock solution prepared made by adding 5 mL of the basic solution to a 25-mL measuring flask and adjusting to 25 mL with a 0.01-M $CaCl_2$ millipore water solution making a nominal concentration of 0.56 µCi/mL or 7.6 mg/L.

Kinetic and equilibrium sorption experiments
A high concentration working solution was prepared by adding 5 mL of the stock solution to a 100-mL measuring flask and adjusting to 100 mL with a 0.01-M $CaCl_2$ millipore water solution. This made a nominal concentration of 0.028 µCi/mL or 0.38 mg/L. Three samples of this solution were counted and the concentration was 68558 ± 846 dpm/mL, which equals 0.031 µCi/mL or 0.43 mg/L (S.D. 0.3%).

A low concentration working solution was prepared by adding 5 mL of the high concentration solution to a 50-mL measuring flask and adjusting to 50 mL with a 0.01-M $CaCl_2$ millipore water solution making a nominal concentration of 0.0028 µCi/mL or 0.038 mg/L. Two samples of this solution were counted and the concentration was 6137 ± 12.7 dpm/mL, which equals 0.0028 µCi/mL or 0.038 mg/L (S.D. 0.4%).

A medium concentration ioxynil working solution was prepared by adding 2 mL of the basic solution to a 250-mL measuring flask and adjusting to 250 mL with a 0.01-M $CaCl_2$ millipore water solution making a nominal concentration of 0.022 µCi/mL or 0.30 mg/L. Three samples of this solution were counted and the concentration was 50563 ± 1814 dpm/mL, which equals 0.023 µCi/mL or 0.31 mg/L (S.D. 1.8%).

Experiments with temperature variation, lake sediments
Solution of radiolabelled ioxynil
A medium concentration ioxynil working solution was prepared by adding 2 mL of the basic solution to a 250-mL measuring flask and adjusting to 250 mL with a 0.01-M $CaCl_2$ millipore water solution making a nominal concentration of 0.022 µCi/mL or 0.30 mg/L. Three samples of this solution were counted just before use and the concentration was 50097 ± 1179 dpm/mL, which equals 0.023 µCi/mL or 0.31 mg/L (S.D. 2.3%).

Degradation experiments
Stock solution in acetone
From the basic solution a stock solution (nominal 0.56 µCi/mL or 7.6 mg/L) was prepared by adding 10 mL of the basic solution to 40 mL acetone in a measuring flask. Three 10-µL samples were analysed and the average concentration was 1409600 ± 37700 dpm/mL or 0.63 µCi/mL.

Basic solution
The original solution (2 mL) was added to a 100-mL measuring flask and the volume was adjusted to 100 mL with acetone resulting in a basic solution with a nominal concentration of 2.5 μCi/mL or 7500 mg/L

Stock solution
A stock solution was prepared by adding 5 mL of the basic solution to a 25-mL measuring flask and adjusting to 25 mL with a 0.01-M $CaCl_2$ millipore water solution making a nominal concentration of 0.50 μCi/mL or 1500 mg/L.

Equilibrium sorption experiments
A high concentration working solution was prepared by adding 2 mL of the stock solution to a 100-mL measuring flask and adjusting to 100 mL with a 0.01-M $CaCl_2$ millipore water solution making a nominal concentration of 0.010 μCi/mL or 30 mg/L. Three samples of this solution were counted and the concentration was 31075 ± 601 dpm/mL, which equals 0.014 μCi/mL or 42.0 mg/L (S.D. 0.48%).

A medium concentration working solution was prepared by adding 5 mL of the high concentration solution to a 50-mL measuring flask and adjusting to 50 mL with a 0.01-M $CaCl_2$ millipore water solution making a nominal concentration of 0.001 μCi/mL or 3.0 mg/L. One sample of this solution was counted and the concentration was 2906 dpm/mL, which equals 0.0013 μCi/mL or 3.9 mg/L.

A low concentration working solution was prepared by adding 1 mL of the high concentration solution to a 50-mL measuring flask and adjusting to 50 mL with a 0.01-M $CaCl_2$ millipore water solution making a nominal concentration of 0.00020 μCi/mL or 0.60 mg/L. Two samples of this solution were counted and the concentration was 509 ± 45.2 dpm/mL, which equals 0.00023 μCi/mL or 0.69 mg/L.

Experiments with temperature variation, lake sediments
A medium concentration working solution was prepared by adding 0.5 mL of the stock solution to a 200-mL measuring flask and adjusting to 200 mL with a 0.01-M $CaCl_2$ millipore water solution making a nominal concentration of 0.0013 μCi/mL or 3.75 mg/L. Three samples of this solution were counted and the concentration was 4028 ± 56 dpm/mL, which equals 0.0018 μCi/mL or 5.4 mg/L.

Degradation experiments
Stock solution in acetone
From the basic solution, a stock solution (nominal 0.50 μCi/mL or 1500 mg/L) was prepared by adding 10 mL of the basic solution to 40 mL of acetone in a measuring flask. Three samples of 10 μL were analysed and the concentration was 1656400 ± 22000 dpm/mL or 0.75 μCi/mL.

Preparation of other solutions
A 30-mmol/L NaN_3 solution was prepared from a 1-M stock solution by adding 6 mL of stock solution to a 200-mL measuring flask and adding millipore water. $CaCl_2 \cdot H_2O$ was added to a concentration of 0.01 M $CaCl_2$.

0.01-M $CaCl_2$ solutions were prepared by adding 1.47 g $CaCl_2 \cdot 2H_2O$ to a 1000-mL measuring flask and adjusting the volume to 1000 mL with millipore water.

Appendix B.
Results

In this appendix, raw data for the performed experiments are given in tables.

Two types of Kd(t) = $C_s(t)/C_w(t)$ are given. The Kd[1] has been calculated from measured C_w and C_s whereas the Kd[2] has been calculated from measured C_w and C-control. The reason for this second approach was that Cs, as mentioned, was not measured in all cases and that the measurement of C_s, when performed, was very uncertain for some sediments. The uncertainty is expected to be associated with the procedure where activity is determined in a small 0.1-g subsample, extracted from 1.0 g of centrifuged sediment. If the sediment is inhomogeneous, this subsample is likely to be un-representative causing erroneous Kds. The Kd values considered to be trustworthy are presented with an *. The C_s that were not measured but calculated from C_w and $C_{control}$ are indicated by #.

10.1 B.1 "Kinetic" sorption experiments with pendimethalin and pond sediment

Table B.1
Pendimethalin low concentration, pond sediment

Time	Kd[1]	Kd[2]	C_w		C_s[3]	C_s[4]	C_T[5]	Recovery[6]	C-control
hours	L/kg	L/kg	dpm/L	mg/L	dpm/kg DW	dpm/L	dpm/L		dpm/L
3	433*	441	159888	0.00130	69292591	5606925	5766813	73%	6037125
3	444*	456	154663	0.00126	68601802	5551029	5705692	73%	6037125
24	525*	579	126750	0.00103	66579967	5387429	5514179	70%	6242000
24	333*	579	126788	0.00103	42256397	3419247	3546034	45%	6242000
168	605*	609	117350	0.00095	70954415	5741395	5858745	75%	6071250
168	601*	595	120013	0.00098	72159478	5838904	5958917	76%	6071250
480	540*	574	123425	0.00100	66681680	5395659	5519084	70%	6031625
480	586*	584	121363	0.00099	71070661	5750801	5872164	75%	6031625
						Average	5742228		6095500

1 Kd calculated from measured C_w and C_s,
2 Kd calculated from measured C_w and calculated C_s where C_s = C-control - C_w.
3 C_s is given as measured C_s in the sediment sample corrected for the amount of pesticide present in the water that was evaporated prior to counting (the pesticide concentration in the evaporated sediment water is assumed to be equal to measured C_w in the supernatant).
4 C_s in the unit [dpm/L] is calculated as C_s[dpm/kg dry weight] · CP [kg dry weight/L slurry] where CP is sediment concentration.
5 $C_T = C_s+C_w$.
6 Recovery is calculated as C_T/C_T-nominal.

1 Kd beregnet ud fra målt C_w og C_s,
2 Kd beregnet ud fra målt C_w og beregnet C_s hvor C_s = C-control - C_w.
3 C_s angives som målt C_s i sedimentprøven korrigeret for den mængde pesticid, som var tilstede i det vand, som blev afdampet inden tælling (pesticidkoncentrationen i det afdampede sedimentvand antages at være lig med målt C_w i supernatanten).
4 C_s i [dpm/L] er beregnet som C_s[dpm/kg tørvægt] · CP [kg tørvægt/L slam] hvor CP er sedimentkoncentration.
5 $C_T = C_s+C_w$.
6 Genfinding er beregnet som C_T/C_T-nominel.

