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Pesticides in Streams and Subsurface Drainage Water within Two Arable Catchments in Denmark: Pesticide Application, Concentration, Transport and Fate

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

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

Table i. Sub-projects of ”Pesticides in Surface Water”.
Tabel i. Oversigt over delprojekter i ”Pesticider i overfladevand”.

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

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

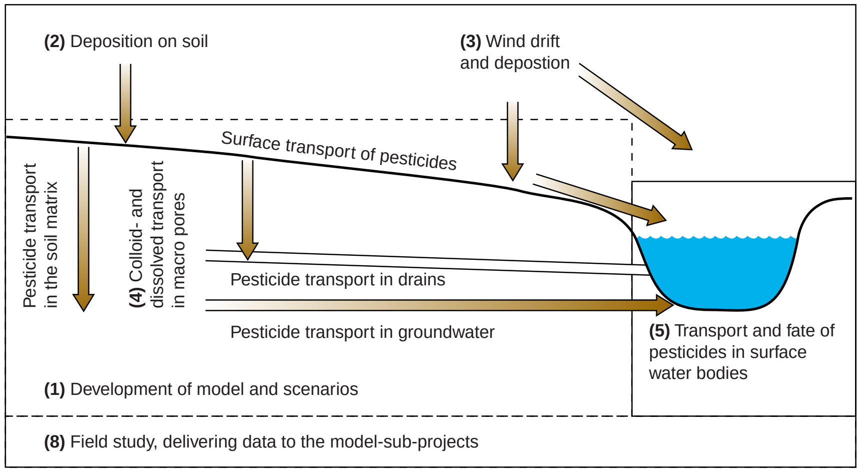


Figure i. Links between the different sub-projects. The sub-projects are illustrated on a cross-section of the catchment to illustrate interactions.
Figur i. Sammenhæng mellem delprojekterne. Delprojekterne er placeret på et tværsnit af et opland for at illustrere interaktionerne.

The reports produced by the project are:

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

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

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

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

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

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

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

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

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

The original considerations behind the project are described in detail in the report ”Model Based Tool for Evaluation of Exposure and Effects of Pesticides in Surface Water”, Inception Report – J. nr. M 7041-0120, by DHI, VKI, NERI, DIAS and Funen County, 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, Funen County (1999-2002)
- Hanne Bach, National Environmental Research Institute (1999-2002).

October 2002

Merete Styczen, project co-ordinator

Sammenfatning og konklusioner

Fundhyppighed, koncentration og tab af 49 pesticider og metabolitter blev målt gennem 2 år (1999 og 2000) i to mindre dyrkede danske vandløbsoplande. Lillebæk på Fyn har et opland på 4.35 km^2. Oplandet er 86% dyrket og består overvejende af lerede jorder. Odderbæk i Nordjylland har et opland på 11.43 km^2. Det er 83% dyrket og består hovedsageligt af sandede jorder. To vandløbsstationer blev oprettet i Lillebæk som delte oplandet i et øvre rørlagt delopland og et ned opland med åbent vandløbsforløb. Pesticiders forekomst, transport og skæbne i vand, suspenderet stof og vandløbssediment blev målt ved prøver udtaget ved 3 vandløbsstationer og 3 drænstationer i de to oplande. Hovedresultaterne fra de 2 oplande er vist i tabellerne i-iii.

Table i. Number of pesticides (active substances and metabolites) detected in water samples collected during the two study years from the four monitoring stations in the Lillebæk catchment and two monitoring stations in the Odderbæk.
Tabel i. Antal pesticider (aktiv stoffer og metaboliter) fundet i de indsamlede vandprøver fra de 4 målestationer i Lillebæk oplandet på Fyn og de to målestationer i Odderbæk oplandet i Nordjylland vist for de to måleår (1999 og 2000).

	Size of catchment/field	Number of pesticides detected
Lillebæk catchment		
Upstream station (Topenden) (470032)	229 ha	42
Downstream station (Fredskovvej) (470033)	435 ha	40
Drain 2 (470041)	4.2 ha	17
Drain 6 (470045)	2.1 ha	16
Odderbæk catchment		
Stream station (130011)	1143 ha	39
Drain station (130013)	32 ha	27

Ud af de 49 pesticider der blev analyseret for i vandløbsvand og drænvand blev 39-42 fundet i vandløbsvand (tabel i). Antallet af fundne pesticider og metabolitter i drænvand var mindre i begge oplande hvilket skyldes at et færre antal pesticider blev anvendt i de små drænoplande end i de meget større vandløbsoplande.

Table ii. Detection frequencies for 12 pesticides at the 3 stream stations and 3 drain stations in the two studied catchments during the two study years.
Tabel ii. Fundhyppighed for 12 pesticider ved de 3 vandløbsstationer og de 3 drænstationer i de to oplande gennem de to måleår.

Pesticide	Upstream Lillebæk	Downstream Lillebæk	Odderbæk	Drain 2 Lillebæk	Drain 6 Lillebæk	Drain Odderbæk
	Stream stations			Drain stations		
Herbicides						
BAM (metabolite)	75%	70%	12%	3.6%	0%	14%
Bentazone	62%	87%	69%	57%	67%	61%
Ethofumesate	24%	1.0%	1.8%	0%	0%	2.0%
Ioxynil	17%	7.3%	2.9%	7.1%	0%	0%
Isoproturon	76%	84%	56%	54%	46%	47%
Pendimethalin	34%	26%	25%	0%	13%	12%
Terbuthylazine	97%	87%	32%	7.1%	21%	6.1%
Fungicides						
Fenpropimorph	20%	4.8%	1.8%	0%	0%	2.9%
Prochloraz	3.5%	3.1%	1.5%	0%	0%	4.1%
Propiconazole	55%	18%	5.9%	7.1%	4.2%	6.1%
Insecticides						
Dimethoate	12%	3.1%	1.5%	0%	0%	0%
Pirimicarb	12%	9.4%	2.9%	0%	0%	0%

Fundprocenten af 12 udvalgte persticider og metabolitter i vandløb og dræn er vist i tabel i. Rester af herbicider måles generelt meget hyppige i vandløb og dræn end fungicider og insekticider. Pesticidrester er for de alle stoffer fundet hyppigere i vandløbsvand end i drænvand. Enkelte pesticider som isoproturon og bentazone er dog fundet næsten lige så hyppigt i vandløbsvand og drænvand. Generelt er de pesticider der findes i både vandløbsvand og drænvand anvendt indenfor oplandet eller marken i det samme eller det foregående år.

Table iii Aggregated results from the 2 stream stations in the Lillebæk catchment and the stream station in the Odderbæk catchment. In the table the average annual pesticide use in the two catchments is shown together with the average detection frequency and average maximum concentration for 18 pesticides applied in the two catchments during the two -year period. Moreover, the loss:applied ratio is shown for each catchment for a one-year period (4th quarter 1999 to 3rd quarter 2000). Note that the ratio is a minimum because of the pesticide loss only being calculated for the period covered with sampling.
Tabel iii Gennemsnitlig årlig anvendelse af pesticider i de tre målte oplande i Lillebæk og Odderbæk. Derudover er vist den gennemsnitlige fundhyppighed og gennemsnitlig maximum koncentration af 18 pesticider der blev anvendt i oplandene i de 2 måleår. Endelig er det beregnede tabs:anvendelse ratio vist for året omfattet af 4 kvartal 1999 til 3 kvartal 2000. Den viste ratio er et minimums estimat da tabet kun er beregnet for perioder med prøvetagning.

	Average use of pesticides (herbicides - %) (kg active substances)	Average detection Frequency (%) (±stdv)	Average maximum concentration (ng/l) (±stdv)	Minimum loss:applied ratio (%)
Lillebæk upstream culverted sub-catchment (229 ha)	150 (58%)	36 (±29)	521 (±1078)	0.0233
Entire Lillebæk catchment (435 ha)	184 (53%)	28 (±32)	211 (±455)	0.0109
Odderbæk catchment (1143 ha)	1034 (86%)	13 (±20)	204 (±678)	0.0031

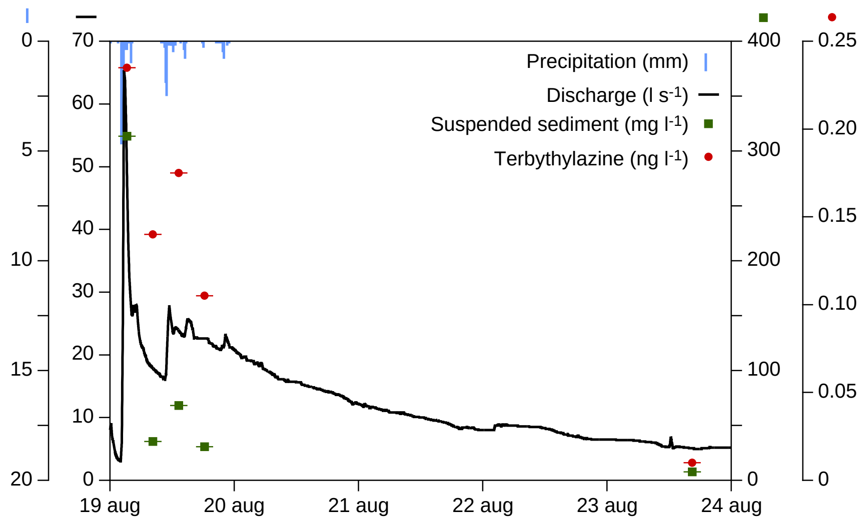
Forekomsten og den maksimale koncentration af 18 anvendte pesticider i landbruget i de 2 måleperioder (efterår 1999 til efterår 2001) var højest i den rørlagte det af Lillebæk, næsthøjest i hele Lillebæk oplandet og mindst i Odderbæk (tabel i). Tilsvarende var tabsraten af pesticider (målt transport i vandløb divideret med anvendte mængder aktivstof) 2 til 8 gange højere fra oplandet hvor Lillebæk var rørlagt end fra hele Lillebæk oplandet og Odderbæk oplandet. Vinddrift og atmosfærisk deposition af pesticider til

Lillebæk kan ikke forekomme i den rørlagte del af oplandet. Da den rørlagte del af Lillebæk oplandet stadig har den største tabsrate af pesticider må det antages at vinddrift og atmosfærisk deposition generelt er af mindre betydning som pesticide transportvej til tilsvarende små vandløb. Tab af pesticider til vandløb via drænvand må i den rørlagte del af Lillebæk oplandet være den største transportvej da oplandet er intensivt drænet. Pesticider målt i vandløbet kan være tilført ved udvaskning eller makropore transport i jorden under regnhændelser efter udsprøjtning på markerne (se f.eks. Laubel et al., 1998; Kronvang et al., 2002).

Punktkilder, som gårdspladser og vaskepladser med kontakt til drænsystemer, kan også være en vigtig kilde og transportvej for pesticider til grundvand og vandløb (se f.eks. Bay og Hansen, 2001). Målinger af punktkilders betydning var dog ikke omfattet af det forsøgsdesign som blev anvendt i undersøgelsen, hvorfor betydningen af punktkilder i de to oplande ikke kan opgøres. De to drænsystemer som der blev målt på i Lillebæk oplandet var begge uden kontakt til gårdspladser og vaskepladser. I begge drænsystemer blev der fundet mange pesticidrester, dog for de fleste pesticider med en lavere fundhyppighed og koncentration end i vandløbet. Da Lillebæk oplandet indeholder mange drænsystemer er der ingen sikkerhed for at de 2 drænsystemer der indgik i undersøgelsen er repræsentative. Andre undersøgelser har konstateret meget høje pesticidkoncentrationer i dræn hvor der ikke var tale om punktkilder men transport af pesticider gennem sprækker og store porer (makroporer) i jorden (Kronvang, 2002; Holm et al., 2003). Efter målingernes afslutning blev der interviewet tre lodsejere om mulige tabsposter for pesticider i det rørlagte Lillebæk opland. De pegede på at en overset kilde og transportvej i det rørlagte opland kunne være overfladisk afstrømning fra marker der på grund af stuvning af regnvand (underdimensionerede drænsystemer) slap ind i drænbrønde.

En nærmere analyse af hvor betydningsfuld punktkilder er for fund af pesticider i vandløb i modsætning til markbidrag vil kræve en målrettet opsporings undersøgelse i vandløbsoplande af punktkilder kombineret med målinger af markbidrag og pesticidforekomst i vandløb.

Der blev opstillet signifikante empiriske sammenhænge mellem pesticid tab og henholdsvis pesticide anvendelsen på markerne og pesticidernes fysisk-kemiske egenskaber for i alt 16 pesticider anvendt i undersøgelsesperioden. Disse empiriske sammenhænge viser at små mængder udsprøjtede pesticider hurtigt transporteres gennem jorden til dræn eller øvre grundvand og derfra til overfladevand. Den hurtige stigning i koncentrationen af pesticider efter regnvejr og stigende vandføring i vandløbene viser at pesticider hurtigt finder vej mellem mark og vandløb i de to undersøgte oplande (figur i). Måden hvorpå koncentrationen af pesticid stiger efter regn og stigende vandføring i vandløb er påvist at være afhængig af det enkelte pesticids fysisk-kemiske egenskaber. Hydrofobe pesticider udviser en stor stigning i starten af en regnhændelse ofte samtidig med stigninger i koncentrationen af suspenderet stof (figur i).



	no.	Kd, mean	Kd, median
Correlation to suspended sediment	4	5.3	3.31
No correlation	6	0.85	0.72

Figure i Concentration of terbuthylazine and suspended sediment during a storm event in December 1999 at the upstream station in the Lillebæk. The Kd values of 4 pesticides with a significant relationship to suspended sediment concentration and 6 pesticides with no significant relationship are shown in the Table below.
Figur i Koncentrationen af terbuthylazin og suspenderet stof ved en afstrømningshændelse i december 1999 ved den opstrøms vandløbsstation i Lillebæk. I tabelln under figuren er Kd værdien for 4 pesticider der korrelerer til suspenderet stof og 6 pesticider der ikke korrelerer desuden vist.

Mange af de hydrofobe pesticider udvist stærke sammenhænge til koncentrationen af suspenderet stof i perioder med regn og stigende vandføring i vandløb uanset årstid. Pesticid indholdet i suspenderet stof og vandløbssediment udviste stigninger især i forårets sprøjtesæsonen (april-juni).