Table B.2
The mass balance for pendimethalin (low concentration) sorption to pond sediment. The recoveries were calculated relative to theoretical total activity and relative to the activity of controls

Time	Water	Sediment	Test glass	Centrifuge tubes	Total	Theoretical total	Control	Balance theoretical	Balance control
hours	dpm	dpm	dpm	dpm	dpm	dpm	dpm		
3	1919	67283	42	101	69345	94179	73531	76%	94%
3	1856	66612	64	47	68579	94179	73531	75%	93%
24	1521	64649	56	25	66251	94179	77240	72%	86%
24	1521	41031	79	35	42666	94179	77240	47%	55%
168	1408	68897	65	29	70399	94179	73787	77%	95%
168	1440	70067	27	12	71546	94179	73787	78%	97%
480	1481	64748	134	59	66422	94179	73017	73%	91%
480	1456	69010	69	31	70566	94179	73017	77%	97%
							Average	72%	89%

Table B.3
Pendimethalin, high concentration, pond sediment

Time	Kd[1]	Kd[2]	C_w		C_s	C_s	C_T	Recovery	C-control
hours	L/kg	L/kg	dpm/L	mg/L	dpm/kg DW	dpm/L	dpm/L		dpm/L
3	448*	438	338000	0.0027	158066486	12790213	13128213	81%	12661000
3	360*	472	314075	0.0026	113037247	9146597	9460672	58%	12661000
24	513*	511	282713	0.0023	137333830	11112596	11395308	70%	12328000
24	482*	509	283750	0.0023	136873372	11075337	11359087	70%	12328000
168	476*	584	258288	0.0021	122860780	9941485	10199772	63%	12828750
168	490*	577	261463	0.0021	128008451	10358017	10619480	66%	12828750
480	542*	538	262950	0.0021	142546414	11534381	11797331	73%	12043875
480	599*	548	258200	0.0021	154563074	12506729	12764929	79%	12043875
						Average	11340599		12465406

Table B.4
The mass balance for pendimethalin (high concentration) sorption to pond sediment

Time	Water	Sediment	Test glass	Centrifuge tubes	Total	Theoretical total	Control	Balance theoretical	Balance control
hours	dpm	dpm	dpm	dpm	dpm	dpm	dpm		
3	4056	147122	41	18	151237	194279	158467	80%	95%
3	3769	109759	24	11	113563	194279	158467	60%	72%
24	3393	140830	23	10	144255	194279	153598	76%	94%
24	3405	132904	8	3	136320	194279	153598	72%	89%
168	3099	119298	22	10	122430	194279	155309	65%	79%
168	3138	124296	16	7	127456	194279	155309	68%	82%
480	3155	138413	20	9	141597	194279	145631	75%	97%
480	3098	150081	8	3	153190	194279	145631	81%	105%
							Average	72%	89%

10.2 B.2 "Kinetic" sorption experiments with pendimethalin and stream sediments

In the kinetics experiment with pendimethalin and stream sediments, the activity of the sediment phase was only determined for the replicate test tubes removed at the termination time. Therefore, the C_s given at other times

(marked with #) have been calculated from C_s = C-control – C_w. The C_s measured at time 197 hour is not considered representative of the actual C_s.

Table B.5
Pendimethalin, high concentration, Lillebæk stream sediment

Time	Kd[1]	Kd[2]	C_w	C_s	C_s	C_T	Recovery	C-control
hours	L/kg	L/kg	dpm/L	dpm/kg DW	dpm/L	dpm/L		dpm/L
2		172*	501500	86387260#	7119750#			7621250
2		151*	566000	85604651#	7055250#			7621250
6		188*	558000	104855915#	8641875#			9199875
6		211*	500750	105550556#	8699125#			9199875
24		221*	477000	105182002#	8668750#			9145750
24		227*	465000	105327604#	8680750#			9145750
197	941	229*	456000	429019967	35358396	35814396	367%	9059250
197	881	208*	499250	439853750	36251280	36750530	377%	9059250
					Average	15562334		8756531

Table B.6
Pendimethalin, high concentration, Odderbæk stream sediment

Time	Kd[1]	Kd[2]	C_w	C_s	C_s	C_T	Recovery	C-control
hours	L/kg	L/kg	dpm/L	dpm/kg DW	dpm/L	dpm/L		dpm/L
2		359*	258750	92804622#	7362500#			7621250
2		346*	267750	92691176#	7353500#			7621250
6		482*	234250	113012080#	8965625#			9199875
6		480*	235250	112999475#	8964625#			9199875
24		580*	194500	112830882#	8951250#			9145750
24		503*	223750	112462185#	8922000#			9145750
197	1491	559*	199750	297829516	23627808	23827558	244%	9059250
197	704	666*	168167	118349268	9389042	9557209	98%	9059250
					Average	10664815		8756531

10.3 B.3 "Kinetic" sorption experiments with ioxynil and stream sediments

Table B.7
Ioxynil, medium concentration, Lillebæk stream sediment

Time	Kd[1]	Kd[2]	C_w		C_s	C_s	C_T	Recovery	C-control
hours	L/kg	L/kg	dpm/L	mg/L	dpm/kg DW	dpm/L	dpm/L		dpm/L
2	16	5*	24506250	0.153	390828441	32210777	56717027	168%	33910250
2	14	5*	24524000	0.153	338095697	27864720	52388720	155%	33910250
6	15	8*	20040000	0.125	308590116	25432969	45472969	135%	33985167
6	4	5*	24363750	0.152	93876039	7736950	32100700	95%	33985167
24	16	5*	22770500	0.142	373233541	30760664	53531164	159%	32979250
24	16	4*	25199250	0.157	395701974	32612438	57811688	172%	32979250
198	15	6*	24004250	0.149	372050896	30663195	54667445	162%	35998500
198	18	6*	23699250	0.148	417820267	34435354	58134604	172%	35998500
						Average	49670378		33624889

Table B.8
Ioxynil, medium concentration, Odderbæk stream sediment

time	Kd[1]	Kd[2]	C_w		C_s	C_s	C_T	Recovery	C-control
h	L/kg	L/kg	dpm/L	mg/L	dpm/kg DW	dpm/L	dpm/L		dpm/L
2	37	16*	14981750	14981750	551773058	43773996	58755746	174%	33910250
2	24	15*	15291250	15291250	369124221	29283855	44575105	132%	33910250
6	23	20*	13302500	13302500	305104483	24204956	37507456	111%	33985167
6	26	17*	14586000	14586000	386282884	30645109	45231109	134%	33985167
24	46	18*	13704750	13704750	623722300	49481969	63186719	187%	32979250
24	38	18*	13508750	13508750	515834598	40922878	54431628	161%	32979250
198	27	19*	14144250	14144250	384596205	30511299	44655549	132%	35998500
198	43	21*	13575750	13575750	584899485	46402026	59977776	178%	35998500
						Average	50614627		33624889

10.4 B.4 "Kinetic" sorption experiments with pendimethalin and Lake Vaparanta sediments

Table B.9
Sorption of pendimethalin to Lake Vaparanta sediment at very low concentration

Time	Kd[1]	Kd[2]	C_w		C_s	C_s	C_T	Recovery	C-control
hours	L/kg	L/kg	dpm/L	mg/L	dpm/kg DW	dpm/L	dpm/L		dpm/L
1		94*	172300	0.00140	16135013	664638#	836938		836938
1		86*	183250	0.00149	15793273	653688#	836938		836938
4		105*	166250	0.00135	17476164	719450#	885700		885700
4		102*	169850	0.00138	17378269	715850#	885700		885700
24		103*	161300	0.00131	16539846	679813#	841113		841113
24		98*	166775	0.00136	16406640	674338#	841113		841113
48	85*	102*	156700	0.00127	13321844	550735	707435	103%	816988
48	85*	99*	160750	0.00131	13730075	567612	728362	106%	816988
						Average	820412		845184

Table B.10
Sorption of pendimethalin to Lake Vaparanta sediment at low concentration

Time	Kd[1]	Kd[2]	C_w		C_s	C_s	C_T	Recovery	C-control
hours	L/kg	L/kg	dpm/L	mg/L	dpm/kg DW	dpm/L	dpm/L		dpm/L
1		83*	383150	0.00311	31894799	1321713#	1704863		1704863
1		81*	390450	0.00317	31750245	1314413#	1704863		1704863
4		100*	358075	0.00291	35907181	1480875#	1838950		1838950
4		99*	360000	0.00293	35788913	1478950#	1838950		1838950
24		100*	354025	0.00288	35337753	1455350#	1809375		1809375
24		99*	356125	0.00289	35265569	1453250#	1809375		1809375
48	98*	97*	344950	0.00280	33933979	1405656	1750606	127%	1729788
48	82*	103*	327550	0.00266	26737781	1106904	1434454	104%	1729788
						Average	1736429		1770744

Table B.11
Sorption of pendimethalin to Lake Vaparanta sediment at medium concentration

Time	Kd[1]	Kd[2]	C_w		C_s	C_s	C_T	Recovery	C-control
hours	L/kg	L/kg	dpm/L	mg/L	dpm/kg DW	dpm/L	dpm/L		dpm/L
1		75	827175	0.00672	61635772	2553663#	3380838		3380838
1		77	809675	0.00658	62169571	2571163#	3380838		3380838
4		72	799375	0.00650	57378855	2364038#	3163413		3163413
4		75	770600	0.00626	58077268	2392813#	3163413		3163413
24		84	735900	0.00598	61872673	2554800#	3290700		3290700
24		80	762300	0.00620	61038185	2528400#	3290700		3290700
48	73	116	702425	0.00571	51410517	2116442	2818867	102%	4068275
48	63	118	694925	0.00565	43578431	1791139	2486064	90%	4068275
						Average	3121854		3475806

Table B.12
Sorption of pendimethalin to Lake Vaparanta sediment at high concentration

Time	Kd[1]	Kd[2]	C_w		C_s	C_s	C_T	Recovery	C-control
hours	L/kg	L/kg	dpm/L	mg/L	dpm/kg DW	dpm/L	dpm/L		dpm/L
1		72	1627750	0.01323	116821718	4831425#	6459175		6459175
1		69	1671975	0.01359	115775472	4787200#	6459175		6459175
4		77	1591800	0.01294	122845289	5074463#	6666263		6666263
4		67	1758600	0.01429	118688783	4907663#	6666263		6666263
24		68	1615250	0.01313	109880961	4525338#	6140588		6140588
24		78	1457800	0.01185	113227729	4682788#	6140588		6140588
48	79*	33	1404500	0.01142	111125481	4588510	5993010	109%	3289763
48	198	584	131625	0.00107	26116073	1073625	1205250	22%	3289763
						Average	5716289		5638947

Table B.13
Sorption of pendimethalin to Lake Vaparanta sediment at very high concentration

Time	Kd[1]	Kd[2]	C_w		C_s	C_s	C_T	Recovery	C-control
hours	L/kg	L/kg	dpm/L	mg/L	dpm/kg DW	dpm/L	dpm/L		dpm/L
1		62*	3627625	0.02949	225072748	9300963#	12928588		12928588
1		64*	3541775	0.02879	226968972	9386813#	12928588		12928588
4		61*	3696725	0.03005	226494945	9387763#	13084488		13084488
4		70*	3352750	0.02725	235591082	9731738#	13084488		13084488
24		75*	3131975	0.02546	234794859	9687225#	12819200		12819200
24		78*	3040350	0.02471	236637084	9778850#	12819200		12819200
48	53	72*	2772275	0.02253	146179684	6011822	8784097	80%	10928175
48	83*	79*	2555250	0.02077	210973361	8700911	11256161	102%	10928175
						Average	12213101		12440113

10.5 B.5 "Kinetic" desorption experiments with pendimethalin and pond sediment

Table B.14
Desorption of pendimethalin (low concentration) from pond sediment

Time	Kd[1]	Kd[2]	C_w	C_s[3]	C_s[4]
hours	L/kg	L/kg	dpm/L	dpm/kg TS	dpm/kg TS
1	1083	835	85035	92129964	71042233
1	1413	1089	87110	123063145	94887101
3.5	1471	1134	82330	121108052	93397727
3.5	1418	1093	85603	121388364	93601492
24	1220	875	79228	96661182	69322681
24	1287	923	76280	98200028	70437462
240	1180	973	88753	104704857	86400501
240	1254	895	76750	96276045	79555373

1 Kd calculated as $Kd=(C_T-C_w)/C_w$ where C_T is nominal total concentration.
2 Kd calculated from $Kd=(C_{control}-C_w)/C_w$. For the times 1 and 3.5 hours, no controls were analysed but an average of the controls at 24 and 240 hours was used.
3 $C_s=C_T-C_w$ where C_T is nominal.
4 $C_s = C_{control}-C_w$.

1 Kd beregnet som $Kd=(C_T-C_w)/C_w$ hvor C_T er nominel totalkoncentration.
2 Kd beregnet ud fra $Kd=(C_{control}-C_w)/C_w$. Der blev ikke analyseret nogle kontroller for tidspunkterne 1 og 3,5 time, men et gennemsnit af kontrollerne for 24 og 240 timer blev anvendt.
3 $C_s=C_T-C_w$ hvor C_T er nominel.
4 $C_s = C_{control}-C_w$.

Table B.15
Desorption of pendimethalin (high concentration) from pond sediment

Time	Kd	Kd	C_w	C_s	C_s
hours	L/kg	L/kg	dpm/L	dpm/kg TS	dpm/kg TS
1	1157	869	178433	206533366	155124667
1	1140	856	178943	203973830	153200520
3,5	1168	877	168345	196605930	147700901
3,5	1249	939	162170	202606443	152229356
24	1182	811	166585	196841819	135111224
24	1717	1179	150143	257769712	177019515
240	1154	942	172528	199137817	162515938
240	1041	849	189800	197610478	161227958

10.6 B.6 "Equilibrium" sorption experiments with pendimethalin and stream sediments

Table B.16
Pendimethalin "equilibrium" sorption to stream sediments

Time	Kd	Kd	C_w	C_s	C_s	C_T	Recovery	C-control
hours	L/kg	L/kg	dpm/L	dpm/kg DW	dpm/L	dpm/L		dpm/L
Lillebæk sediment, low concentration								
213	1772	581*	106000	187859993	7733656	7839656	266%	2641375
213	2199	654*	94500	207849451	8568556	8663056	293%	2641375
Lillebæk sediment, medium concentration								
215	1438	447*	145000	208546796	17191169	17336169	226%	5488750
215	1667	427*	151500	252614347	20836288	20987788	274%	5488750
Odderbæk sediment, low concentration								
213	3458	2101*	31250	108068999	4297025	4328275	147%	2641375
213	5271	2240*	29250	154185278	6146596	6175846	209%	2641375
Odderbæk sediment, medium concentration								
215	2561	1261*	54250	138923182	11035567	11089817	145%	5488750
215	2300	1223*	56000	128817700	10216472	10272472	134%	5488750

10.7 B.7 "Equilibrium" sorption experiments with ioxynil and stream sediments

Table B.17
Ioxynil "equilibrium" sorption to stream sediments

Time	Kd	Kd	C_w	C_s	C_s	C_T	Recovery	C-control
hours	L/kg	L/kg	dpm/L	dpm/kg DW	dpm/L	dpm/L		dpm/L
Lillebæk sediment, low concentration								
213	20	5*	3002500	60093903	4966607	7969107	195%	4320250
213	23	6*	2816750	64512248	5326455	8143205	199%	4320250
Lillebæk sediment, high concentration								
212	7	3*	34007000	252059243	20817508	54824508	120%	34115750
212	12	3*	34224500	413658915	34133300	68357800	150%	34115750
Odderbæk sediment, low concentration								
213	55	20*	1657500	91659918	7271687	8929187	218%	4320250
213	52	20*	1666750	86809999	6899323	8566073	209%	4320250
Odderbæk sediment, high concentration								
213	24	14*	20488250	488170153	38735911	59224161	130%	34115750
213	25	11*	23396250	593741782	47079963	70476213	154%	34115750

10.8 B.8 "Equilibrium" sorption experiments with bentazone and stream sediments

Table B.18
Bentazone "equilibrium" sorption to stream sediment

Time	Kd	Kd	C_w	C_s	C_s	C_T	Recovery	C-control
hours	L/kg	L/kg	dpm/L	dpm/kg DW	dpm/L	dpm/L		dpm/L
Lillebæk sediment, low concentration								
213	2.4	0.52*	359000	853442	70493	429493	126%	374375
213	2.9	0.52*	359000	1031639	85186	444186	131%	374375
Lillebæk sediment, medium concentration								
213	2.1	0.44*	1886750	4008618	330674	2217424	114%	1955250
213	0.69	0.57*	1868250	1289647	106288	1974538	102%	1955250
Lillebæk sediment, high concentration								
213	3.3	0.38*	18982250	61770165	5092927	24075177	116%	19576750
213	0.68	0.59*	18661750	12781694	1054899	19716649	95%	19576750
Odderbæk sediment, low concentration								
213	4.4	0.93*	348750	1530838	121556	470306	138%	374375
213	6.7	1.0*	346250	2330220	185012	531262	156%	374375
Odderbæk sediment, medium concentration								
213	1.6	0.82*	1835750	3008896	239183	2074933	107%	1955250
213	2.4	0.78*	1841000	4416454	350933	2191933	113%	1955250
Odderbæk sediment, high concentration								
213	1.1	0.78*	18433500	19838404	1575735	20009235	97%	19576750
213	1.5	0.63*	18638750	27436167	2180303	20819053	100%	19576750

10.9 B.9 "Equilibrium" sorption experiments with pendimethalin and lake sediments

Table B.19
Sorption of pendimethalin to lake sediments at 4°C

Sediment	Kd	pH	Cw	Cw	Cs	Cs	C_{total} (nominal)	C-control
	L/kg		dpm/L	mg/L	dpm/kg TS	dpm/L	dpm/L	dpm/L
Høytiäinen	374	5.4	334825	0.0027	125291626#	9749675#	10189444	10084500
Høytiäinen	384	5.4	327175	0.0027	125515312#	9757325#	10189444	10084500
Kuorinka	276	5.8	424525	0.0035	117096069#	9659975#	10189444	10084500
Kuorinka	329	5.8	358525	0.0029	117907898#	9725975#	10189444	10084500
Mekrijärvi	2514	5.0	53850	0.0004	135370230#	10030650#	10189444	10084500
Mekrijärvi	2522	5.0	53675	0.0004	135386126#	10030825#	10189444	10084500
Vaparanta	76	6.2	1378950	0.0112	105477528#	8705550#	10189444	10084500
Vaparanta	78	6.2	1358975	0.0110	105445253#	8725525#	10189444	10084500

Table B.20
Sorption of pendimethalin to lake sediments at 20°C

Sediment	Kd	pH	C_w		C_s		C_{total} (nominal)	C-control
	L/kg		dpm/L	mg/L	dpm/kg TS	dpm/L	dpm/L	dpm/L
Høytiäinen	331	5.7	348675	0.0028	115323286#	8991908#	11016389	9340583
Høytiäinen	357	5.8	324625	0.0026	115793342#	9015958#	11016389	9340583
Kuorinka	302	5.9	360275	0.0029	108781146#	8980308#	11016389	9340583
Kuorinka	309	6.0	352500	0.0029	109060619#	8988083#	11016389	9340583
Mekrijärvi	2608	5.2	47925	0.0004	124998176#	9292658#	11016389	9340583
Mekrijärvi	2634	5.2	47500	0.0004	125103617#	9293083#	11016389	9340583
Vaparanta	76	6.4	1288000	0.0105	97488073#	8052583#	11016389	9340583
Vaparanta	81	6.4	1216250	0.0099	98238859#	8124333#	11016389	9340583

10.10 B.10 "Equilibrium" sorption experiments with ioxynil and lake sediments

Table B.21
Sorption of ioxynil to lake sediments at 4°C

Sediment	Kd	pH	C_w		C_s		C_{total} (nominal)	C-control
	L/kg		dpm/L	mg/L	dpm/kg TS	dpm/L	dpm/L	dpm/L
Høytiäinen	9.0	5.6	20551250	0.13	185212752#	14392333#	34043611	34943583
Høytiäinen	8.7	5.6	20850500	0.13	180927393#	14093083#	34043611	34943583
Kuorinka	5.0	5.9	24642500	0.15	124444289#	10301083#	34043611	34943583
Kuorinka	4.5	6.0	25466750	0.16	114876066#	9476833#	34043611	34943583
Mekrijärvi	295	5.1	1526950	0.01	450619095#	33416633#	34043611	34943583
Mekrijärvi	294	5.1	1533475	0.01	450846352#	33410108#	34043611	34943583
Vaparanta	1.0	6.3	32298750	0.20	31977943#	2644833#	34043611	34943583
Vaparanta	1.0	6.3	32219000	0.20	32981693#	2724583#	34043611	34943583

Table B.22
Sorption of ioxynil to lake sediments at 20°C

Sediment	Kd	pH	C_w		C_s		C_{total} (nominal)	C-control
	L/kg		dpm/L	mg/L	dpm/kg TS	dpm/L	dpm/L	dpm/L
Høytiäinen	7.6	5.9	21904000	0.14	166344910#	12923583#	32752222	34827583
Høytiäinen	7.3	5.9	22163500	0.14	162728000#	12664083#	32752222	34827583
Kuorinka	4.9	6.1	24849250	0.15	120701639#	9978333#	32752222	34827583
Kuorinka	4.6	6.1	25188250	0.16	116682483#	9639333#	32752222	34827583
Mekrijärvi	291	5.3	1540550	0.01	448289320#	33287033#	32752222	34827583
Mekrijärvi	290	5.3	1546925	0.01	449324086#	33280658#	32752222	34827583
Vaparanta	0.9	6.4	32479250	0.20	28384542#	2348333#	32752222	34827583
Vaparanta	0.9	6.5	32527000	0.20	27765813#	2300583#	32752222	34827583