En statistisk beregning af gentagelses intervaller for koncentrationen af pesticider i Lillebæk blev gennemført for udvalgte pesticider pesticider baseret på en generaliseret ekstremværdi fordelingsfunktion. Gentagelsesintervaller for koncentrationen af terbuthylazin og diuron i den rørlagte del af Lillebæk og for isoporturon i den åbne del af Lillebæk viser at meget høje maksimum koncentrationer må kunne forventes at forekomme i korte tidsrum. At kortlægge maksimum forekomster af pesticider i små oplande vil derfor stille store krav til prøvetagningsfrekvens.

Summary and conclusions

Detection frequency, concentration and loss of 49 pesticides and metabolites were measured during two years (1999 and 2000) in two small Danish arable catchments. The Lillebæk catchment on Funen has an area of 4.35 km^2 with 86% agricultural land on loamy soils, and the Odderbæk catchment in Northern Jutland has an area of 11.43 km^2 with 83% agricultural land, mainly on sandy soils. Two stream stations were established in the Lillebæk catchment dividing the entire catchment into 2 sub-catchments: an upstream culverted and a downstream sub-catchment with an open stream channel. The fate of pesticides in water, suspended sediment and streambed sediment was measured based on samples/results from 3 stream stations and 3 tile drain stations in the two catchments. The main aggregated results from the two catchments are shown in Tables i-iii.

Table i. Number of pesticides (active substances and metabolites) detected in water samples collected during the two study years from the 4 monitoring stations in the Lillebæk catchment and 2 stations in the Odderbæk.
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Most of the 49 pesticides and metabolites analysed for in stream water was detected (39-42) (Table i). The number of pesticides detected in tile drainage water was only lesser than in stream water (Table i). This could be explained by the fewer pesticides applied within the smaller subdrained fields especially concerning the two drains in the Lillebæk catchment.

Table ii. Detection frequencies for 12 pesticides at the 3 stream stations and 3 drain stations in the two studied catchments during the two study years.
Tabel ii. Fundhyppighed for 12 pesticider ved de 3 vandløbsstationer og de 3 drænstationer i de to oplande gennem de to måleår.

Pesticide	Upstream Lillebæk	Downstream Lillebæk	Odderbæk	Drain 2 Lillebæk	Drain 6 Lillebæk	Drain Odderbæk
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Insecticides						
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The detection frequency for 12 selected pesticides and metabilites measured in streams and drains are shown in Table ii. Herbicides were detected much more frequently in streams and drains than fungicides and insecticides. Moreover, pesticides were found more frequently in the studied streams than in the studied drains. Pesticides like isoproturon og bentazone were, however, experienced nearly the same detection frequency in streams and drains. In general, the pesticides found in streams and drains have been applied within the same or previous year within the catchment or the tile drained field.

Table iii Aggregated results from the 2 stream stations in the Lillebæk catchment and the stream station in the Odderbæk catchment. In the table the average annual pesticide use in the two catchments is shown together with the average detection frequency and average maximum concentration for 18 pesticides applied in the two catchments during the two -year period. Moreover, the loss:applied ratio is shown for each catchment for a one-year period (4th quarter 1999 to 3rd quarter 2000). Note that the ratio is a minimum because of the pesticide loss only being calculated for the period covered with sampling.
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	Average use of pesticides (herbicides - %) (kg active substances)	Average detection Frequency (%) (±stdv)	Average maximum concentration (ng/l) (±stdv)	Minimum loss:applie d ratio (%)
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Odderbæk catchment (1143 ha)	1034 (86%)	13 (±20)	204 (±678)	0.0031

Detection frequency and maximum concentration of 18 applied pesticides in the catchments were highest for the upstream culverted sub-catchment in the Lillebæk, followed by the entire Lillebæk catchment and the Odderbæk catchment (Table i). Similarly, the loss:applied ratio was 2 and 8 times, respectively, higher from the upstream culverted sub-catchment than from the entire Lillebæk catchment and the Odderbæk catchment (Table i). Clearly, wind drift and atmospheric deposition of pesticides can be excluded as a pesticide source to the upstream culverted stream. As the culverted stream experienced the highest detection frequency, highest concentrations and highest loss:applied ratio, it indicates that wind drift and atmospheric depostion of pesticides are no major pesticide pathway to any of the streams. Instead, tile drainage water must be a major transport route for at least pesticides as indicated by the results from the upstream culverted catchment which is intensively tile drained. The pesticides measured in the stream can be lost through leaching and macropore flow during rain events following an application (e.g. Laubel et al., 1998; Kronvang et al., 2002).

The existence of point sources in the catchment can, however, also play an important role for increased pesticide losses to groundwater and to surface water through tile drains (Bay and Hansen, 2001). Point sources were not investigated in this study as the two tile drains monitored were without contact to farmyards. Pesticides were detected in both tile drains but with a lower detection frequency and concentration than in the stream for most of the pesticides. Moreover, the 2 tile drained fields chosen for this investigation may not be representative for the many tile drains in the entire Lillebæk catchment. Other investigations have shown that high pesticide concentrations can occur in subsurface drainage water without influence from point sources due to translocation of pesticides through macropores (Kronvang, 2002; Holm et al., 2003). An interview with three farmers revealed that pesticide losses from surface runoff could also be a pesticide pathway due to underdimensioned drainage systems in the upstream part of the culverted catchment.

A more throrough investigation on the importance of point sources as opposed to field losses of pesticides in catchments will demand a screening for the existence of point sources followed by tracer experiments, together with monitoring of field losses and occurrence of pesticides in streams.

Significant relationships were developed between pesticide loss and pesticide application and pesticide physico-chemical properties based on data for 16 pesticides. Such relationships show that small amounts of applied pesticides are quickly transported through the upper soil layer to tile drains and upper groundwater and thereafter carried to surface waters. The steep increases in pesticide concentration and loss during rain and increasing discharge in the streams (storm events) confirm that pesticides are indeed transferred quickly from field to stream in the two studied catchments (Fig. i). The pattern of increase in the pesticide concentration has been documented as depending on pesticide physico-chemical properties, the hydrophobic pesticides peaking early in the storm event together with a peak in suspended sediment concentration (Fig. i).

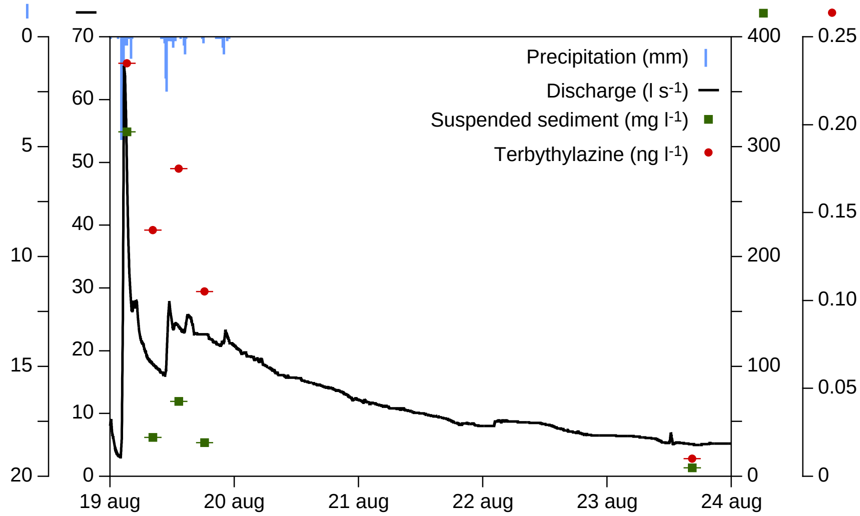

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Figure i Concentration of terbuthylazine and suspended sediment during a storm event in December 1999 at the upstream station in the Lillebæk. The Kd values of 4 pesticides with a significant relationship to suspended sediment concentration and 6 pesticides with no significant relationship are shown in the Table below.
Figur i Koncentrationen af terbuthylazin og suspenderet stof ved en afstrømningshændelse i december 1999 ved den opstrøms vandløbsstation i Lillebæk. I tabelln under figuren er Kd værdien for 4 pesticider der korrelerer til suspenderet stof og 6 pesticider der ikke korrelerer desuden vist.

Many of the hydrophobic pesticides expirienced strong relationships to the concentration of suspended sediment during storm events during all seasons of the year. Moreover, the pesticide content increased in suspended sediment and streambed sediment, especially during the spring spraying season (April-June). Recurrence intervals for pesticide concentrations were calculated for selected pesticides measured in the Lillebæk catchment based on a generalised extreme value distribution. The recurrence intervals for terbuthylazine and diuron at the upstream station in the Lillebæk and isoproturon at the downstream station reveal that high peak concentrations are likely to occur. However, it requires intense sampling programmes in order to detect these peak pesticide concentrations.

1 Introduction

1.1 Objectives

The main objective of the measuring programme presented is to generate data for validating and testing a new Danish pesticide model developed to predict the transport of pesticides to surface waters and the fate of pesticides in streams within small agricultural catchments. Therefore, we have measured the occurrence, concentration and transport of selected pesticides in stream water and subsurface drainage water during the study years 1999 and 2000. Water samples were mainly collected during spates, as the hypothesis was that precipitation and/or snow-melt would transport dissolved and more hydrophobic pesticides with surface runoff or through the soil to tile drainage runoff and would eventually reach the stream channel. However, water samples were also collected during periods with steady or decreasing discharge conditions. During such periods pesticides from groundwater, and during the spraying season also pesticides from wind drift, are believed to act as the main contributing pesticide pathways. Transport of selected key pesticides is quantified and compared with the application in the catchment in order to achieve an estimate of the loss ratio (pesticide transport divided by pesticide application). Finally, we have measured the fate of pesticides in streams by sampling suspended sediment and streambed sediment at different times of the year.

1.2 Background

In recent years there has been a growing awareness of the occurrence and concentration of pesticides in surface water due to the deterioration of surface water as a drinking water resource and the possible impact of pesticides on biota. Funen County was the first to monitor pesticides in streams in Denmark and link the presence to biota (macroinvertebrates) (Pedersen, 1996; Funen County, 1997, 1999 and 2001).

Other international studies have shown that pesticides applied in agriculture may risk being delivered to surface waters via different hydrological pathways, wind drift, atmospheric deposition or by accidental loss during cleaning of spraying equipment (Bellamie and Gouy, 1992; Kreuger, 1996; Kreuger, 2000). Many investigations have documented the presence of a large number of pesticides in surface water, especially in the spraying season and for certain pesticides all the year round (Harris et al., 1994; Mogensen and Spliid, 1995; Kreuger, 1998; Mogensen and Kronvang, 1999).

The importance of wind drift for pesticide loss to a large stream and the possible ecological consequences were investigated in a controlled field experiment on Zealand in spring 2000 (Bønding, 2001). The experiment was conducted with the insecticide esfenvalerate that was sprayed in normal doses at three different distances to the stream edge (2 m, 10 m and 20 m). The wind direction was changing during the experiment, but mainly along the stream channel with a wind speed of up to 2 m/s. Each experimental reach and an upstream control reach were equipped with automatic water samplers and 12 caves with the macroinvertebrate ***B. rhodani*** were installed prior to the experiment. Esfenvalerate was not detected in the stream water at any of the experimental reaches, nor could any significant effects be seen on the macroinvertebrates.

An important source for pesticides to stream water could be point sources due to bad handling of pesticides in the filling and cleaning procedure. The importance of these sources is, however, difficult to measure and interpret (Kreuger, 1998). Kreuger (1998) investigated a culverted stream and measured high concentrations of many pesticides. The author failed, however, to trace the source of pesticides to farm yards using bromide as a conservative tracer. Point sources were believed to play an important role for the high pesticide concentrations measured in culvert water during dry periods, possibly due to spillage of pesticides during filling and cleaning of spraying equipment.

Kreuger (2000) has shown a large decrease in the loss of pesticides from a small Swedish catchment during the period 1990-1998. The reason for this was four-fold: 1) Improved handling of pesticides due to information to farmers, etc.; 2) Change from high-dose pesticides to low-dose pesticides; 3) A small reduction in the number of farmers applying pesticides which could reduce the number of point sources; 4) An increase in the use of glyphosate which was not included in the investigation. The above findings show that point sources could be uncertain in investigations of the dynamics and fate of pesticides in catchments.

The existing knowledge on pesticide occurrence and concentration in surface water is in most cases based on routine monitoring programmes (Aiken, 1999; Ludvigsen, 2000; Iversen et al., 2001). The presence and concentration of pesticides in streams during spates has until now only been investigated in a few number of studies (Liess et al., 1999, Kreuger, 1998, Spalding and Snow, 1989). Results from these investigations have revealed that high concentrations of pesticides are often detected during high-flow periods, especially during spates in the spraying season (Kreuger, 1996). In Denmark, very few studies have focused on the concentration and transport of pesticides in subsurface drainage water and streams. Vilholdt et al. (1999) and Kronvang et al. (2002) have shown that both soluble and more hydrophobic pesticides are transported through the upper soil column during rain events.

The importance of Koc (partition coefficient between pesticide adsorbed to soil organic carbon and water), sprayed area, and dosage for the occurrence of pesticides in Danish streams has been demonstrated by using partial order ranking (Dobel et al., 2000; Iversen et al., 2001). However, the amount of pesticides applied on fields in the catchments has not yet been compared with the resulting concentration and transport in subsurface drainage water and streams in Denmark.

Kreuger and Törnqvist (1998) compared applied amount of pesticides and pesticide physico-chemical properties with the mean pesticide concentration and pesticide transport in a stream draining the Vemmehög catchment. They developed statistically significant relationships revealing log Pow (octanol/water partition coefficient) and applied amount of pesticides to be the most important predictors. The loss ratio (applied/transport) of pesticides has been calculated in a large number of small and large-scale investigations (Kladivko et al., 1991; Frank et al., 1991; Gomme et al., 1991; Battaglin et al., 1993; Albanis et al., 1994, Traub-Eberhard et al., 1994; Harris et al., 1995; Kreuger, 1998).

This study focuses on measurement of concentration, transport and loss ratio (applied/transport) of a range of pesticides in two hydrologically contrasting arable catchments. In this report, we will present and discuss the results from simultaneous measurements of pesticide concentrations and transport in subsurface tile drainage water and stream water within two agricultural catchments with different soil types. Pesticide concentrations in suspended sediment and streambed sediments in the two streams are furthermore presented.

2 Description of the two investigated catchments

2.1 Lillebæk on Funen

The catchment area of Lillebæk stream is situated on south-east Funen. The stream flows through the catchment area from NW to SE and discharges into the open sea, the Great Belt (Fig. 2.1). Geomorphologically, Lillebæk stream is characterized by moraine clay from the second-last glaciation and, in the northern part, also the last glaciation.