10.11 B.11 "Equilibrium" sorption experiments with bentazone and lake sediments

Table B.23
Sorption of bentazone to lake sediments at 4°C

Sediment	Kd	pH	C_w		C_s		C_{total} (nominal)	C-control
	L/kg		dpm/L	mg/L	dpm/kg TS	dpm/L	dpm/L	dpm/L
Høytiäinen	0.7	5.7	2617250	3.5	1837855#	143200#	2652500	2760450
Høytiäinen	0.7	5.6	2614425	3.5	1880490#	146025#	2652500	2760450
Kuorinka	0.4	6.0	2666900	3.6	1129924#	93550#	2652500	2760450
Kuorinka	0.7	5.8	2618550	3.5	1715106#	141900#	2652500	2760450
Mekrijärvi	4.0	5.2	2124375	2.9	8566267#	636075#	2652500	2760450
Mekrijärvi	3.8	5.2	2154125	2.9	8167242#	606325#	2652500	2760450
Vaparanta	0.4	6.4	2680875	3.6	964237#	79575#	2652500	2760450
Vaparanta	0.2	6.4	2719525	3.7	494566#	40925#	2652500	2760450

Table B.24
Sorption of bentazone to lake sediments at 20°C

Sediment	Kd	pH	C_w		C_s		C_{total} (nominal)	C-control
	L/kg		dpm/L	mg/L	dpm/kg TS	dpm/L	dpm/L	dpm/L
Høytiäinen	0.6	6.0	2640700	3.6	1694782#	131683#	2717861	2772383
Høytiäinen	0.7	6.0	2629300	3.6	1840765#	143083#	2717861	2772383
Kuorinka	0.5	6.1	2667500	3.6	1268328#	104883#	2717861	2772383
Kuorinka	0.4	6.1	2680875	3.6	1107582#	91508#	2717861	2772383
Mekrijärvi	3.9	5.3	2155700	2.9	8300144#	616683#	2717861	2772383
Mekrijärvi	4.0	5.3	2141625	2.9	8523577#	630758#	2717861	2772383
Vaparanta	0.3	6.5	2712000	3.7	730516#	60383#	2717861	2772383
Vaparanta	0.4	7.2	2675925	3.6	1169637#	96458#	2717861	2772383

10.12 B.12 Accuracy in sorption experiments

Table B.25
Variability in measured concentrations. Average relative standard deviations are given with maximum values in parenthesis.

Substance	Sediment	Conc.	n	Between centrifuge tubes (test tubes) C_w	n	Between test tubes C_w	n	Between test tubes C_s
Pendimethalin	pond	low	16	1.4% (2.6%)	8	1.3% (2.4%)	8	9.5% (32%)
Pendimethalin	pond	high	16	1.3% (2.4%)	8	1.9% (5.2%)	8	8.3% (21%)
Pendimethalin	Lillebæk	low			2	8.1%	2	7.1%
Pendimethalin	Lillebæk	medium			2	3.1%	2	13%
Pendimethalin	Lillebæk	high			8	6.1% (8.5%)	2	1.8%
Pendimethalin	Odderbæk	low				4.7%	2	25%
Pendimethalin	Odderbæk	medium			2	2.2%		5.3%
Pendimethalin	Odderbæk	high			8	6.2% (12%)	2	52%
Ioxynil	Lillebæk	low			2	4.5%	2	5.0%
Ioxynil	Lillebæk	medium			8	5.5% (14%)	8	25%(75%)
Ioxynil	Lillebæk	high			2	0.5%	2	34%
Ioxynil	Odderbæk	low			2	0.4%	2	3.8%
Ioxynil	Odderbæk	medium			8	3.0% (6.5%)	8	22% (29%)
Ioxynil	Odderbæk	high			2	9.4%	2	14%
Bentazone	Lillebæk	low			2	0.0%	2	13%
Bentazone	Lillebæk	medium			2	0.7%	2	72.57%
Bentazone	Lillebæk	high			2	1.2%	2	92.93%
Bentazone	Odderbæk	low			2	0.5%	2	29.28%
Bentazone	Odderbæk	medium			2	0.2%	2	26.81%
Bentazone	Odderbæk	high			2	0.8%	2	22.73%

10.13 B.13 Degradation experiments

Table B.26
Average relative disappearance of activity in % + S.D

Time	Pelagic	Pelagic	Lillebæk	Odderbæk
[hours]	high	low	low	low
Pendimethalin				
0.04	16.5 ± 1.8	18.8 ± 4	16.9 ± 1.4	9.5 ± 3.2
5	62.6 ± 0.8	61.8 ± 2	41.9 ± 1.5	27.6 ± 2
10	70.8 ± 2	73.1 ± 2.2	48.4 ± 3	20.5 ± 6.7
14	88.2 ± 3.8	87.6 ± 1.5	71.5 ± 2.5	53.3 ± 3.4
19	68 ± 3.8	71.4 ± 1.3	34.7 ± 9.2	17.5 ± 7.3
24	65.2 ± 5.5	69.1 ± 1.8	46.5 ± 3.6	24.6 ± 1.8
31	73.3 ± 2.5	73.9 ± 0.9	51.6 ± 2.1	27.4 ± 4.6
34	71.9 ± 3.3	71.4 ± 1.7	44 ± 4.3	27.1 ± 3.1
40	70.6 ± 5.7	67.2 ± 2.5	50.6 ± 3.5	50.6 ± 3.5
47	68.8 ± 5.5	66.4 ± 4	45.2 ± 3.7	29.2 ± 5.8
54	78 ± 5.7	74.4 ± 3.1	49.9 ± 3.1	33.2 ± 5.2
61	75.3 ± 5.3	68.8 ± 2.6	44.7 ± 3.6	30.7 ± 4.8
75	65.6 ± 5.3	61 ± 3.6	41.8 ± 3	28.9 ± 3.5
89	60.7 ± 4.6	55.9 ± 6	38 ± 3.6	26.9 ± 2.6
103	68.6 ± 8	63.2 ± 5.5	38.1 ± 6.3	33.8 ± 6
Ioxynil				
0.04	2.4 ± 1.1	4.4 ± 0.6	3.6 ± 0.5	1.7 ± 1.2
5	2.5 ± 0.7	2.6 ± 1.4	5 ± 1.7	4.9 ± 0.7
10	6.1 ± 1	6.9 ± 1.8	10 ± 2.9	8.4 ± 1.9
14	4.8 ± 1.3	4.9 ± 0.5	9.1 ± 1.7	11.7 ± 1.2
19	3.1 ± 1.2	3.4 ± 1.6	7.4 ± 0.4	11.9 ± 0.5
24	2.3 ± 1	3.4 ± 1	8.4 ± 2.4	15.5 ± 1.2
31	1.9 ± 0.3	1.7 ± 0.4	14.7 ± 2.2	20.8 ± 1.4
34	3.5 ± 1.3	2 ± 1.2	12.4 ± 0.7	24.2 ± 1.7
40	6 ± 2.2	3.1 ± 1.1	14.9 ± 1.6	26.5 ± 2
47	4.9 ± 1	5 ± 1.7	18.1 ± 1.2	29.8 ± 0.9
54	7.7 ± 1.9	8.8 ± 0.9	21.4 ± 2.4	37.3 ± 1.3
61	5 ± 0.7	5 ± 0.8	21.5 ± 0.9	38.3 ± 1
75	8.4 ± 2.5	7 ± 0.4	26.5 ± 2.1	44.3 ± 0.6
89	9 ± 1.9	7.8 ± 1.4	29.4 ± 3.2	48 ± 2.5
103	9.7 ± 1.3	8.5 ± 1.2	35.4 ± 3.1	57.2 ± 3.3
Bentazone				
0.04	4.4 ± 2.3	4.4 ± 0.4	2.8 ± 1.5	3.1 ± 0.9
5	3.7 ± 1.3	4.5 ± 1.4	3.4 ± 0.2	1.7 ± 2.6
10	7.7 ± 0.9	6.9 ± 1.4	5.5 ± 0.9	5.3 ± 1.3
14	5.9 ± 2.3	6.5 ± 2.6	6.7 ± 0.9	5 ± 1.5
19	3.4 ± 0.8	3.8 ± 0.4	5.1 ± 0.7	5.1 ± 0.7
24	4.1 ± 1.1	3.7 ± 1.4	5.1 ± 0.7	5.2 ± 1.3
31	3.7 ± 2.4	2.7 ± 0.3	4.1 ± 0.7	4.2 ± 0.9
34	4.6 ± 0.4	5.4 ± 0.9	5.5 ± 1	4.6 ± 0.2
40	5.7 ± 1.7	5.2 ± 2.1	5.6 ± 1.2	6.4 ± 0.2
47	4.7 ± 1.6	4.2 ± 1.1	5 ± 1.5	5.1 ± 0.8
54	7.7 ± 0.4	8.2 ± 0.7	7.2 ± 1.1	9.7 ± 2.4
61	4.7 ± 0.8	4.7 ± 1.9	5.7 ± 1.2	4 ± 1.3
75	6.2 ± 0.8	5.3 ± 0.8	6.4 ± 0.9	6 ± 1
89	4.7 ± 0.8	4.5 ± 0.4	7.7 ± 1.1	5.4 ± 0.9
103	6.1 ± 1.1	4.4 ± 0.9	7.2 ± 1.1	7.4 ± 0.6

10.14 B.14 Sediment particle size distribution

Table B.27
Relative weight percentage of particle size fractions determined by sieving and weighing, for pond and stream sediments

Diameter [mm]	Relative weight % of fraction		
	Lillebæk	Odderbæk	Pond
1.4-2	7.08%	0.10%	0.19%
1-1.4	5.89%	0.20%	0.31%
0.71-1	5.55%	0.05%	0.50%
0.5-0.71	10.10%	0.60%	1.02%
0.355-0.5	12.60%	0.35%	1.35%
0.25-0.355	14.89%	0.91%	1.98%
0.18-0.25	12.96%	2.52%	2.59%
0.125-0.18	9.79%	7.15%	3.32%
0.09-0.125	5.72%	12.34%	3.38%
0.063-0.09	3.76%	20.50%	4.82%
<0.063	11.66%	55.26%	80.53%

Table B.28
Relative weight percentage of particle size fractions determined by sieving and weighing, for lake sediments

Diameter [mm]	Relative weight % of fraction			
	Höytiäinen	Varparanta	Kuorinka	Mekrijärvi
0.4-2	3.2%	11.0%	1.9%	3.5%
0.125-0.400	10.7%	21.0%	4.5%	24.7%
0.063-0.125	7.2%	30.7%	15.7%	17.5%
0.037-0.063	5.6%	7.1%	12.2%	13.3%
0.020-0.037	4.7%	2.7%	3.3%	8.1%
<0.020	68.6%	27.4%	62.4%	32.9%

Appendix C.
Experiment with glass surfaces

10.15 C.1 Introduction

In batch sorption experiments as reported here, sorption to glassware may be the reason for poor mass balances. As the pesticide in these experiments is found either dissolved in the water, associated with particles or sorbed to glass surface, the knowledge of glass sorption can be used in calculating concentration on particles indirectly.

The equilibrium sorption to glass surfaces was investigated for pendimethalin, the most hydrophobic of the model pesticides. The sorption to both new smooth glass and old rough glass was investigated.

10.16 C.2 Experimental set-up

In order to investigate the linearity of the equilibrium sorption, a series of glass-water systems with different glass surface to water ratios but with the same pesticide concentration was set up.

Rough glass systems were made by shaking two sets of five "used" 30-mL round-bottomed glass tubes with 0, 50, 100, 150 and 200 new 5-mm glass spheres, 20 g of clean quartz sand and water for three days. After the three days, the sand was removed and the bottles and the now rough spheres were rinsed thoroughly with millipore water. The smooth glass systems were made by adding 0, 50, 100, 150 og 200 new 5 mm-glass spheres to two sets of five new 30-mL glass tubes.

Nine mL of millipore water was added to all 20 tubes together with one mL 0.11 mg/L pendimethalin solution. The tubes were shaken for 48 hours, 5 mL of the water was withdrawn and activity was determined by LSC.

10.17 C.3 Results

For the smooth and rough glass, the results are given in Tables C.1-C.2 below. The area of glass is calculated as the inner areas of the glass bottle $2 \cdot \pi \cdot r \cdot h + 2 \cdot \pi \cdot r^2$ plus the area of the spheres: No. of spheres $\cdot 4 \cdot \pi \cdot r^2$. The activity in the water phase (m_w) is calculated from the scintillation counts while the activity on the glass surfaces (m_g) is calculated as difference between total activity and m_w: m_g = m-total – m_w. Kd is calculated as C_g/C_w, where C_g is concentration on glass.

Table C.1
Kd for smooth glass

Area	C_w	m_w	m_g	C_w	C_g	Kd
cm^2	dpm/5ml	dpm/glass	dpm/glass	dpm/L	dpm/m^2	Smooth
69.8	4436	8871	1736	887142	248622	0.28
69.8	4354	8708	1899	870800	272032	0.31
109	4321	8642	1965	864168	180175	0.21
109	4419	8837	1770	883724	162246	0.18
148	3908	7816	2791	781612	188130	0.24
148	4123	8246	2360	824646	159121	0.19
188	4078	8155	2452	815544	130667	0.16
188	3599	7198	3409	719812	181692	0.25
227	3409	6817	3790	681710	167038	0.25
227	3335	6670	3937	667004	173520	0.26

Table C.2
Kd for rough glass

Area	C_w	m_w	m_g	C_w	C_g	Kd
cm^2	dpm/5ml	dpm/glass	dpm/glass	dpm/L	dpm/m^2	Rough
69.8	3641	7281	3326	728142	476395	0.65
69.8	3569	7137	3470	713728	497044	0.70
109	3744	7487	3120	748730	297138	0.40
109	3256	6511	4096	651104	390124	0.60
148	3433	6866	3741	686622	266864	0.39
148	3323	6646	3961	664566	282599	0.43
188	3279	6558	4049	655828	230881	0.35
188	3179	6357	4250	635744	242334	0.38
227	3130	6261	4346	626078	206429	0.33
227	3181	6362	4245	636176	201632	0.32

The results are shown graphically in Figure C.1 below.

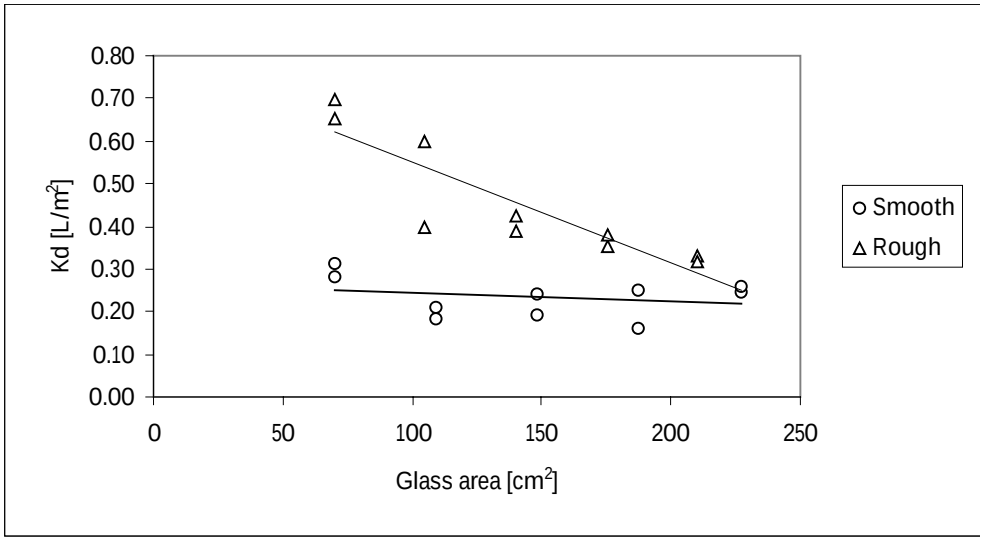

Figure C.1
Kd as a function of glass area for smooth and rough glass

As it can be seen from Figure C.1, there is apparently no relationship between Kd and glass area for smooth glass bottle and spheres, while for rough spheres Kd may vary with glass surface indicating non-linearity of Kd. Kd for smooth

glass was found to be 0.23 L/m^2 in average. For rough glass, an average Kd of 0.37 L/m^2 was found if the three high Kd values are considered outliers.

From this experiment and using a three-compartment model, it can be seen that the pendimethalin amount sorbed to glass in the sorption experiment should be around 0.4% of the total amount while 97.5% is on the sediment and 2.1% is in the water. With pendimethalin in this experimental set-up, the error in Kd caused by measuring only the water concentration and assuming the rest is sorbed to sediment is low.

Appendix D.
Experiment with filters

10.18 D.1 Introduction

In order to evaluate the usefulness of filters for separation of dissolved and sorbed pesticide, an experiment to determine the take up of pesticide by different filters was performed.

10.19 D.2 Materials

Solutions of radiolabelled pendimethalin, ioxynil and bentazone in three concentrations were used.

- Pendimethalin, high concentration: 0.5 mL of 1.21 µCi/mL stock solution was added to a 50-mL measuring flask and the volume was adjusted to 50 mL with millipore water. From this, medium and low concentration solutions were prepared by diluting the high concentration 10 and 100 times with millipore water.

- Ioxynil, high concentration: 2.5 mL of 0.56 µCi/mL stock solution was added to a 50-mL measuring flask and the volume was adjusted to 50 mL with millipore water. From this, medium and low concentration solutions were prepared by diluting the high concentration 10 and 100 times with millipore water.

- Bentazone, high concentration: 2.5 mL of 0.50 µCi/mL stock solution was added to a 50-mL measuring flask and the volume was adjusted to 50 mL with millipore water. From this, medium and low concentration solutions were prepared by diluting the high concentration 10 and 100 times with millipore water.

Three filter types were tested:

- GF-filter: Glass fibre filter, pore size of approx. 0.4 µm
- CA-filter: Celluloseacetate filter, pore size of 0.2 µm
- PC-filter: Polycarbonate filter, pore size of 0.22 µm

10.20 D.3 Experimental procedure

A set-up of glass filtering equipment was used. Filtering was made in this order:

- Bentazone, low
- Bentazone, medium
- Bentazone, high
- Ioxynil, low
- Ioxynil, medium
- Ioxynil, high

- Pendimethalin, low
- Pendimethalin, medium
- Pendimethalin, high

For each solution, all three filter types were tested using the following procedure.

Three mL of the solution was poured through the first filter and 2 mL of the filtrate was mixed with 15 mL scintillation liquid and the activity was determined using LSC. The remaining filtrate was discarded. Using the same filter, another 3 mL was filtered and again 2 mL was collected for determination of activity. Finally, the filter was transferred to a scintillation vial and the activity was determined. A new type of filter was mounted in the equipment and the procedure was repeated. After filtering with all three filter types had been performed, the same procedure was performed with the next, stronger solution. The glass equipment was cleaned between pesticides.

For control, the same procedure was performed without filter.