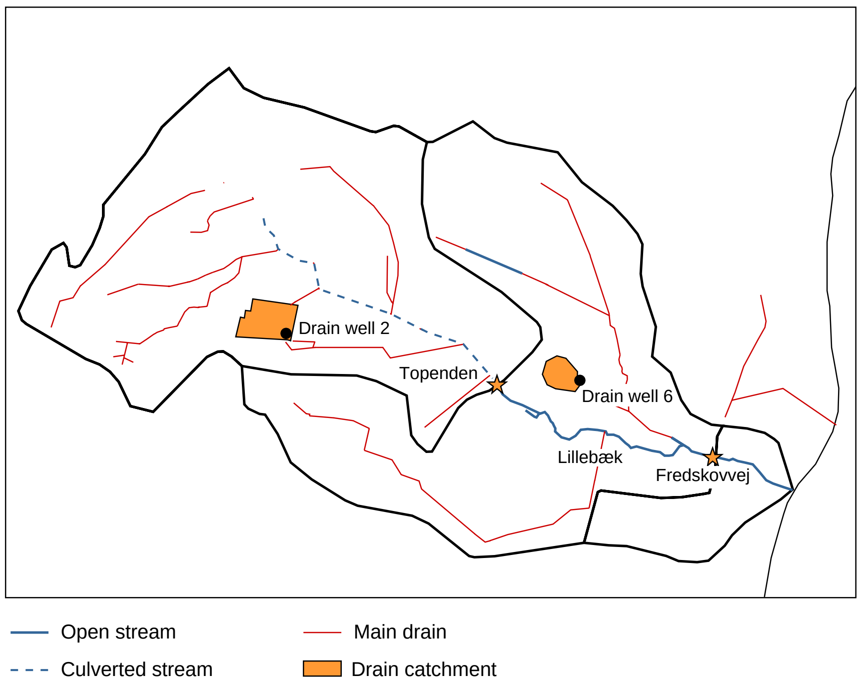


Figure 2.1. The catchment area of Lillebæk stream with indication of the two stream sampling stations (upstream station of Lillebæk=Topenden) and downstream station of Lillebæk=Fredskovvej) and the two tile drainage stations (drain 2 and 6).
Figur 2.1. Lillebæk-oplandet med indtegnelse af vandløbet og hoveddræn, samt de fire målestationer, Topenden og Fredskovvej i Lillebæk og de to drænstationer, dræn 2 og dræn 6.

The upstream sampling station (upstream station of Lillebæk=Topenden) drains through a culverted stream, whereas the 1.4 km long section further downstream to the second monitoring station (downstream station of Lillebæk=Fredskovvej) is an open stream channel. The catchment area of Lillebæk can be divided into three sub-catchments as shown in Figure 2.1. Both of the two upper sub-catchments include tile stations in drained fields. The upper sub-catchment covers an area with drains connected to a culverted channel. Runoff at the upstream sampling station (upstream station of Lillebæk) mainly derives from subsurface runoff from the upper sub-catchment.

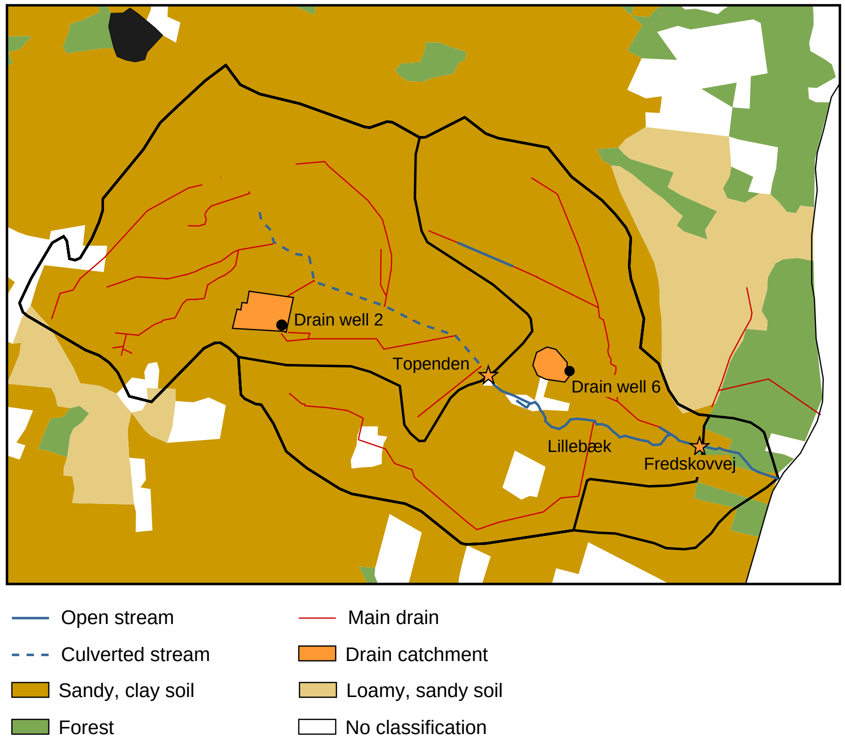


Figure 2.2. Soil characterization of the upper 20 cm soil in the catchment area of Lillebæk. Sandy, clay soil is the dominant soil type.
Figur 2.2. Jordbonitetsbeskrivelse for pløjelaget i Lillebæk-oplandet.

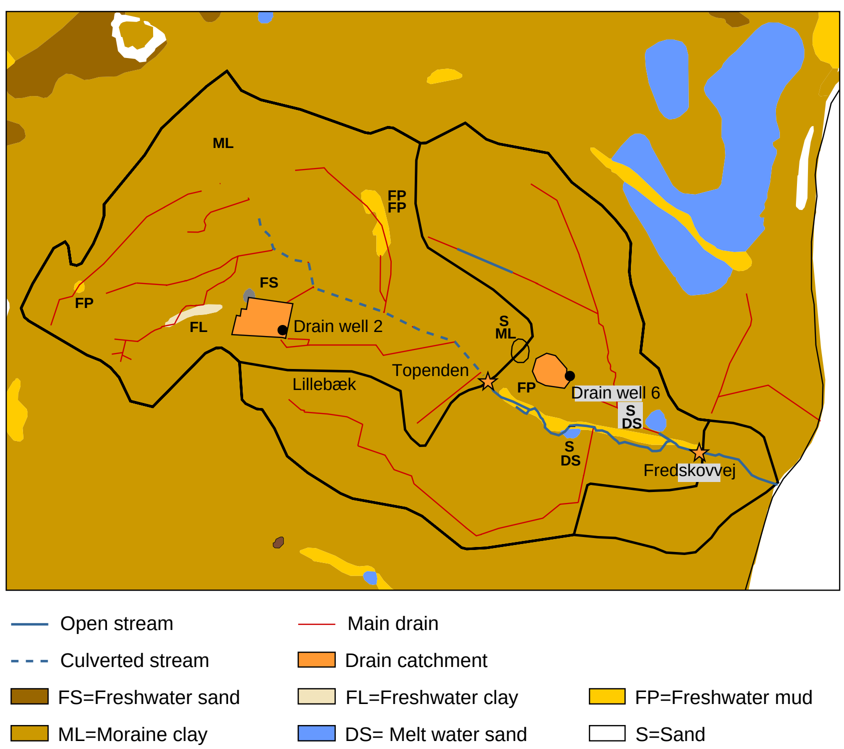


Figure 2.3. Surface geology up to one metre in depth of the catchment area of Lillebæk. Moraine clay is the dominant surface geology.
Figur 2.3. Beskrivelse af overfladegeologien til en meters dybde i Lillebæk-oplandet, hvor moræneler er den typiske jordart.

The catchment area of the downstream station of Lillebæk stream is 435 hectares with about 86 % being agricultural land. The upper sub-catchment is 229 hectares. The dominant soil of the upper 20 cm topsoil is sandy, clay soil (Fig. 2.2). Surface geology up to a depth of one metre is mainly moraine clay (Fig. 2.3).

Catchment fields of the two tile stations are shown in Figure 2.1. Drain 2 is situated in the upper sub-catchment of Lillebæk stream and drains to the culverted channel. Drain 6 is situated in the downstream sub-catchment of Lillebæk stream and drains to the open channel. Drain 2 drains a catchment area of 4.2 hectares and drain 6 drains a catchment area of 2.1 hectares.

2.2 Odderbæk stream in northern Jutland

The Odderbæk stream catchment is situated in northern Jutland. The stream flows through the catchment area from N to S and discharges into the Lerkenfeldt stream (Fig. 2.4).

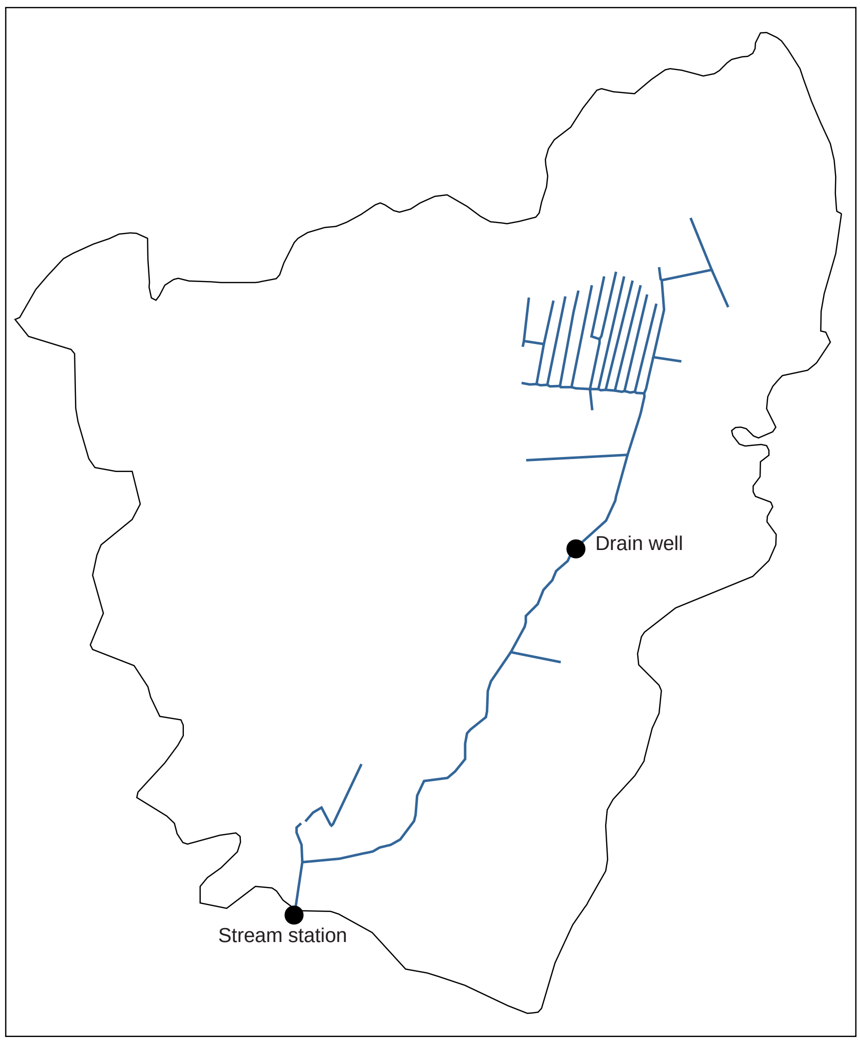


Figure 2.4: The catchment area of Odderbæk stream. The monitoring stations in the stream and the monitoring station at the outlet of the tile drainage to the stream are indicated on the map.
Figur 2.4. Odderbæk-oplandet med indtegnelse af vandløbet og de to målestationers beliggenhed.

Odderbæk stream is characterized by a melt water river terrace and peripheral moraine. It is a moraine landscape formed during the last glaciation. Odderbæk stream drains a catchment area of 1,143 hectares. A larger drained sub-catchment of 32 hectares is located within the Odderbæk stream catchment.

The catchment area of Odderbæk is 1,143 hectares with about 83% being agricultural land. The dominant soil type (upper 20 cm topsoil) is sandy soil (Fig. 2.5). Surface geology up to the depth of one metre is a mixture of sand and moraine clay (Fig. 2.6).

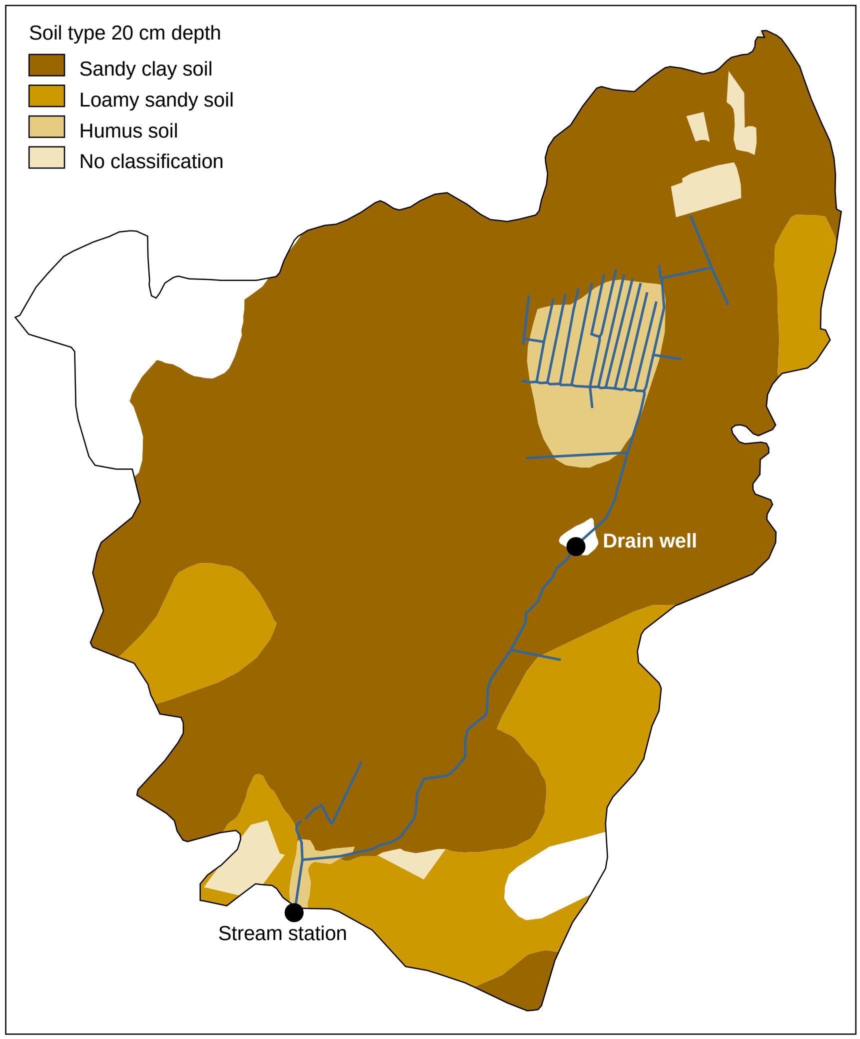


Figure 2.5. Soil characterization of the upper 20 cm soil in the catchment area of Odderbæk. Sandy soil is the dominant soil type.
Figur 2.5. Jordbonitetsbeskrivelse for pløjelaget i Odderbæk-oplandet.