10.21 D.4 Results

Table D.1
Mass balance for filtering of bentazone solutions. % relative to control

Filter	Solution	Filtrate	Filter	Total
GF-F	low concentration	91.8%	3.9%	96%
GF-F	medium concentration	93.0%	3.3%	96%
GF-F	high concentration	93.0%	2.9%	96%
CA	low concentration	96.5%	4.9%	101%
CA	medium concentration	94.9%	3.6%	98%
CA	high concentration	97.1%	4.4%	102%
PC	low concentration	99.3%	0.9%	100%
PC	medium concentration	97.7%	1.6%	99%
PC	high concentration	99.8%	1.7%	101%

Table D.2
Mass balance for filtering of ioxynil solutions. % relative to control

Filter	Solution	Filtrate	Filter	Total
GF-F	low concentration	102.5%	2.5%	105%
GF-F	medium concentration	96.1%	2.9%	99%
GF-F	high concentration	86.9%	3.4%	90%
CA	low concentration	92.9%	7.5%	100%
CA	medium concentration	97.7%	4.0%	102%
CA	high concentration	81.6%	20.8%	102%
PC	low concentration	101.5%	1.6%	103%
PC	medium concentration	101.9%	1.1%	103%
PC	high concentration	95.1%	1.0%	96%

Table D.3
Mass balance for filtering of pendimethalin solutions. % relative to control

Filter	Solution	Filtrate	Filter	Total
GF-F	low concentration	80.8%	13.1%	94%
GF-F	medium concentration	74.3%	13.3%	88%
GF-F	high concentration	98.8%	17.2%	116%
CA	low concentration	1.8%	130.2%	132%
CA	medium concentration	11.2%	118.9%	130%
CA	high concentration	16.3%	169.0%	185%
PC	low concentration	0.0%	122.7%	123%
PC	medium concentration	6.8%	106.2%	113%
PC	high concentration	15.8%	115.4%	131%

The results show that only the glass fibre filter has any potential for use for separation of sorbed and freely dissolved pendimethalin while all three types of filters can apparently be used for ioxynil and bentazone. In general, there was no difference between first and second filtering. But for pendimethalin, less pendimethalin was retained in the second filtering indicating that the filter could be saturated.

Appendix E.
Experiment with glass and plastic pipettes

Plastic pipettes were used in the procedure of adding pesticide work solutions to the test glasses. Therefore, the retention of the pesticide, pendimethalin, with plastic pipettes was compared with that of glass pipettes. The results showed (t-test) that for this compound at a 95% confidence level, there was a measurable difference in the retention by glass and plastic pipettes for both a high and a low concentration. The activity of the glass-pipetted solution was about 2-3% higher than that of the plastic-pipetted solution. Therefore, a small systematic error is introduced when using plastic pipettes, which may account for at least 2-3% of the deficit in the mass balance.

Table E.1
The activity of pendimethalin solution when dispensed by either plastic or glass pipettes

	C_w	C_w
	dpm/mL	dpm/mL
High concentration		
	Glass	Plastic
1	24138	23506
2	25023	23379
3	23694	23858
average	24285	23581
Low concentration		
	Glass	Plastic
1	11567	11480
2	11919	11632
3	11832	11388
average	11772	11500

Appendix F.
The influence of pH on sorption coefficients

Bentazone and ioxynil are reasonably strong acids and they will be dissociated at neutral pH. The level of dissociation can be calculated from:

$$\alpha_a = \frac{[HA]}{[HA]+[A^-]} = \frac{1}{1+10^{pH-pKa}}$$

where α_a is the fraction of the total amount present as non-dissociated (neutral) acid. α_a is given for different pHs in the table below.

Table F.1
dissociation as a function of pH for bentazone and ioxynil

pH	Bentazone	Ioxynil
	pKa = 2.92	pKa = 3.96
4	7.68E-02	4.77E-01
5	8.25E-03	8.36E-02
6	8.31E-04	9.04E-03
7	8.32E-05	9.11E-04
8	8.32E-06	9.12E-05
9	8.32E-07	9.12E-06

From Table F.1 it can be seen that, at pH around 7, only 0.008% of the bentazone will occur in the neutral form. The remainder will be charged. Thus, the Kd values determined in this study at pH around 7 are for a mixture of the neutral and charged form but mainly for the charged form. The hydrophobicity of organic compounds falls drastically when the compound becomes charged and if the dissolution into organic matter is the main responsible mode of sorption. Kd decreases drastically. The relationship between Kd for the charged and the neutral acid is called ω.

If only the sorption/dissolution to organic matter is considered, the following expression can be written

$$Kd(HA,A^-) = \frac{\left[K_{om}(HA) + K_{om}(A^-)\cdot\frac{K_a}{[H^+]}\right]\cdot f_{om}}{1+\frac{K_a}{[H^+]}} = \frac{Kd(HA) + Kd(A^-)\cdot\frac{K_a}{[H^+]}}{1+\frac{K_a}{[H^+]}}$$

$$Kd(HA) = \left[1+\frac{K_a}{[H^+]}\right]\cdot Kd(HA,A^-) - \frac{K_a}{[H^+]}\cdot Kd(A^-)$$

and if $Kd(A^-) = \omega \cdot Kd(HA)$

$$Kd(HA) = \frac{\left[1 + \frac{K_a}{[H^+]}\right]}{1 + \omega \cdot \frac{K_a}{[H^+]}} \cdot Kd(HA, A^-)$$

Equation 6

This relationship has been tabulated as function of ω and pH in Tables F.2-F.3 below.

Table F.2
The relationship Kd(HA)/Kd(HA.A$^-$) for Ioxynil (pKa = 3.96)

pH	ω						
	1.0	0.50	0.100	0.050	0.010	0.001	0.0001
2	1.0	1.0	1.0	1.0	1.0	1.0	1.0
3	1.0	1.1	1.1	1.1	1.1	1.1	1.1
4	1.0	1.4	1.9	2.0	2.1	2.1	2.1
5	1.0	1.8	5.7	7.7	10.8	11.8	12.0
6	1.0	2.0	9.2	17.1	52.8	99.7	109.4
7	1.0	2.0	9.9	19.7	91.7	523.5	989.0
8	1.0	2.0	10.0	20.0	99.1	916.5	5230.6
9	1.0	2.0	10.0	20.0	99.9	991.0	9164.3
10	1.0	2.0	10.0	20.0	100.0	999.1	9909.6
11	1.0	2.0	10.0	20.0	100.0	999.9	9990.9

Table F.3
The relationship Kd(HA)/Kd(HA.A$^-$) for Bentazone (pKa = 2.92)

pH	ω						
	1.0	0.50	0.100	0.050	0.010	0.001	0.0001
2	1.0	1.1	1.1	1.1	1.1	1.1	1.1
3	1.0	1.4	2.0	2.1	2.2	2.2	2.2
4	1.0	1.9	5.9	8.1	11.6	12.9	13.0
5	1.0	2.0	9.3	17.3	55.0	108.2	119.8
6	1.0	2.0	9.9	19.7	92.4	546.4	1074.1
7	1.0	2.0	10.0	20.0	99.2	923.3	5459.7
8	1.0	2.0	10.0	20.0	99.9	991.8	9232.2
9	1.0	2.0	10.0	20.0	100.0	999.2	9917.5
10	1.0	2.0	10.0	20.0	100.0	999.9	9991.7
11	1.0	2.0	10.0	20.0	100.0	1000.0	9999.2

For bentazone, K_{ow} has been measured at different pH (Chapter 2). At low pH, at which the neutral HA form dominates, a K_{ow} of 219 was reported. At high pH, at which the charged A^- form dominates, a K_{ow} of 0.28 has been reported. This gives a K_{ow}-ω around 0.001, which means that for the neutral form K_{ow}(HA) is 900 times higher than the K_{ow}(HA.A$^-$) at pH around 7. The relationship between Kd(HA) and Kd(HA.A$^-$) will be similar because Kd for

a soil with 2% of organic matter (268), at pH 7, is similar to K_{ow} (219) in numeric size.

Unfortunately, ω is not known for ioxynil but, for organic acids, it is often 0.01 to 0.001 (Schwarzenbach et al., 1993). Assuming that ω is 0.001. Kd(HA) is 500 times higher than Kd($HA.A^-$) at pH 7.

Conversely, the tables show that the effective Kd($HA.A^-$) will change drastically at low pH but at pH above 7, it is more or less independent of pH. This means that an increase in pH as may be caused by photosynthesis, will have no effect on the partitioning of these pesticides. A decrease below a pH of 6 will, however, lead to a stronger sorption.

Appendix G.
Sorption model

Description of the two-rate sorption model used in the pesticide river fate sub model and fitted to laboratory data.

The model is defined as given below:

$$V \cdot \frac{dC_w}{dt} = -k_{sorp}\left[h^{-1}\right] \cdot V \cdot C_w\left[g/m^3\ water\right] + k_{desorp}\left[h^{-1}\right] \cdot m_s \cdot C_s[g/kg\ sediment]$$

$$m_s \cdot \frac{dC_s}{dt} = +k_{sorp}\left[h^{-1}\right] \cdot V \cdot C_w\left[g/m^3\ water\right] - k_{desorp}\left[h^{-1}\right] \cdot m_s \cdot C_s[g/kg\ sediment]$$

$$\frac{dC_w}{dt} = -k_{sorp}\left[h^{-1}\right] \cdot C_w\left[g/m^3\ water\right] + k_{desorp}\left[h^{-1}\right] \cdot \frac{m_s}{V} \cdot C_s[g/kg\ sediment]$$

$$\frac{m_s}{V} \cdot \frac{dC_s}{dt} = +k_{sorp}\left[h^{-1}\right] \cdot C_w\left[g/m^3\ water\right] - k_{desorp}\left[h^{-1}\right] \cdot \frac{m_s}{V} \cdot C_s[g/kg\ sediment]$$

$m_s/V = Cp$ and as $Cp \cdot Cs[g/kg\ sediment] = Cs[g/m^3\ water]$, the model can be written as

$$\frac{dC_w}{dt} = -k_{sorp}\left[h^{-1}\right] \cdot C_w\left[g/m^3\ water\right] + k_{desorp}\left[h^{-1}\right] \cdot C_s\left[g/m^3\ water\right]$$

$$\frac{dC_s}{dt} = +k_{sorp}\left[h^{-1}\right] \cdot C_w\left[g/m^3\ water\right] - k_{desorp}\left[h^{-1}\right] \cdot C_s\left[g/m^3\ water\right]$$

where C_w is the concentration in water [g/m^3]. C_s is the concentration in the sediment [g/m^3 water] and k_{sorp} and k_{desorp} are sorption and desorption coefficients. t is time [h].

k_{sorp} is a pseudo first order rate constant as the sorption rate actually depends both on water concentration and particle concentration.