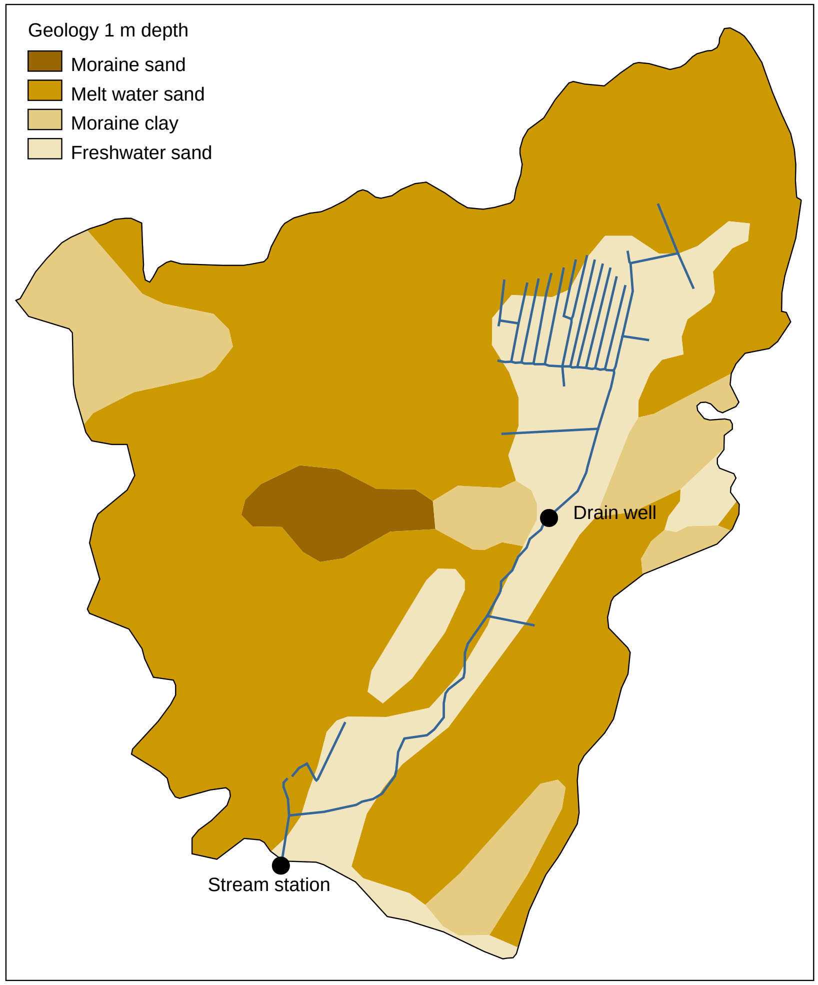


Figure 2.6. Surface geology up to one metre in depth of the catchment area of Odderbæk. Sandy deposits are the dominant surface geology.
Figur 2.6. Beskrivelse af overfladegeologien til en meters dybde i Odderbæk-oplandet, hvor sandede aflejringer er den typiske jordart.

3 Methods

3.1 Field sampling and measurements

The catchments, Lillebæk on Funen, Denmark (4.65 km^2), and Odderbæk in northern Jutland, Denmark (11.43 km^2) were selected as study areas. Both catchments are included in the Danish Nationwide Monitoring Programme under the Action Plan on the Aquatic Environment.

In the Lillebæk catchment, four pesticide monitoring stations were installed during the two study years 1999 and 2000. Two stream monitoring stations were installed, one covering the water and pesticide loss from two upper subcatchments (435 ha) and one covering the upstream culverted sub-catchment of 229 ha (see chapter 2). Moreover, two drain stations were installed covering catchment areas of 4.2 and 2.1 hectares, respectively.

In the Odderbæk catchment we have installed two pesticide monitoring stations consisting of one stream station covering the entire catchment (1143 ha) and one drain station covering a sub-catchment of 32 hectares.

At all monitoring stations water stage was recorded continuously and stored on a datalogger. Discharge was measured at regular intervals at each stream and drain station, which enabled the establishment of stage-discharge relationships for the stream stations, and V-notsch weir-formulas for the drain stations. Instantaneous discharge has thus been calculated for each station.

Each pesticide monitoring station had an automatic ISCO-sampler installed where each sampler was linked to a mechanical contact switch, which initiated water sampling at a predetermined rise in water level. Each pesticide monitoring station consisted of an automatic ISCO-sampler (2700 for drain stations and 3700 for stream stations) (see photo 3.1 and photo 3.2). The drain station samplers had 24 x 300-ml glass bottles and the stream stations had 12 x 900-ml glass bottles.

The monitoring stations were visited at least once a week and the contact switch was thenadjusted according to the water stage of that time. The predetermined rise in water level initiating the samplers was 5-10 cm at the three stream stations and 2-3 cm at the three drain stations. Normally, the contact switch was set at lowest rise in water level during low-flow periods and at the highest rise in water level during high-flow periods.

Photo 3.1. ISCO-sampler in sampling house at stream monitoring station in the Odderbæk catchment.
Foto 3.1. Isco-prøvetager i instrument-hus, Vandløbsmålestationen i Odderbæk oplandet.

Photo 3.2. Sampling wheel for drain station in the Odderbæk catchment with two stage recorders, V-notched weir and contact switch installed.
Foto 3.2. Målebrønd, drænstationen i Odderbæk-oplandet med 2 vandstandsmålere, V-overfald og flydekontakt installeret.

The stream and drain monitoring stations undertook a pre-programmed time-proportional sampling during each event covering 24 hours. Sampling was conducted every two hours at stream stations and every hour at drain stations. The sampling programme makes it possible to both analyse a composite water sample covering the entire storm event and to analyse water samples taken at predetermined times during the storm event. The sampling programme thus made it possible to both determine total pesticide losses during storm events (spates) and to investigate maximum concentrations and losses at a certain time or stage during a specific event. Based on an on-line permission to extract data by telephone from the stage-recorders at all stations, we decided how to pool water samples and in some cases to store water samples as single point samples for each storm event.

In order to cover the presence and transport of pesticides during periods without precipitation (both rain and snow), point samples were manually taken in 1000 ml glass bottles during different times of the year at all stream and drain stations. All water samples were transported to the laboratory in Silkeborg. On return to the laboratory the water samples were kept at 5° C, and conserved within 1-2 days. Glass bottles were cleaned according to the technical description given for NOVA 1998-2003 (Kronvang et al., 1999), which includes an ignition at 450°C. The pesticide analysis required one water sample of approx. 1000 ml. Conservation of the water samples kept for pesticide analysis was conducted at the laboratory by solid phase extraction (SPE) (Vejrup & Ljungqvist, 1998). The dissolved pesticide and part of the sediment or organically bound pesticides were retained this way, and kept frozen until laboratory analysis.

In order to determine the fate of pesticides in the streams we collected samples of the upper fine (< 250 µm) and newly accumulated streambed sediment by means of a kajak-corer. Sediment samples were collected from two sub-reaches of the Lillebæk stream and one sub-reach of the Odderbæk stream. Sediment samples were brought to the laboratory and kept frozen until analysis.

For storm event samples with high concentrations of suspended sediment, the suspended sediment was saved for pesticide analysis. A special sampling device called SubMarie designed for separating suspended sediment and colloids from stream and drain water was installed at the three stream stations (see photo 3.3). The suspended sediment sampler enabled us to extract suspended sediment and colloids during different periods of the year. We collected composite suspended sediment samples at almost monthly intervals during the year of 2000. All sediment samples (streambed sediment and suspended sediment) were brought to the laboratory and kept frozen until analysis.

Water samples were analysed for 49 different pesticides and metabolites. The streambed sediment samples and suspended sediment samples were analysed for 19 pesticides.

Photo 3.3 prototype of the suspended sediment sampler installed in Odderbæk in December 1999.
Foto 3.3.Prototypen af prøvetageren til suspenderet stof installeret i Odderbæk i December 1999.

3.2 Laboratory analysis

3.2.1 Analysis of pesticides in water samples

Analysis of pesticides is a multi-step process including

1) Pre-concentration by solid phase extraction (SPE)
2) Clean-up from the SPE column
3) Separation and analysis of analytes using LC/MS/MS,
4) Integration of chromatograms and calculation of concentrations.

Step 1 was carried out within 1-2 days after the water samples were collected. As part of the quality control one blank and two recovery samples were prepared with each batch of samples as described below. SPE cartridges were kept frozen until they were eluted. Sample preparation was carried out in the same way for all samples while the LC/MS analysis was carried out on either of two instruments. The analytical method utilised was adapted from existing LC/MS multimethods (Køppen & Spliid 1998, Vejrup & Lundquist 1998 and Bossi et al. 2002.).

Chemicals
Methanol, acetonitrile (LC grade), glacial acetic acid and ammonium acetate (analytical grade) were purchased from Merck (Darmstad, Germany). Propylene glycol and formic acid (analytical grade) were from Fluka (Buchs, Switzerland). For LC and standard dilution, deionized water was further purified with a Milli-Q water purification system (Millipore, Bedford, MA). The pesticides and pesticide degradation products were purchased from Dr. Ehrenstorfer (Augsburg, Germany) in ampoules as mixed stock standard solutions. Calibration standards were prepared by appropriate dilution of the

mix stock solutions with 10:90 methanol/water. These standards were kept at 4° C and used within two weeks. Isotope labelled 2,4-D (D_3) and Atrazine (D_5) from Cambridge Isotope Laboratories (Woburn, MA) were used as surrogate standards. A stock solution (100 μg /mL) was prepared in acetonitrile. A 50 ng/mL solution in 10:90 methanol/water was prepared from the stock solution and used for sample fortification.

Sample cleanup

All water samples were extracted by solid phase extraction (on SPE-cartridges) within 1-2 days after arrival at the laboratory using the procedure described below. The water samples (1 L) were spiked with isotope labelled 2.4-D (D_5) and Atrazine (ethylamin D_5) at 50 ng/L as internal standard. One blank sample and two recovery samples were added to each batch of samples. Spiking 1L tap water with isotope labelled 2.4-D (D5) and Atrazine (ethylamin D5) at 50 ng/l made up the blank sample. Spiking tap water with all standards at 50 ng/l L level made up the recovery samples. All the samples were adjusted to pH 4.5 with an acetic acid buffer and filtered through GF/C glass fibre filters (Whatman, Maidstone, UK). Five ml of methanol was used to wash the filters in order to prevent loss of pesticides. The filtrates were applied to Porapak RDX cartridges (500 mg Waters, preconditioned with acetonitril and methanol). The SPE cartridges were air-dried by continuous suction for 30 minutes and stored at -21° C until analysis. The SPE cartridges were eluted with 2 x 5 mL methanol-acetonitril (1:1, v/v) and 50 μl of propylene glycol was added. The eluents were evaporated under a stream of nitrogen at 40° C and redissolved in 1.00 ml of methanol-water (1:9, v/v).

LC/MS/MS analysis

The samples were analysed on one of two different LC/MS/MS systems.

LC/MS/MS System 1:

The LC/MS/MS system consisted of a TSQ 700 triple quadrupole mass spectrometer (Finnigan, San Jose, MA, USA) coupled to a Waters HPLC gradient pump model 600 MS and a Waters autosampler model 717 (Waters, Milford, MA, USA) via an API-interface (Atmospheric Pressure Ionization). The analytes were separated on a Hypersil BDS C18 column, 250 x 2.1 mm, 5 μm particle size (Hypersil, Cheshire, UK) at a constant temperature of 30° C. The sample injection volume was 50 μl. A binary mobile phase gradient was used for analyte separation at a flow rate of 200 μl/min. The gradient was programmed as follows: linear from 100% A to 50% A in 3 minutes; linear from 50% A to 100% B in 27 minutes; maintaining 100% B for 3 minutes; linear to 100% A in 3 minutes. Equilibration time prior to the next injection was 9 minutes.

The acidic pesticides were analysed with the ESI-inlet (Electro Spray Ionization) in negative mode (Spray voltage 5 kV and Capillary temperature 250°C) using an A-eluent of 10:90 methanol/20 mM acetic acid and an B-eluent of 20 mM acetic acid in methanol.

For the neutral and basic pesticides, the APCI-inlet (Atmospheric Pressure Chemical Ionization) was used in positive mode (Corona current 5 μA, Vaporizer temperature 500°C and Capillary temperature 170°C). The A-eluent was 1:99 methanol/10 mM Ammonium acetate and the B-eluent was 10 % Ammonium acetate in methanol. All analyses were done using time scheduled SIM-mode (Single Ion Monitoring) and all findings were verified by using LC/MS/MS and corrected for recovery.

LC/MS/MS System 2:

The LC/MS/MS system consisted of a bench-top triple quadrupole mass spectrometer, model API 2000 (PE Sciex, Concorde, Ontario, Canada), coupled to a Perkin Elmer Series 200 pump and a Perkin Elmer Series 200 autosampler (Perkin Elmer, Norwalk, CT). The analytes were separated on a Hypersil BDS C18 column, 250 x 2.1 mm, 5 µm particle size (Hypersil, Cheshire, UK) at a constant temperature of 30° C. The sample injection volume was 50 µl. A binary mobile phase gradient was used for analyte separation at a flow rate of 200 µl/min. The gradient was programmed as follows: linear from 100% A to 50% A in 3 minutes; linear from 50% A to 100% B in 27 minutes; maintaining 100% B for 3 minutes; linear to 100% A in 3 minutes. Equilibration time prior to the next injection was 14 minutes.