At equilibrium, traditional Kd is given as:

$$Kd\left[m^3\ water/g\ sed\right] = \frac{C_s[g/g\ sed]}{C_w\left[g/m^3\ water\right]}$$

which by multiplication with CP can be transformed to Kd'

$$Kd\left[m^3\ water/g\ sed\right] \cdot CP\left[g\ sed/m^3\ water\right] = \frac{C_s[g/g\ sed] \cdot CP\left[g\ sed/m^3\ water\right]}{C_w\left[g/m^3\ water\right]}$$

$$= \frac{C_s\left[g/m^3\ water\right]}{C_w\left[g/m^3\ water\right]} = Kd'$$

Kd' is thus dependent on CP. The value of Kd' is a direct expression of the relationship between sorbed and freely dissolved fractions of pesticide. Kd' of 2 means that 2/3 of the pesticide is sorbed while 1/3 is freely dissolved.

At equilibrium $\frac{dC_w}{dt} = 0$, which yields

$$\frac{dC_w}{dt} = -k_{sorp}\left[h^{-1}\right]\cdot C_w\left[g/m^3 water\right] + k_{desorp}\left[h^{-1}\right]\cdot C_s\left[g/m^3 water\right] = 0$$
$$\wedge C_s\left[g/m^3 water\right] = Kd'\cdot C_w\left[g/m^3 water\right]$$
$$\Downarrow$$
$$Kd' = \frac{k_{sorp}\left[h^{-1}\right]}{k_{desorp}\left[h^{-1}\right]}$$

Kd' thus gives the relationship between k_{sorp} and k_{desorp} at equilibrium.

In order to fit the model, an analytical solution must be derived. This is done below for an experimental sorption set-up where $C_{s.start} = 0$ and $C_{w.start} = C_T$. It is a closed system and thus $C_T = C_w + C_s$ at all times.

$$\frac{dC_s}{dt} = k_{sorp}\cdot C_w - k_{desorp}\cdot C_s \wedge C_T = C_w + C_s$$
$$\frac{dC_s}{dt} = k_{sorp}\cdot C_T - \left(k_{desorp} + k_{sorp}\right)\cdot C_s = a\cdot C_s + b;$$
$$a = -\left(k_{desorp} + k_{sorp}\right); b = k_{sorp}\cdot C_T$$

The analytical solution is:

$$\int_{C_s(0)}^{C_s(t)} \frac{1}{a\cdot C_s + b} dC_s = \int_0^t dt$$
$$\frac{1}{a}\int_{u(0)}^{u(t)} \frac{1}{u} du = \int_0^t dt$$
$$\frac{1}{a}\left[\ln(u)\right]_{u(0)}^{u(t)} = \left[t\right]_0^t$$
$$\frac{1}{a}\cdot\left(\ln(a\cdot C_s + b) - \ln(b)\right) = t$$
$$C_s = \frac{b\cdot e^{a\cdot t} - b}{a} = \frac{k_{sorp}}{k_{sorp} + k_{desorp}}\cdot C_T\cdot\left(1 - e^{-(k_{sorp}+k_{desorp})\cdot t}\right)$$

The same can be done with C_w

$$\int_{C_w(0)}^{C_w(t)} \frac{1}{a \cdot C_w + b} dC_w = \int_0^t dt$$

$$\frac{1}{a} \int_{u(0)}^{u(t)} \frac{1}{u} du = \int_0^t dt$$

$$\frac{1}{a} [\ln(u)]_{u(0)}^{u(t)} = [t]_0^t$$

$$\frac{1}{a} \cdot (\ln(a \cdot C_w(t) + b) - \ln(a \cdot C_w(0) + b)) = t, C_w(0) = C_T$$

$$C_w = \frac{(a \cdot C_T + b) \cdot e^{a \cdot t} - b}{a} = C_T \cdot \frac{k_{sorp} \cdot e^{-(k_{sorp} + k_{desorp}) \cdot t} + k_{desorp}}{k_{sorp} + k_{desorp}}$$

k_{sorp} and k_{desorp} can be fitted to laboratory sorption data using the equations for either C_w or C_s and non linear regression.

Alternatively, k_{sorp} and k_{desorp} can be fitted with the analytical expression for $Kd'_{apparent}$:

$$Kd'_{apparent}(t) = \frac{C_s(t)}{C_w(t)} = \frac{1 - e^{-(k_{sorp} + k_{desorp}) t}}{\frac{k_{desorp}}{k_{sorp}} + e^{-(k_{sorp} + k_{desorp}) t}}$$

with which both measured water concentrations and sorbent concentrations can be taken into account. However, depending on the partition coefficient and the experimental set-up, either C_w or C_s will be more reliable for fitting. If only C_w or C_s is used for fitting, C_T becomes important and it should be the actual sum of C_w and C_s excluding pesticide sorbed to glass and other.

From experiment to model

If it is assumed that Kd is independent of particle (sorbent) concentration CP and thereby $Kd_{model} = Kd_{experiment}$, the following will be true:

$$Kd_{model} = \frac{k_{sorp,model}}{k_{desorp,model} \cdot CP_{model}} = Kd_{exp} = \frac{k_{sorp,exp}}{k_{desorp,exp} \cdot CP_{exp}}$$

$$\Downarrow$$

$$\frac{k_{sorp,model}}{k_{desorp,model}} \cdot \frac{CP_{exp}}{CP_{model}} = \frac{k_{sorp,exp}}{k_{desorp,exp}}$$

As mentioned earlier, it can be theorized that the sorption rate will be dependent on particle concentration because the probability of a pesticide molecule meeting a particle to sorp to is proportional to particle concentration. On the other hand, the desorption rate, i.e., the probability of a pesticide molecule to desorp from a particle, is not dependent on the particle concentration but rather on the sorbing tendency (attractive forces).

Therefore, the following can be written:

$$k_{sorp,model} = k_{sorp,exp} \cdot \frac{CP_{model}}{CP_{exp}} \text{ and } k_{desorp.model} = k_{desorp.exp}$$

This means that sorption rate constants derived from experiments at one particle concentration must be adjusted with the relevant particle concentration when entered into the model.

The actual fitting of k_{sorp} and k_{desorp} is based on data sets of time and C_w and $C_T = C_w$ [g/m^3 water] + C_s [g/g sediment]CP [g sediment/m^3 water]

The time it takes to reach a certain concentration can be calculated as:

$$C_S = \frac{k_{sorp}}{k_{sorp} + k_{desorp}} \cdot C_T \cdot \left(1 - e^{-(k_{sorp}+k_{desorp})\cdot t}\right)$$

$$\Downarrow$$

$$t = \frac{\ln\left(1 - \frac{(k_{sorp} + k_{desorp}) \cdot C_s}{k_{sorp} \cdot C_T}\right)}{-(k_{sorp} + k_{desorp})}$$

The time that it takes for C_s to reach a certain degree of equilibrium can then be calculated to be:

$$t = \frac{\ln\left(1 - \frac{(k_{sorp} + k_{desorp}) \cdot C_s}{k_{sorp} \cdot C_T}\right)}{-(k_{sorp} + k_{desorp})} \wedge C_s = \beta \cdot C_{s,\infty} = \beta \cdot \frac{Kd' \cdot C_T}{1 + Kd'}$$

$$t = \frac{\ln\left(1 - \frac{(k_{sorp} + k_{desorp}) \cdot \beta \cdot \frac{Kd' \cdot C_T}{1+Kd'}}{k_{sorp} \cdot C_T}\right)}{-(k_{sorp} + k_{desorp})} = \frac{\ln(1-\beta)}{-(k_{sorp} + k_{desorp})}$$

Likewise for C_w:

$$t = \frac{\ln\left(\left(\frac{C_w}{C_T} - 1\right) \cdot \frac{k_{sorp} + k_{desorp}}{k_{sorp}} + 1\right)}{-(k_{sorp} + k_{desorp})} \wedge C_w = \beta \cdot C_{w,\infty} = \beta \cdot \frac{C_T}{1 + Kd'}$$

$$t = \frac{\ln\left(\left(\frac{\beta \cdot \frac{C_T}{1 + \frac{k_{sorp}}{k_{desorp}}}}{C_T} - 1\right) \cdot \frac{k_{sorp} + k_{desorp}}{k_{sorp}} + 1\right)}{-(k_{sorp} + k_{desorp})} = \frac{\ln\left(\frac{(\beta - 1)k_{desorp}}{k_{sorp}}\right)}{-(k_{sorp} + k_{desorp})}$$

The last two formulas show that the time to reach equilibrium is dependent on the rate constants and larger values of either a single or both rate constants

will lead to faster equilibrium. If the particle concentration differs between the model situation and the experiment, so will the time to equilibrium. In general, the particle concentration of suspended matter in the stream will be lower than in the experiment and thus the time to equilibrium will be longer.

Another way of solving the equation:

$$C_s = \frac{1}{k_{desorp}} \frac{dC_w}{dt} + \frac{k_{sorp}}{k_{desorp}} \cdot C_w$$

$$\frac{dC_s}{dt} = k_{sorp} \cdot C_w - k_{desorp} \cdot C_s =$$

$$k_{sorp} \cdot C_w - k_{desorp} \cdot \left(\frac{1}{k_{desorp}} \frac{dC_w}{dt} + \frac{k_{sorp}}{k_{desorp}} \cdot C_w \right) = -\frac{dC_w}{dt}$$

$$\frac{dC_s}{dt} = \frac{d\left(\frac{1}{k_{desorp}} \frac{dC_w}{dt} + \frac{k_{sorp}}{k_{desorp}} \cdot C_w \right)}{dt} =$$

$$\frac{1}{k_{desorp}} \frac{d^2C_w}{dt^2} + \frac{k_{sorp}}{k_{desorp}} \cdot \frac{dC_w}{dt} = -\frac{dC_w}{dt}$$

$$\frac{d^2C_w}{dt^2} + (k_{sorp} + k_{desorp}) \cdot \frac{dC_w}{dt} = 0$$

$$R^2 + (k_{sorp} + k_{desorp})R = 0$$

$$R = \frac{-(k_{sorp} + k_{desorp}) \pm \sqrt{(k_{sorp} + k_{desorp})^2}}{2}, R_1 = -(k_{sorp} + k_{desorp}), R_2 = 0$$

$$C_w = c_1 \cdot e^{-(k_{sorp} + k_{desorp})t} + c_2$$

$$C_w(\infty) = c_1 \cdot e^{-(k_{sorp} + k_{desorp})\infty} + c_2 = c_2$$

$$c_2 = C_w(\infty) = C_T(1 + Kd') = C_T \frac{k_{desorp}}{k_{sorp} + k_{desorp}}$$

$$C_w(0) = C_T = c_1 \cdot e^{-(k_{sorp} + k_{desorp})0} + c_2 = c_1 + C_T \frac{k_{desorp}}{k_{sorp} + k_{desorp}}$$

$$c_1 = \left(1 - \frac{k_{desorp}}{k_{sorp} + k_{desorp}} \right) C_T = C_T \frac{k_{sorp}}{k_{sorp} + k_{desorp}}$$

When degradation of a pesticide in the water phase is included, the model will be

$$\frac{dC_w}{dt} = -k_{sorp} \cdot C_w + k_{desorp} \cdot C_s - k_{deg} \cdot C_w$$

$$\frac{dC_s}{dt} = k_{sorp} \cdot C_w - k_{desorp} \cdot C_s$$

$$C_s = \frac{1}{k_{desorp}} \frac{dC_w}{dt} + \frac{k_{sorp} + k_{deg}}{k_{desorp}} \cdot C_w$$

$$\frac{dC_s}{dt} = k_{sorp} \cdot C_w - k_{desorp} \cdot C_s =$$

$$k_{sorp} \cdot C_w - k_{desorp} \cdot \left(\frac{1}{k_{desorp}} \frac{dC_w}{dt} + \frac{k_{sorp} + k_{deg}}{k_{desorp}} \cdot C_w \right) = -\frac{dC_w}{dt} - k_{deg} \cdot C_w$$

$$\frac{dC_s}{dt} = \frac{d\left(\frac{1}{k_{desorp}} \frac{dC_w}{dt} + \frac{k_{sorp} + k_{deg}}{k_{desorp}} \cdot C_w \right)}{dt} =$$

$$\frac{1}{k_{desorp}} \frac{d^2 C_w}{dt^2} + \frac{k_{sorp} + k_{deg}}{k_{desorp}} \cdot \frac{dC_w}{dt} = -\frac{dC_w}{dt} - k_{deg} \cdot C_w$$

$$\frac{d^2 C_w}{dt^2} + (k_{sorp} + k_{deg} + k_{desorp}) \cdot \frac{dC_w}{dt} + k_{deg} \cdot k_{desorp} \cdot C_w = 0$$

$$R^2 + (k_{sorp} + k_{deg} + k_{desorp}) \cdot R + k_{deg} \cdot k_{desorp} = 0$$

$$R = \frac{-(k_{sorp} + k_{desorp} + k_{deg}) \pm \sqrt{(k_{sorp} + k_{desorp} + k_{deg})^2 - 4k_{desorp}k_{deg}}}{2}$$

$$C_w = c_1 \cdot e^{R_1 t} + c_2 \cdot e^{R_2 t}$$

Border conditions

$$C_w(0) = c_1 + c_2 = C_T(0)$$

$$\frac{dC_w}{dt} = c_1 \cdot R_1 \cdot e^{R_1 t} + c_2 \cdot R_2 \cdot e^{R_2 t} \quad C_s = \frac{1}{k_{desorp}} \frac{dC_w}{dt} + \frac{k_{sorp} + k_{deg}}{k_{desorp}} \cdot C_w$$

$$\Downarrow t = 0; C_s(0) = 0; C_w(0) = C_T(0)$$

$$c_1 \cdot R_1 + c_2 \cdot R_2 + (k_{sorp} + k_{deg}) C_T(0) = 0 \wedge c_1 + c_2 = C_T(0)$$

$$c_1 \cdot R_1 + (C_T(0) - c_1) \cdot R_2 + (k_{sorp} + k_{deg}) C_T(0) = 0$$

$$c_1 = \frac{k_{sorp} + k_{deg} + R_2}{R_2 - R_1} C_T(0) =$$

$$\frac{k_{sorp} + k_{deg} + \left[\frac{-(k_{sorp} + k_{desorp} + k_{deg}) - \sqrt{(k_{sorp} + k_{desorp} + k_{deg})^2 - 4k_{desorp}k_{deg}}}{2} \right]}{-\sqrt{(k_{sorp} + k_{desorp} + k_{deg})^2 - 4k_{desorp}k_{deg}}} C_T(0)$$

$$c_2 = -\frac{k_{sorp} + k_{deg} + R_1}{R_2 - R_1} C_T(0) =$$

$$\left(-\frac{k_{sorp} + k_{deg} + \left[\frac{-(k_{sorp} + k_{desorp} + k_{deg}) + \sqrt{(k_{sorp} + k_{desorp} + k_{deg})^2 - 4k_{desorp}k_{deg}}}{2} \right]}{-\sqrt{(k_{sorp} + k_{desorp} + k_{deg})^2 - 4k_{desorp}k_{deg}}} \right) C_T(0)$$

For the fitting of degradation data (C_{total} measured), an expression for C_{total} is derived:

$$\frac{dC_T}{dt} = \frac{dC_w}{dt} + \frac{dC_s}{dt} = -k_{deg} \cdot C_w$$

$$\frac{dC_T}{dt} = -k_{deg}\left(c_1 \cdot e^{R_1 t} + c_2 \cdot e^{R_2 t}\right)$$

$$\int dC_T = \int -k_{deg}\left(c_1 \cdot e^{R_1 t} + c_2 \cdot e^{R_2 t}\right)dt + c_3$$

$$C_T = -k_{deg}\left(\frac{c_1}{R_1} \cdot e^{R_1 t} + \frac{c_2}{R_2} \cdot e^{R_2 t}\right)$$

In calculations, c_1' and c_2' is used. $c_1'=c_1/(R_1 \cdot C_T(0))$ and $c_2'=c_2/(R_2 \cdot C_T(0))$ and thus

$$C_T = -k_{deg} \cdot C_T(0) \cdot \left(c'_1 \cdot e^{R_1 t} + c'_2 \cdot e^{R_2 t}\right)$$

Fejl! Ugyldig kæde.

	k1>>k2. k1>k3	k3>k1>>k2	k1~k2~k3	k1~k2>k3	k1~k2<<k3	k1~k2<k3
k1	1.5	1.5000	0.1	0.8	0.1	0.8
k2	0.001	0.0010	0.05	0.6	0.05	0.6
k3	0.1	1.8000	0.1	0.1	1.2	1.8

In the model, a strongly sorbing pesticide will be modelled by relatively fast sorption and relatively slow desorption. If the degradation rate is not high (lower than sorption rate), a very slow degradation will occur as both the desorption and degradation rates are slow. If the degradation rate is very high (faster than desorption k2>k1 and similar to sorption), an initial fast degradation will occur until sorption has taken place. The degradation will subsequently be limited by desorption. If the sorption, desorption and degradation rates are comparable, the disappearance will be similar to first order. If the sorption is weak and much slower than degradation, a fast initial almost complete disappearance will occur followed by a long period of slow desorption-limited degradation (for the same relationship between the rate constants, the curve will be compressed on the timescale with a decrease in values and expanded with an increase in values).

10.22 G.1 Centrifugation

Centrifugation was conducted in a small ultracentrifuge at 9000 rpm. This was the maximum speed that the centrifuge tubes could withstand without breaking. The centrifuge had 6 slots for 7-mL glass centrifuge tubes.

$$RCF = \frac{\omega^2 x}{g} = \frac{\left(\frac{2\pi \cdot rpm}{60}\right)^2}{g} \cdot x$$

RCF: relative centrifugation factor [g]. ω: rotational speed [rad/s]. rpm: rotations per minute. g: gravitational force. x distance of particle from rotor centre [m].

The sedimentation speed is given by

$$\frac{dx}{dt} = \frac{\frac{4}{3}\pi \cdot r^3 \cdot (\sigma_p - \sigma_M) \cdot \omega^2 \cdot x}{6 \cdot \pi \cdot \eta \cdot r} = \frac{2 \cdot r^2 \cdot (\sigma_p - \sigma_M) \cdot \omega \cdot x}{9 \cdot \eta}$$

$$\Downarrow$$

$$\Delta t = \frac{9 \cdot \eta \cdot \ln\left(\frac{x_2}{x_1}\right)}{2 \cdot r_p^2 \cdot (\sigma_p - \sigma_M) \cdot \omega^2} \Leftrightarrow r_p = \sqrt{\frac{\ln\left(\frac{x_2}{x_1}\right) \cdot 9 \cdot \eta}{2 \cdot (\sigma_p - \sigma_M) \cdot \omega^2 \cdot \Delta t}}$$

r: particle diameter. η: viscosity of liquid. σ_P: particle density. σ_M: media density. x1: distance from centre to top of solution. x1: distance from centre to bottom of solution. t: time

The centrifuge used had the data x1 =4 cm, x2 = 8 cm and if it is anticipated that the density of the particles is 1.8 kg/L and the viscosity of the water is $\eta = 8.95 \cdot 10^{-3}$ g/s · cm, it can be calculated from the expressions above that particles with a radius larger than approx. 0.05 μm will be sedimentated within the 60 min of 9000 rpm used for centrifugation in this experiment. If the density of the particles is higher (e.g. quartz), even smaller particles will be sedimentated.

10.23 G.2 Three-compartment model

$$C_s = K_1 \cdot C_w$$

$$C_g = K_2 \cdot C_w$$

$$m_{tot} = C_w \cdot V_w + C_s \cdot m_s + C_g \cdot A_g$$

$$C_s = \frac{m_{tot}}{\frac{V_w + K_2 \cdot A_g}{K_1} + m_s}$$

$$C_w = \frac{m_{tot}}{V_w + K_2 \cdot A_g + m_s \cdot K_1}$$

$$C_g = \frac{m_{tot} \cdot K_2}{V_w + K_2 \cdot A_g + m_s \cdot K_1}$$

$$\frac{mg}{m_{tot}} = \frac{A_g \cdot K_2}{V_w + A_g \cdot K_2 + m_s \cdot K_1}$$

$$C_s = \frac{T_{total} - m_v \cdot T_v}{m_s} = \frac{T_{total} - m_s \cdot \omega \cdot T_v}{m_s}$$

T_{total} = count on boat

m_v = amount of water in boat

T_v = activity of water in boat

ω = water amount per dry material in boat

C_s corrected = Count sediment – $V_{Sediment\ water}$ C_w.