For separation of acid pesticides, mobile phase A was 10:90 methanol/water with 0.1% acetic acid added, and mobile phase B was 100% methanol with 0.1% acetic acid added. For separation of neutral pesticides, mobile phase A was 1:99 methanol/5 mM ammonium acetate with 0.1% formic acid added, and mobile phase B was 90:10 methanol/5 mM ammonium acetate with 0.1% formic acid added. The Sciex turbo ion spray (TISP) probe was employed in this study. The TISP probe corresponds to the commonly named electrospray interface. The TISP probe was maintained at 375° C with a spray voltage of -4500 V for negative ionization mode and +5500 V for positive ionization mode. All analysis was performed as LC/MS/MS analyses in time-scheduled SRM mode (Single Reaction Mode). All results were corrected for recovery.

Limits of quantification and uncertainty of measurements

For both LC/MS/MS-systems the limit of quantification was determined by analysing six samples of tap water spiked with all pesticides at the 20 ng/l level. The limit of quantification was determined as three times the standard deviation, see Table 3.1.

The uncertainty of measurements for both LC/MS/MS-systems was determined by making a budget of uncertainty for the method. Utilising that the recovery samples have been prepared on different days using different dilutions of standards and have been analysed on different days with different dilutions of standards and calibration curves, the budget becomes real simple. All variations and uncertainties, except the uncertainty of the sample volume and the uncertainty of the mixed stock solution in the ampoules, are included in the variation of the recovery samples.

As the sample volume in the method is determined to the nearest 50 ml, the maximum error is estimated at $\boldsymbol{u}_{\boldsymbol{sample}}$ = 2/3*50 ml/1000 ml = 3,3%. According to the certificate of the ampoules with the standards, the maximum error of the concentration is $\boldsymbol{u}_{\boldsymbol{ampoule}}$ = 0.5%. Assuming a squared distribution, the following formula gives the uncertainty of measurements (ref.):

$$u_{total} = \sqrt{u_{\text{recovery}}{}^{2} + \left(\frac{u_{\text{sample}}}{\sqrt{3}}\right)^{2} + \left(\frac{u_{\text{ampoul}}}{\sqrt{3}}\right)^{2}}$$

Table 3.1 provides an overview of the performance of the analytical method. For each batch of samples, calculation of the concentration of each compound took into account the actual recovery and blank values.

Table 3.1. Performance of the analytical method using two LC-MS systems. Limit of quantification is determined as three times the standard deviation of samples at the 20 ng/l level. Recovery and uncertainty are determined at the 100 ng/l level using data from the recovery samples obtained from quality control during the study.

Tabel 3.1. Ydeevne for den analytiske metode med brug af to LC-MS systemer. Kvantificeringsgrænsen er bestemt som tre gange standardafvigelsen af prøver på 20 ng/l niveau. Genfinding og usikkerhed er bestemt på 100 ng/l niveau ud fra genfindingsprøver, der er anvendt til kvalitetskontrol i forbindelse med dette projekt.

Compound	Limit of quantification, μg/l		Recovery (%)		Uncertainty of measurements (%)	
	1st System	2nd System	1st System	2nd System	1st System	2nd System
Atrazine	0,001	0,004	94 ± 7	109 ± 2	16	8
BAM (2,6-dichlorobenzamide)	0,010	0,006	84 ± 12	65 ± 3	25	9
Carbofuran	0,008	0,023	82 ± 11	73 ± 7	20	21
Chloridazon	0,003	0,004	112 ± 8	79 ± 2	17	6
Cyanazine	0,006	0,004	89 ± 19	88 ± 4	32	11
Desethylatrazine	0,007	0,007	105 ± 9	95 ± 3	19	9
Desethylterbuthylazin	0,002	0,006	112 ± 9	117 ± 2	21	7
Desisopropylatrazine	0,005	0,010	95 ± 7	82 ± 4	15	11
Dimethoate	0,011	0,004	123 ± 11	77 ± 3	23	9
Diuron	0,009	0,006	108 ± 6	121 ± 4	13	13
Ethofumesate	0,035	0,004	116 ± 7	131 ± 11	15	32
Fenpropimorph	0,058	0,023	109 ± 6	135 ± 6	6	18
Hexazinone	0,002	0,006	95 ± 18	112 ± 4	29	10
Hydroxy-atrazine	0,010	0,005	96 ± 10	36 ± 6	21	9
Hydroxy-carbofuran	0,007	0,029	54 ± 10	42 ± 3	16	7
Hydroxy-simazine	0,013	0,008	59 ± 16	58 ± 16	41	40
Hydroxy-terbuthylazine	0,006	0,004	105 ± 10	95 ± 4	21	12
Isoproturon	0,003	0,005	91 ± 6	118 ± 5	13	14
Linuron	0,009	0,002	101 ± 14	125 ± 3	28	9
Metamitron	0,010	0,004	76 ± 6	58 ± 3	12	9
Methabenzthiazuron	0,005	0,003	97 ± 2	120 ± 3	6	10
Metribuzin	0,007	0,011	113 ± 20	92 ± 3	40	9
Pendimethalin	0,026	0,006	38 ± 6	73 ± 10	12	31
Primicarb	0,004	0,004	96 ± 7	68 ± 3	15	9
Prochloraz	0,006	0,003	78 ± 7	124 ± 7	15	19
Propiconazol	0,007	0,003	116 ± 8	140 ± 7	17	21
Propyzamide	0,011	0,005	94 ± 7	126 ± 4	14	12
Simazine	0,003	0,008	45 ± 10	106 ± 2	21	7
Terbuthylazine	0,003	0,005	82 ± 8	96 ± 3	16	8
Triadimenol	0,004	0,005	107 ± 5	127 ± 8	9	23
2,4-D	0,002	0,005	96 ± 4	100 ± 2	29	11
2,4-dichlorophenol	0,021	0,014	76 ±16	113 ± 3	25	19
Benazolin	0,003	0,005	70 ± 12	40 ± 1	23	7
Bentazone	0,001	0,004	76 ± 11	45 ± 3	23	13
Bromoxynil	0,001	0,005	71 ± 10	97 ± 3	24	16
Chlorsulfuron	0,004	0,007	62 ± 11	30 ± 2	33	10
Dicamba	0,003	0,004	73 ± 18	34 ± 2	9	8
Dichlorprop	0,004	0,004	105 ± 4	115 ± 2	30	13
Dinoseb	0,004	0,008	96 ± 15	128 ± 3	19	18
DNOC	0,001	0,007	85 ± 9	84 ± 3	16	17
Flamprop	0,004	0,004	86 ± 7	87 ± 2	20	14
Fluazifop	0,009	0,009	91 ± 10	105 ± 2	19	13
Ioxynil	0,003	0,005	71 ± 9	108 ± 4	8	20
Lenacil	0,003	0,005	32 ± 4	31 ± 4	13	13
MCPA	0,003	0,005	84 ± 7	101 ± 2	18	11
Mecoprop	0,003	0,006	87 ± 9	111 ± 2	31	13
Metsulfuron-methyl	0,004	0,024	28 ± 12	30 ± 11	48	45
p-nitrophenol	0,003	0,007	30 ± 3	37 ± 4	10	10
Thifensulfuron-methyl	0,003	0,025	20 ± 6	19 ± 6	19	19
Triasulfuron	0,003	0,010	19 ± 6	20 ± 6	20	20

3.2.2 Analysis of pesticides in sediment

Sediment samples were thawed at room temperature and the water was decanted from the wet samples. Sediment dry weight was measured after drying for 16 hours at 105 °C using 10-25 g sediment. The organic matter content was measured as loss on ignition in a sub-sample after 4 hours at 550 °C. Fourteen grammes of the wet sediment sample (without decanted water) were mixed in a mortar with 7 g Hydromatrix (pelletized diatomaceous earth) as a drying agent.

Nine grammes of the mixture (corresponding to 6 g wet sediment sample) were extracted with acetone/dichlormethane, 1:1, (60 ml) in a Soxtec Avanti 2050 Auto system. Soxtec Avanti represents the new generation of automated Soxhlet extraction. Ethion was added before extraction as an internal standard. The extraction was carried out at 170° C for 2 hours in the boiling extraction solvent followed by extraction for 1 hour in the rinse position. The extract was evaporated and the volume adjusted to 2 ml with cyclohexane/dichlormetane, 1:1.

One ml of this extract was purified by Gel Permeation Chromatography (GPC) and the volume adjusted to 1 ml with cychlohexane/acetone 9:1. Half of this extract was purified with concentrated sulphuric acid for analysing DDE-p,p by GC-EC (hexabromobenzene was added as internal standard). The other half of the extract was analysed with GC-MS using both EI-ionisation and NCI-ionisation. The detection limits and mean recovery of the analysed pesticides are shown in Table 3.2. The results presented are not corrected for percentage recovery.

Table 3.2: Pesticides encompassed by the streambed sediment and suspended sediment analysis with detection limit and mean recoveries.
Tabel 3.2. Pesticider indeholdt i analyser af bund-sediment og suspenderet stof, med detektionsgranser og middel genfindingsprocent.

Pesticide	Pesticide class	Detection limit (ng/g DW)	Mean recovery ± STDV (%)
Alpha-cypermethrin	Insecticide	10	93 ± 17
Atrazine	Herbicide	10	103 ± 15
DDT-p,p	Insecticide	5	73 ± 17
DDE-p,p	Metabolite	5	90 ± 23
Dimethoate	Insecticide	20	109 ± 11
Diuron	Herbicide	10-20	114 ± 43
Ethofumesate	Herbicide	10-20	122 ± 2
Esfenvalerate	Insecticide	5-10	96 ± 19
Fenpropimorph	Fungicide	10	124 ± 56
Isoproturon	Herbicide	10	167 ± 82
Lambda-cyhalothrin	Insecticide	5	102 ± 17
Malathion	Insecticide	20-40	86 ± 18
Pendimethalin	Herbicide	10-20	84 ± 26
Pirimicarb	Insecticide	10	121 ± 16
Prochloraz	Fungicide	50-100	88 ± 1
Propiconazole	Fungicide	20-30	107 ± 8
Terbuthylazine	Herbicide	10	97 ± 18

3.3 Transport estimation and statistical analysis

Descriptive statistics as calculation of the median value was done for pesticides revealing positive (above detection limit or traces) analytical values, whereas zero values were not incorporated in the statistical calculations.

Transport of pesticides was only calculated for the period during which water sampling was conducted. The calculated pesticide transport is therefore a minimum estimate when annual losses or quarter losses from the catchments aret taken into consideration. The transport was calculated minute by minute by multiplying values of concentration and discharge. The length of the calculation periods was defined as one hour before and one hour after the actual measurements and it was assumed that the concentration was constant within these defined time intervals. Instantaneous discharges were calculated from the stage record and subsequently linearly interpolated to minute by minute values in the following way:

$$Q_j = \frac{Q_i(t_{i+1} - j) + Q_{i+1}(j - t_i)}{t_{i+1} - t}, \mathit{for}\, t_i < j < t_{i+1}$$

where Q_j is linear interpolated discharges for minutes between t_i and t_{i+1}. Calculations were made in the statistical software programme, SAS.

We fitted a generalized extreme-value (GEVD) distribution (Kite, 1978) to the pesticide samples by the maximum likelihood method. The GEVD distribution has 3 parameters (location, scale and shape) The distribution has been extensively used to fit maximum and minimum discharges in hydrological applications (e.g. Ovesen ***et al.***, 2000). In this report, the GEVD distribution is used to calculate the concentration with 95% confidence interval at different recurrence intervals for the different pesticides. The statistical method is described in Prescott and Walden (1983).

4 Crop types and pesticide application in the catchments

Farm practices in the Lillebæk and Odderbæk catchments are followed by annual interviews of farmers in the area. The interviews provide detailed information about each field within the catchment area, including information about field size, crop grown and treatments in the field, such as use of manure, fertilizer and pesticides, with a specification of time and quantity.

4.1 Lillebæk catchment

There were 29 farmers with fields within the catchment area in the agricultural year 1998/1999 and 27 in 1999/2000. The ten most cultured crops in the working years 1998/1999 and 1999/2000 are shown in Table 4.1. These ten crops constitute about 90 – 95 % of the agricultural area grown in the catchment area. Winter crops, such as rape and cereals make up 45 – 48 % of the agricultural area grown. Compared to the rest of Denmark, the Lillebæk catchment area has a relatively high share of area grown with Christmas trees, fruit trees and berries.

Table 4.1. Dominant crops, extent of crop area grown (hectares) and average use of pesticides per hectare crop (kg organic active substance per hectare) within the catchment area of Lillebæk for the working years 1998/99 and 1999/00.
Tabel 4.1. De 10 mest anvendte afgrøder i Lillebæk-oplandet med deres arealudbredelse (hektar) og gennemsnitlige pesticidforbrug pr. hektar afgrøde (kg organisk aktivt stof) i driftsårene 1998/99 og 1999/00.

Crop	Area (ha)		Pesticide use (kg active substance/ha)	
	1998/1999	1999/2000	1998/1999	1999/2000
Winter wheat	99.2	112.5	0.469	0.808
Spring barley	92.5	67.5	0.497	0.296
Winter barley	25.3	51.6	0.733	0.965
Winter rape	50.5	32.8	0.151	0.101
Grass seeds	48.1	41.5	1.238	1.367
Fruit and berry	20.3	29.1	5.864	5.374
Christmas trees	14.1	14.0	0.913	1.715
Sugar beets	8.9	12.4	2.760	2.025
Maize	7.1	3.2	0.925	0.888
Oats	6.4	4.9	0.089	0.153
Total	372.4	369.5	0.918	1.163

Table 4.1 shows the use of pesticides for the ten most cultivated crops. These data show the average quantity of active substances used for each crop within a working year. The data only include the use of active organic substances and not inorganic substances, such as sulphur, copper and boron. The data show pronounced differences in the amount of pesticide use between crops with rather high pesticide use for sugar beets, fruits and berries. Generally, each crop also shows variation in the amount of pesticide used between years. The large increase in the use of pesticides to winter wheat between 1998/1999 and 1999/2000 is possibly due to the wet winter of 1998/1999 causing increased application of fungicides to winter crops. The reduction in the use of pesticides to spring barley from 1998/1999 to 1999/2000 is undoubtedly caused by the spring of the latter year being much dryer than the previous year.

The consumption of pesticides used within the catchment of Lillebæk is calculated on a quarterly basis from July 1998 to December 2000 (Table 4.2 and Appendix 4.1).

Table 4.2. Quarterly report from July 1998 to December 2000 on pesticide use (kg organic active substance) subdivided into herbicide, insecticide, fungicide, plant growth regulator and total within the catchment area of Lillebæk.
Tabel 4.2. Kvartalsvis opgørelse af pesticidforbruget (kg organisk aktivt stof) fra juli 1998 til december 2000 i Lillebæk-oplandet fordelt på bekæmpelsesemnerne: ukrudtsmiddel, insektmiddel, svampemiddel, vækstreguleringsmiddel og totalt forbrug.

Period	Pesticide use (kg active substance)				
	Herbicide	Insecticide	Fungicide	Plant growth regulator	Total
1998					
Jul. – Sep.	21.598	1.221	16.195	0.000	39.014
Oct. – Dec.	23.000	0.000	0.000	0.000	23.000
1999					
Jan. – Mar.	4.032	0.000	0.000	0.000	4.032
Apr.- Jun.	87.233	6.461	123.176	35.688	252.558
Jul. – Sep.	25.846	2.735	23.983	0.000	52.564
Oct. – Dec.	98.557	0.000	0.000	0.000	98.557
2000					
Jan. – Mar.	37.669	0.000	7.700	0.000	45.369
Apr.- Jun.	76.600	4.662	143.526	41.892	266.680
Jul. – Sep.	37.273	1.442	32.750	0.000	71.471
Oct. – Dec.	64.266	0.000	0.000	0.000	64.266

More than half of the total annual amount of pesticides used is sprayed onto the fields during the period April - June. Futhermore, Table 4.2 shows the quantity of pesticides used as herbicide, insecticide, fungicide and plant growth regulator. Herbicides and fungicides are used in high amounts compared the use of plant growth regulators and insecticides. Although herbicides are used throughout the year, most are used in spring and autumn. Fungicides are mainly used from April to June. The use of fungicides is somewhat lower between July and September and little or no fungicide is used in the period October – March. Insecticides are used from April to September whereas plant growth regulators are used only between April and June.

Table 4.3 and Appendix 4.2 show the quantity of pesticides used within the upper sub-catchment of Lillebæk on a quarterly basis from July 1998 to December 2000.

Table 4.3. Quarterly report from July 1998 to December 2000 describing pesticide use (kg active substance) subdivided into herbicide, insecticide, fungicide, plant growth regulator and total within the subcatchment area, Topenden.
Tabel 4.3. Kvartalsvis opgørelse af pesticidforbruget (kg organisk aktivt stof) fra juli 1998 til december 2000 i det øvre delopland, Topenden, fordelt på bekæmpelsesemnerne: ukrudtsmiddel, insektmiddel, svampemiddel, vækstreguleringsmiddel og totalt forbrug.

Period	Pesticide use (kg active substance)				
	Herbicide	Insecticide	Fungicide	Plant growth regulator	Total
1998					
Jul. – Sep.	12.428	0.418	4.803	0.000	17.649
Oct. – Dec.	17.214	0.000	0.000	0.000	17.214
1999					
Jan. – Mar.	0.000	0.000	0.000	0.000	0.000
Apr.- Jun.	36.162	2.001	39.572	22.028	99.763
Jul. – Sep.	12.687	2.416	15.184	0.000	30.287
Oct. – Dec.	58.407	0.000	0.000	0.000	58.407
2000					
Jan. – Mar.	0.112	0.000	0.000	0.000	0.112
Apr.- Jun.	49.789	1.317	52.874	12.083	116.063
July – Sep.	0.000	0.928	10.584	0.000	11.512
Oct. – Dec.	41.768	0.000	0.000	0.000	41.768

The upper-sub catchment resembles the whole catchment area in the pattern of pesticide use. More than half of the total annual amount of pesticides used is sprayed onto fields in the period April - June. Herbicides and fungicides are used in high amounts compared to plant growth regulators and insecticides. Finally, the seasonal spray pattern in the upper sub- catchment area is similar to the whole catchment area of Lillebæk.

Table 4.4 and Table 4.5 shows the consumption of pesticides within drain catchment area 2 and 6, respectively. The total use of pesticides in the two drain catchments is somewhat low due to the small size of the drain catchment areas. Each drain catchment area covers partly two to three fields. Therefore, the spraying of pesticides occurs during a more restricted period (one to two quarters of the year) than in the catchment area of Lillebæk. Herbicides, insecticides and fungicides are used on both drain catchments in the period July 1998 to December 2000, whereas plant growth regulators are not used.

Table 4.4. Quarterly report from July 1998 to December 2000 describing pesticide use (grammes active substance) subdivided into herbicide, insecticide, fungicide, plant growth regulator and total within the drain catchment area no. 2.
Tabel 4.4. Kvartalsvis opgørelse af pesticidforbruget (kg organisk aktivt stof) fra juli 1998 til december 2000, i drænoplandet nr. 2, fordelt på bekæmpelsesemnerne: ukrudtsmiddel, insektmiddel, svampemiddel, vækstreguleringsmiddel og totalt forbrug.

Period	Pesticide use (gram active substance)				
	Herbicide	Insecticide	Fungicide	Plant growth regulator	Total
1998					
Jul. – Sep.	1.739	12	21	0	1.772
Oct. – Dec.	0	0	0	0	0
1999					
Jan. – Mar.	0	0	0	0	0
Apr.- Jun.	1.529	0	1.023	0	2.552
Jul. – Sep.	0	2	0	0	2
Oct. – Dec.	67	0	0	0	67
2000					
Jan. – Mar.	0	0	0	0	0
Apr.- Jun.	0	30	194	0	224
July – Sep.	0	0	0	0	0
Oct. – Dec.	0	0	0	0	0

Table 4.5. Quarterly report from July 1998 to December 2000 describing pesticide use (grammes active substance) subdivided into herbicide, insecticide, fungicide, plant growth regulator and total within the drain catchment area no. 6.
Tabel 4.5. Kvartalsvis opgørelse af pesticidforbruget (kg organisk aktivt stof) fra juli 1998 til 2000 i drænoplandet nr. 6, fordelt på bekæmpelsesemnerne: ukrudtsmiddel, insektmiddel, svampemiddel, vækstreguleringsmiddel og totalt forbrug.

Period	Pesticide use (gram active substance)				
	Herbicide	Insecticide	Fungicide	Plant growth regulator	Total
1998					
Jul. – Sep.	24	0	0	0	24
Oct. – Dec.	0	0	0	0	0
1999					
Jan. – Mar.	0	0	0	0	0
Apr.- Jun.	1.130	8	216	0	1.346
Jul. – Sep.	0	0	0	0	0
Oct. – Dec.	0	0	0	0	0
2000					
Jan. – Mar.	0	0	0	0	0
Apr.- Jun.	941	4	0	0	941
July – Sep.	0	0	0	0	0
Oct. – Dec.	0	0	0	0	0

4.2 Odderbæk catchment

There were 26 farmers with fields within the catchment area in both agricultural years (1998/1999 and 1999/2000). The ten most cultured crops in the working years 1998/1999 and 1999/2000 are shown in Table 4.6. These ten crops constitute about 90 – 93 % of the agricultural area grown in the catchment area. Winter crops, such as rape and cereals make up 28 – 27 % of the agricultural area grown. Compared to the rest of Denmark, the Odderbæk catchment area has a relatively large area grown with peas.

Table 4.6. Dominant crops, extent of crop area grown (hectares) and average use of pesticides per hectare crop (kg organic active substance per hectare) within the catchment area of Odderbæk for the working years 1998/99 and 1999/00.
Tabel 4.6. De 10 mest anvendte afgrøder i Odderbæk-oplandet med deres arealudbredelse (hektar) og gennemsnitlige pesticidforbrug pr. hektar afgrøde (kg organisk aktivt stof) i driftsårene 1998/99 og 1999/00.

Crop	Area (ha)		Pesticide use (kg active substance/ha)	
	1998/1999	1999/2000	1998/1999	1999/2000
Spring barley	370.6	389.3	1.686	0.435
Winter wheat	196.9	164.7	1.268	1.401
Peas	89.6	92.6	0.917	1.307
Maize	54.8	94.8	1.043	0.996
Sugar beets	46.2	31.2	1.678	2.644
Winter triticale	27.0	44.4	1.468	1.980
Winter rye	25.7	14.4	1.011	0.595
Oats	18.5	39.8	1.051	0.666
Spring rape	13.9	2.0	0.008	0.010
Grass	9.5	9.4	0.182	0.390
Total	852.7	882.6	1.477	0.934

Table 4.6 shows the consumption of pesticides for the ten most cultivated crops. These data show the average quantity of active substances used for each crop within a working year. The data include only the use of active organic substances and not inorganic substances, such as sulphur, copper and boron. There are only moderate differences in the consumption of pesticides between crops with the highest pesticide use for spring barley and maize. Generally, each crop also shows variation in the pesticideconsumption between years.

Table 4.7. Quarterly report July 1998 - October 2000 desribing pesticide use (kg organic active substance) subdivided into herbicide, insecticide, fungicide, plant growth regulator and total within the catchment area of Odderbæk.
Tabel 4.7. Kvartalsvis opgørelse af pesticidforbruget (kg organisk aktivt stof) fra juli 1998 til oktober 2000, i Odderbæk-oplandet fordelt på bekæmpelsesemnerne: ukrudtsmiddel, insektmiddel, svampemiddel, vækstreguleringsmiddel og totalt forbrug.

Period	Pesticide use (kg active substance)				
	Herbicide	Insecticide	Fungicide	Plant growth regulator	Total
1998					
Jul. – Sep.	72.289	2.390	9.087	0.000	83.766
Oct. – Dec.	198.195	0.000	0.000	0.000	198.195
1999					
Jan. – Mar.	0.000	0.000	0.000	0.000	0.000
Apr.- Jun.	835.446	3.870	64.284	22.022	925.624
Jul. – Sep.	7.756	0.478	4.950	0.000	13.184
Oct. – Dec.	247.891	0.000	0.000	0.000	247.891
2000					
Jan. – Mar.	0.000	0.000	0.000	0.000	0.000
Apr.- Jun.	413.409	11.874	124.037	29.035	578.353
Jul. – Sep.	71.082	0.103	83.900	0.000	155.085
1.-16.Oct.	218.924	0.000	0.000	0.000	218.924

Pesticide consumption within the catchment of Odderbæk is made up on a quarterly basis from July 1998 to mid-October 2000 (Table 4.7). More than half of the total annual consumption of pesticides is sprayed onto the fields during the period April - June. Futhermore, Table 4.7 shows the quantity of pesticides used as herbicide, insecticide, fungicide and plant growth regulator. Herbicides and fungicides are used in high amounts compared to plant growth regulators and insecticides.

Herbicides are mostly used in spring and autumn. The highest consumption of fungicides is from April to June. There are considerable year-to-year variations in the use of fungicides between July and September. Fungicides are not used in the period October – March. Insecticides are used from April to September whereas plant growth regulators are only used from April to June.

5 Catchment hydrology

5.1 Lillebæk catchment

The instantaneous discharge at the upstream station and the downstream station is shown in Figure 5.1. Stream flow appears rather flashy during the two study years in Lillebæk, indicating quick hydrological response in the catchment. This seems especially to be the case at the downstream station. In summer, discharge gets very low at both stations.

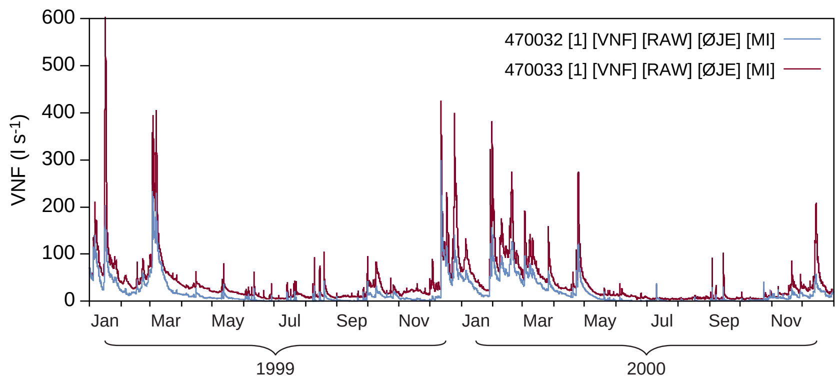


Figure 5.1. Instantaneous discharge at the two stream stations in the Lillebæk catchment during the period 1 January 1999 - 31 December 2000.
Figur 5.1 Øjebliksvandføring ved de to vandløbs-stationer i Lillebæk-oplandet i perioden 1. januar 1999 til 31. december 2000.

Table 5.1 shows the annual mean daily discharge and runoff from the two stream stations and two tile drain stations for the two study years and as average for the period 1989-1998. Mean daily discharge was considerably higher during the first study year (1999) than the second study year (2000). The discharge in 2000 reassembles average conditions in the previous ten years (1989-1998). The difference in mean daily runoff between the two study years was rather high at both stream stations, which means that the influence of groundwater in the Lillebæk catchment is generally weak. There is a remarkable difference in hydrological response between the tile drains, drain no. 2 having higher runoff and lower year–to-year variability than drain no. 6.

Table 5.1 Annual mean discharge and runoff at the two stream stations and two tile drain stations in the Lillebæk catchment.
Tabel 5.1. Årlig middel vandføring og afstrømning ved de to vandløbs-stationer og de to dræn-stationer i Lillebæk-oplandet

	Mean discharge			Mean runoff		
	1999	2000	89-98	1999	2000	89-98
Upstream station	30 l/s	18 l/s	15 l/s	408 mm	244 mm	207 mm
Downstream station	59 l/s	35 l/s	31 l/s	430 mm	252 mm	223 mm
Tile drain 2	0.41 l/s	0.33 l/s	0.28 l/s	312 mm	249 mm	208 mm
Tile drain 6	0.12 l/s	0.05 l/s	0.07 l/s	181 mm	82 mm	110 mm

Table 5.2 shows low-flow characteristics at the two stream stations and two tile drain stations for the two study years and as average for the period 1989-1998. Q95 is the 95 percentile of daily discharges stated in litres per second

and gives the size of the discharge in the low-flow situation recurring in the summer. $Q95_i$ in the right column of Table 5.2 is defined as the 95 percentile normalised by median discharge, and is a measure of the variability of the flow and also gives the proportion of steady and slowly responding water. It appears that the stream at the upstream station runs nearly dry every year and obviously there must be a source of steady contributing water from the lower sub-catchment to the downstream station. Given that the content of pesticides changes with runoff components, presumably the higher proportion of steady flow at the downstream station could be traced in the summer concentrations at this location.

Table 5.2. The 95 Percentile of daily discharges (Q95) and the 95 percentile standardised by the median disharge ($Q95_i$) at the two stream stations and two tile drain stations in the Lillebæk catchment. Q95 is defined as the number that is exceeded by 95 % of the observations.
Tabel 5.2. 95 percentilen af daglig vandføring (Q95) og 95 percentilen normeret med median vandføringen ($Q95_i$) ved de to vandløbs-stationer i Lillebæk-oplandet. Q95 er defineret som den værdi der overskrides af 95 % af observationerne.

	Q95			Q95i		
	1999	2000	89-98	1999	2000	89-98
Upstream station	0.2 l/s	0.1 l/s	0.2 l/s	0.02	0.01	0.06
Downstream station	7.6 l/s	4.6 l/s	2.9 l/s	0.23	0.28	0.24
Tile drain 2	0 l/s	0 l/s	0 l/s	0	0	0
Tile drain 6	0 l/s	0 l/s	0 l/s	0	0	0

The frequency of spates higher than three times the quarterly median of daily discharge at the downstream station is shown in Figure 5.2. The greatest difference in peak flow between the two study years is that more spates were measured during the spring and summer period of 1999 than during the same period in 2000. This can be of importance for the detection of pesticides in drainage and surface water.

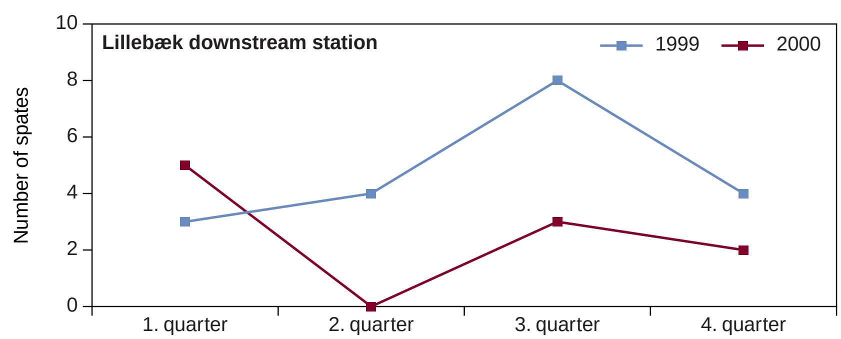


Figure 5.2. Frequency of spates higher than three times the quarterly median daily discharge during the two study years 1999 and 2000 at the downstream station (Fredskovvej) in the Lillebæk catchment. Quarterly median daily discharges are calculated for the period 1989-1998.
Figur 5.2 Frekvensen af flomme større end 3 gange kvartals medianen af daglige vandføringer i undersøgelses årene 1999 og 2000 ved den nedstrøms station (Fredskovvej) i Lillebæk oplandet. Kvartals medianen af daglige vandføringer er beregnet for perioden 1989 til 1998.

5.2 Odderbæk catchment

The instantaneous discharge at the stream station in the Odderbæk is shown in Figure 5.3. Stream flow appears rather flashy during the two study years in Odderbæk, indicating quick hydrological response in the catchment. In summer there is still a substantial amount of water running in the stream.

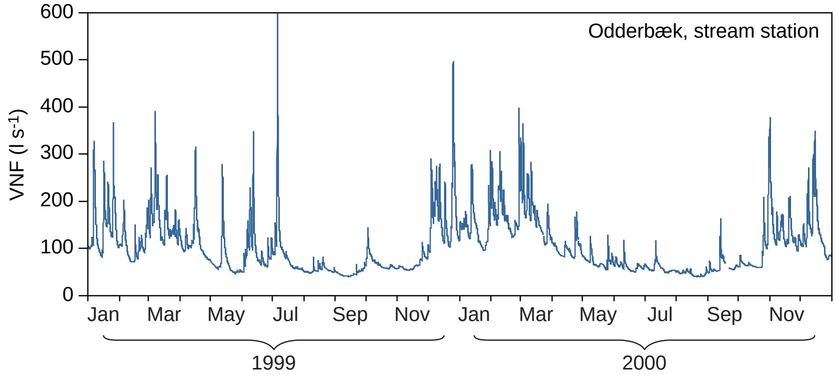


Figure 5.3 Instantaneous discharge at the stream station in the Odderbæk catchment during the period 1 January 1999 - 31 December 2000.
Figur 5.3 Øjebliks vandføring ved vandløbs-stationen i Odderbæk-oplandet i perioden 1. januar 1999 til 31. december 2000.

The annual mean daily discharge and runoff from the stream station and tile drain station is shown for the two study years and as average for the period 1989-1998 in Table 5.3. Mean daily discharge was similar during the two study years, but more wet than average conditions in the previous ten years (1989-1998). Mean runoff at the drainstation is higher than gross precipitation, presumably because the drain receives groundwater from neighbouring catchments.

Table 5.3 Annual mean discharge and runoff at the two stream stations and two tile drain stations in the Lillebæk catchment.
Tabel 5.3 Årlig middel vandføring og afstrømning ved de vandløbs-stationen og dræn-stationen i Odderbæk-oplandet.

	Mean discharge			Mean runoff		
	1999	2000	89-98	1999	2000	89-98
Stream station	100 l/s	105 l/s	73 l/s	277 mm	289 mm	201 mm
Drain station	11 l/s	11 l/s	10 l/s	1116 mm	1090 mm	953 mm

Table 5.4 shows low-flow characteristics at the stream station and tile drain station for the two study years and as average for the period 1989-1998. Q95 is the 95 percentile of daily discharges stated in litres per second and gives the size of the discharge in the low-flow situation recurring in summer. $Q95_i$ in the right column of Table 5.4, is defined as the 95 percentile normalised by median discharge, and is a measure of the variability of the flow and also gives the proportion of steady and slowly responding water. The rather high values of $Q95_i$ suggest that there is a permanent groundwater reservoir contributing to the discharge in the Odderbæk catchment. The content of pesticides in water draining this reservoir can be revealed by looking at summer concentrations.

Table 5.4. The 95 Percentile of daily discharges (Q95) and the 95 percentile standardised by the median discharge ($Q95_i$) at the two stream stations and two tile drain stations in the Odderbæk catchment. Q95 is defined as the number that is exceeded by 95 % of the observations(ref?).
Tabel 5.4. 95 percentilen af daglig vandføring (Q95) og 95 percentilen normeret med median vandføringen ($Q95_i$) ved vandløbs-stationen i Odderbæk-oplandet. Q95 er defineret som den værdi der overskrides af 95 % af observationerne.

	Q95			*$Q95_i$*		
	1999	2000	89-98	1999	2000	89-98
Stream station	48 l/s	49 l/s	26 l/s	0.58	0.57	0.47
Drain station	7.5 l/s	6.8 l/s	4.7 l/s	0.74	0.68	0.55

The frequency of spates higher than three times the quarterly median of daily discharge at the downstream station is shown in Figure 5.4. The greatest difference in peak-flow between the two study years is that five major spates appeared during the spring and summer period of 1999 compared to none in the same period in 2000. This could be important for the detection of pesticides in drainage and surface water.

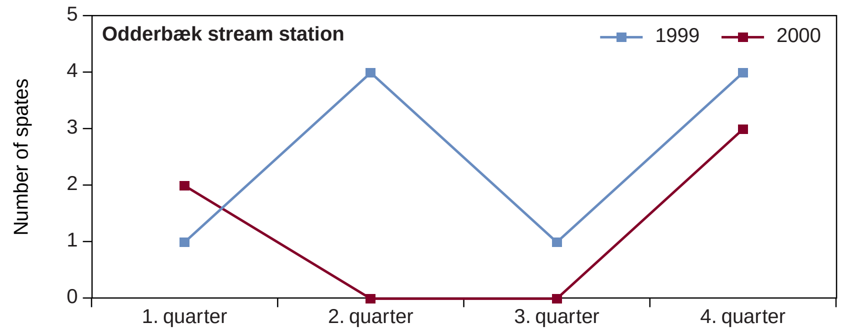


Figure 5.4 Frequency of spates higher than three times the quarterly median daily discharge during the two study years 1999 and 2000 at the stream station in the Odderbæk catchment. Quarterly median daily discharge is calculated for the period 1989-1998.

Figur 5.4. Frekvensen af flomme større end 3 gange kvartals medianen af daglige vandføringer i undersøgelses årene 1999 og 2000 ved Vandløbs-stationen i Odderbæk oplandet. Kvartals medianen af daglige vandføringer er beregnet for perioden 1989 til 1998.

6 Pesticide occurrence and concentration in stream and drains in the Lillebæk catchment

6.1 Water and sediment samples collected from the monitoring stations in the Lillebæk catchment

Table 6.1 shows the number of water samples analysed for pesticides in the Lillebæk catchment. Water samples were collected from the four monitoring stations during both sampling years on sampling dates shown in Figure 6.1.

Table 6.1 Number of water samples (number of days) with water sampling shown on a quarterly basis during the two study years from the four monitoring stations in the Lillebæk catchment.
Tabel 6.1 Antallet af vandprøver og antal måledage i parentes vist kvartalsvis gennem de to måleår 1999 og 2000 for de fire målestationer i Lillebæk.

	1 Q	2 Q	3 Q	4 Q	1 Q	2 Q	3 Q	4Q
	1999				2000			
Upstream station (Topenden) (470032)	1 (1)	20 (7)	13 (7)	17 (10)	10 (5)	43 (39)	14 (8)	8 (6)
Downstream station (Fredskovvej) (470033)	1 (1)	10 (3)	5 (4)	11 (3)	11 (6)	37 (36)	17 (9)	5 (5)
Drain 2 (470041)	1 (1)	0 (0)	3 (3)	6 (3)	10 (8)	8 (7)	0 (0)	0 (0)
Drain 6 (470045)	1 (1)	0 (0)	2 (2)	9 (5)	7 (5)	5 (3)	0 (0)	1 (1)

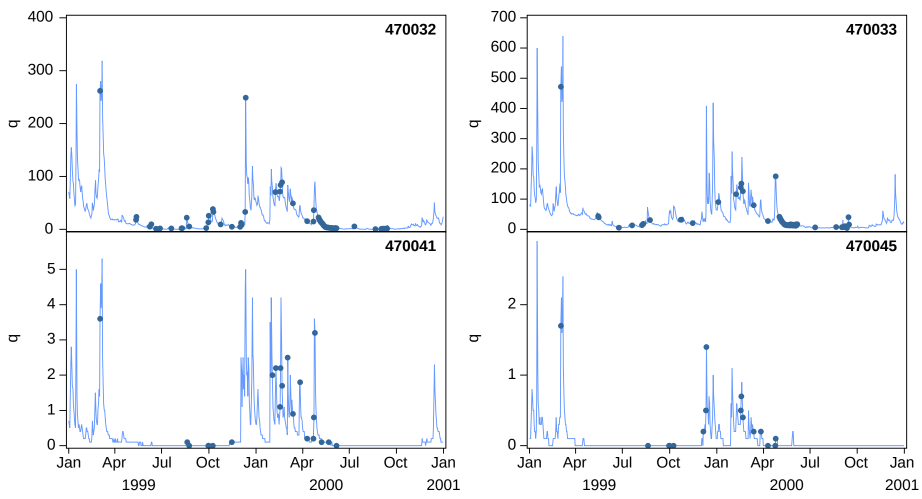


Figure 6.1. Days with water samples collected from the four monitoring stations shown together with the daily mean discharge during 1999 and 2000. On sampling days with storm events (spates), several sub-samples were analysed from the many water samples collected with the automatic sampling equipment.
Figur 6.1. Tidsplot af døgnmiddel vandføring ved de to målestationer i Lillebæk sammen med en angivelse af de dage hvor vandprøver er blevet udtaget. På måledage med stigende vandføring (flom) er der blevet udtaget vandprøver hver time med det automatiske prøvetagningsudstyr.

A total of 24 and 23 storm events, respectively, were sampled at the upstream and downstream monitoring stations in the Lillebæk catchment in 1999 and 2000, whereas 29 and 30 water samples, respectively, were collected during periods with steady or decreasing discharge conditions.

Suspended sediment was collected with an ***in situ*** sediment sampler (SubMarie) from both stream stations during the second study year. A total of eight samples were collected from the upstream station (Topenden) and eight samples from the downstream station (Fredskovvej). Three streambed sediment samples were collected from both stream stations during surveys in the first study year (March, May and June 1999) and another three sediment samples were collected from the downstream and upstream station during surveys in the second study year (May and June 2000).

6.2 Detection of pesticides in stream and sub-surface tile drainage water

Forty-nine different pesticides and metabolites were analysed in the water samples collected from stream and subsurface tile drainage water. The total number of different pesticides detected was 42 and 40, respectively, at the upstream and downstream sampling station in the Lillebæk during the 2- year study period. Much fewer pesticides were detected in the two tile drains: 17 pesticides in drain 2 and 16 pesticides in drain 6. The number of pesticides detected varied between the different seasons of the study years. Generally, more pesticides were detected during the main spraying season in the second quarter of 1999 and 2000 (Table 6.2). More pesticides were detected in stream water than in subsurface tile drainage water during the different seasons of 1999 and 2000 (Table 6.2).

Table 6.2. Number of pesticides (active substances and metabolites) detected in water samples collected on a quarterly basis during the two study years from the four monitoring stations in the Lillebæk catchment.
Tabel 6.2. Antal pesticider (aktiv stoffer og metaboliter) fundet i de indsamlede vandprøver fra de 4 målestationer i Lillebæk oplandet vist kvartalsvis for de to måleår 1999 og 2000.

	1 Q	2 Q	3 Q	4 Q	1 Q	2 Q	3 Q	4 Q
	1999				2000			
Upstream station (Topenden) (470032)	1	38	24	38	20	30	24	22
Downstream station (Fredskovvej) (470033)	0	26	20	25	26	31	24	16
Drain 2 (470041)	0	ns	8	10	7	8	ns	ns
Drain 6 (470045)	2	ns	11	12	11	10	ns	3

ns = no water samples taken

Figure 6.2 shows descriptive statistics for the number of pesticides detected per water sample in each quarter of the study period for the four sampling stations in Lillebæk. The median and average number of pesticides detected in stream water is 2-5 times higher than in tile drainage water. A seasonal trend in the number of pesticides detected per water samples was found for the two stream stations during the first study year, the number of pesticides per water samples being highest in the 2nd quarter of 1999 (Figure 6.2). A similar but less marked trend was also found for the upstream station in 2000. There was a large variation in the average number of pesticides detected in the water samples during the quarters of the first study year (1999). Less variation in the number of pesticides detected per water sample was found during the second study year (Fig. 6.2). The variation was presumably caused by a combination of sampling strategy, changes in hydrology between the two study years and changes in pesticide application factors that will all be discussed later in the report.

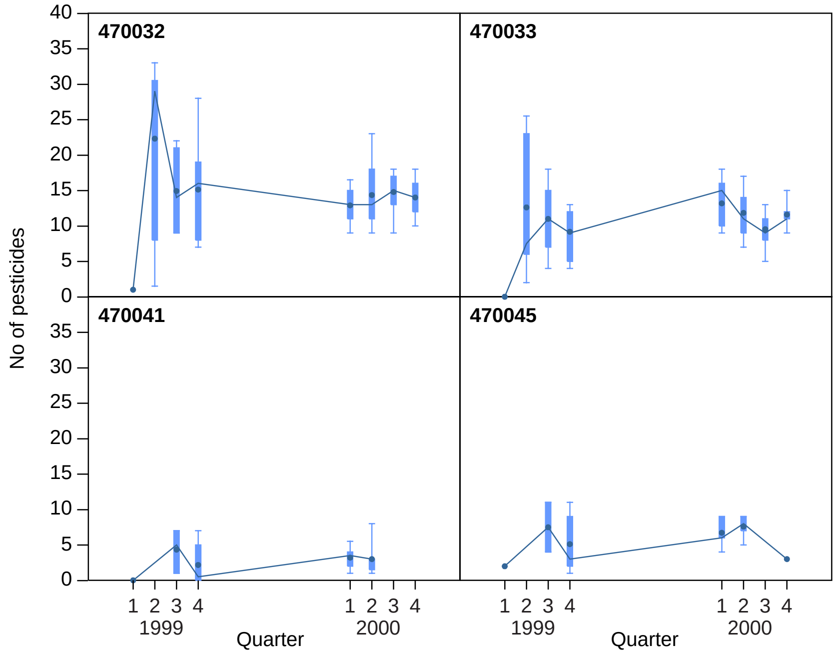


Figure 6.2. Descriptive statistics for the number of pesticides per water sample recovered during each quarter of the two study years at the four stations in the Lillebæk catchment.
Figur 6.2. Deskriptiv statistik vist i et box-plot for antallet af pesticider pr. analyseret vandprøve i de enkelte kvartaler af de to måleår 1999 og 2000.

Figure 6.3 shows the detection frequency for herbicides recovered at the four stations in the Lillebæk catchment. The highest detection frequencies were generally found at the upstream monitoring station (culverted channel) as compared to the downstream monitoring station (open channel). Although generally experiencing the highest detection frequencies, the culverted stream receives no pesticides via wind drift, direct atmospheric deposition and surface runoff.

The ten most commonly detected herbicides at the upstream station were terbuthylazine and its metabolites, hexazinon, atrazine and its metabolites, isoproturon, BAM, MCPA, DNOC, diuron, nitrophenol and bentazone all having detection frequencies above 50% (Fig. 6.3).

The ten most commonly found herbicides detected at the main stream station were the same as for the upstream catchment, which is drained through a culverted channel. In nearly all cases (except for bentazone), the detection frequency was higher at the upstream station than the downstream station covering the entire Lillebæk catchment (Fig. 6.3). The detection frequency was generally lower in tile drainange water than in stream water (Fig. 6.3). However, the herbicides bentazone, isoproturon, atrazine and metabolites, metabolites of terbuthylazine and DNOC were all detected at rather high (>40%) frequencies in tile drainage water (Fig. 6.3). The most commonly detected herbicides in tile drainage water were bentazone, isoproturon and DNOC at drain 2 and metabolites from terbuthylazine, bentazone, isoroturon and metabolites from atrazine at drain 6.

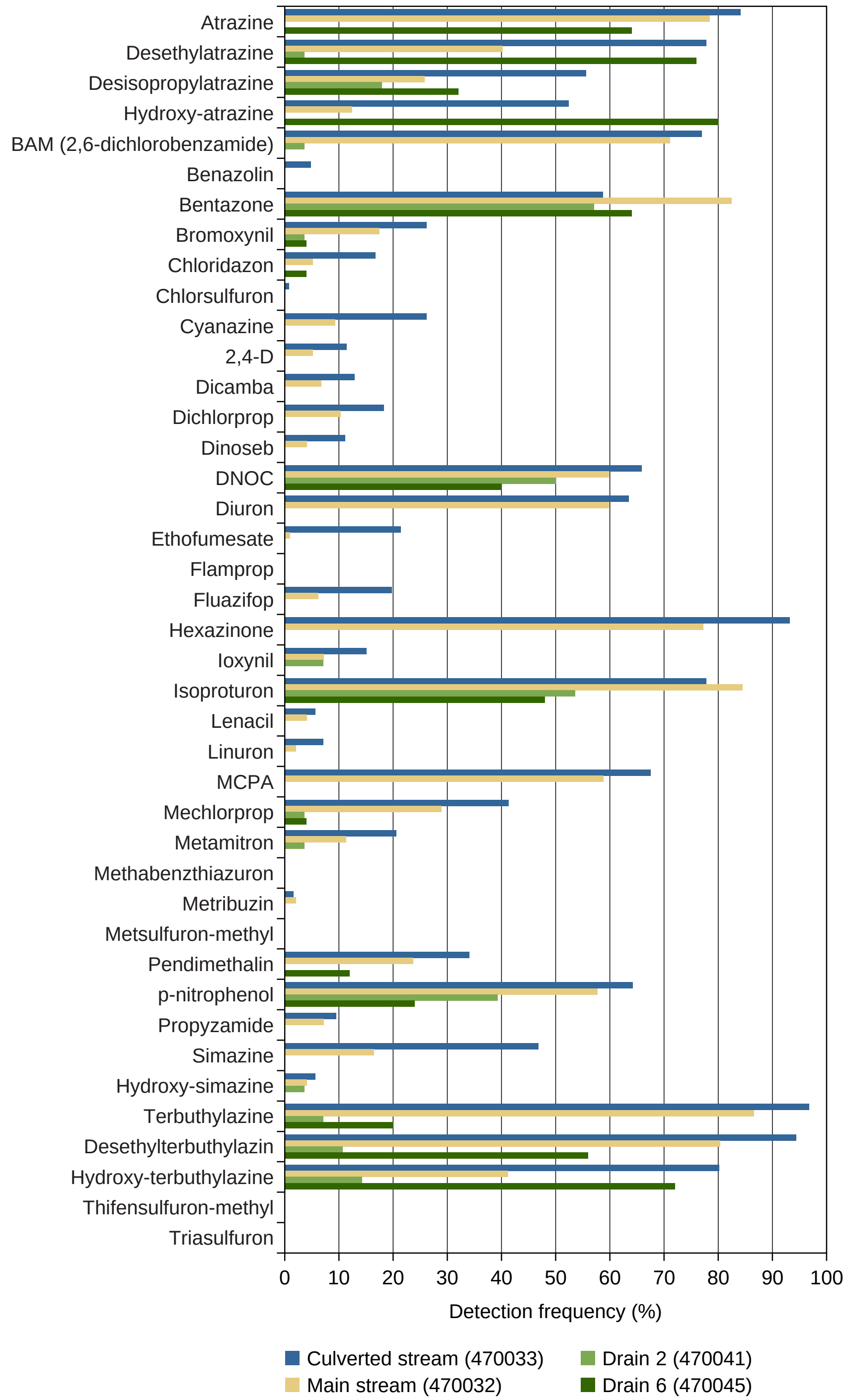


Figure 6.3. Detection frequency for herbicides and metabolites recovered in water samples from the Lillebæk catchment. Number of analysed water samples: Culverted stream: 126; Main stream: 97; Drain 2: 28; Drain 6: 25.
Figur 6.3. Fundhyppighed for herbicider og metaboliter analyseret I vandprøver fra de 4 målestationer I Lillebæk gennem de 2 måleår 1999 og 2000. Antallet af vandprøver analyseret er: Rørlagt vandløb: 126; Hele Lillebæk: 97; Dræn 2: 28 ; Dræn 6: 25.

Fungicides were almost exclusively detected at the two stream stations, with the exception of propiconazole that was also detected at the two drain stations (Fig. 6.4).

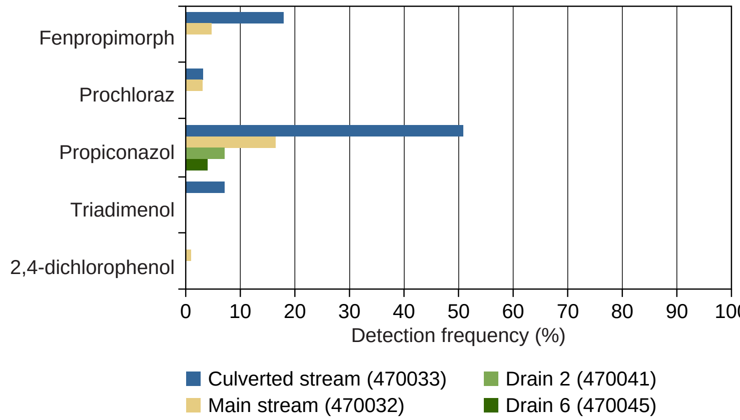


Figure 6.4 Detection frequencies of fungicides recovered in water samples from the four monitoring stations in the Lillebæk catchment. Number of analysed water samples: Culverted stream: 126; Main stream: 97; Drain 2: 28; Drain 6: 25.
Figur 6.4 Fundhyppighed af fungicider i vandprøver udtaget ved de 4 målestationer i oplandet til Lillebæk. *Antallet af vandprøver analyseret er: Rørlagt vandløb: 126; Hele Lillebæk: 97; Dræn 2: 28 ; Dræn 6: 25.*

The detection frequency for fungicides was generally much lower than for herbicides, the only fungicide revealing a frequency above 20% being propiconazol (51%) for the upstream station draining the culverted catchment. The detection frequency for four of the five fungicides was highest at the stream station receiving water from the culverted catchment.

Three insecticides and one metabolite were analysed in water samples from the Lillebæk catchment (Fig. 6.5). The detection frequency for insecticides was generally low, the highest being 13% in case of dimethoate and 16% for pirimicarb at the upstream culverted stream (Fig. 6.5). These two insecticides were detected at both stream stations, whereas only one metabolite was detected at one of the drain stations (Fig. 6.5).

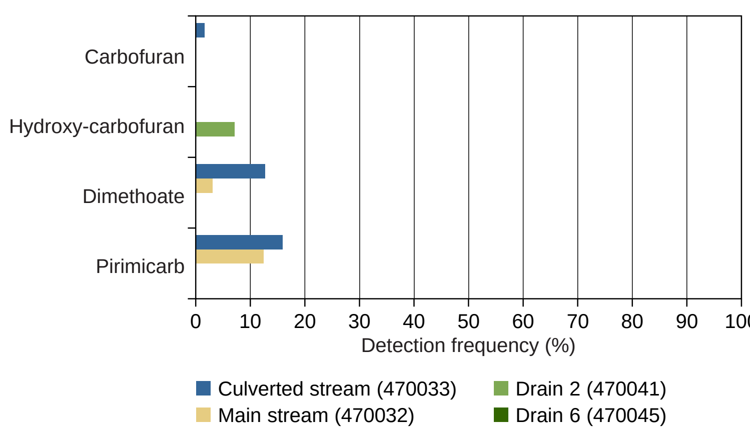


Figure 6.5. Detection frequency of insecticides recovered in water samples from the Lillebæk catchment. Number of analysed water samples: Culverted stream: 126; Main stream: 97; Drain 2: 28; Drain 6: 25.
Figur 6.5. Fundhyppighed af insekticider i vandprøver udtaget ved de 4 målestationer i oplandet til Lillebæk. Antallet af vandprøver analyseret er: Rørlagt vandløb: 126; Hele Lillebæk: 97; Dræn 2: 28 ; Dræn 6: 25.

Nine pesticides were detected at all four monitoring stations (bentazone, propiconazole, terbuthylazine and metabolites, isoproturon, two metabolites from atrazine, DNOC, nitrophenol, mechlorprop and bromoxynil). Six of these pesticides were applied in the catchment during the two study years, whereas atrazine and metabolites, DNOC and the metabolite nitrophenol have been banned for agricultural use for several years. The somewhat high and widespread detection frequency of DNOC and nitrophenol at the four sampling stations in the Lillebæk catchments can, however, be explained by traffic emissions.

The median and maximum pesticide concentrations measured at the four sampling stations in the Lillebæk catchment are shown in Table 6.3 for selected key pesticides from the three groups of herbicides, fungicides and insecticides. The median and maximum concentration of all analysed pesticides in water samples from stream and tile drains can be found in Appendix 6.1.

Table 6.3. Median and maximum concentrations of selected key pesticides among herbicides, fungicides and insecticides detected in water samples from the two stream stations and two drain stations in the Lillebæk catchment.
Tabel 6.3. Median og maximum koncentrationer af udvalgte pesticider (herbicider, fungicider og insekticider) konstateret i vandprøver fra de to vandløbsstationer og 2 drænstationer i Lillebæk oplandet.

Pesticides	Approved (1999)	Upstream station (culverted)		Downstream station (main)		Drain 2		Drain 6	
		Pesticide concentration (ng l^{-1})							
		Med	Max	Med	Max	Med	Max	Med	Max
Herbicides									
Terbuthylazine	+	76	4318	16	330	1	1	2	10
Desethylterbuthylazine	M	17	522	5	51	1	1	2	16
Hydroxyterbuthylazine	M	26	429	11	61	2	50	12	43
Bentazone*	+	2	180	3	90	1	2	2	76
Bromoxynol	+	5	42	2	19	1	1	1	1
Pendimethalin*	+	13	168	13	95	nd	nd	7	26
BAM	M	45	209	38	84	4	4	nd	nd
Ioxynil*	+	5	98	2	14	2	3	nd	nd
Ethofumesate*	+	3	39	1	1	nd	nd	nd	nd
Nitrophenol	M	17	744	14	884	10	125	6	25
MCPA	+	23	1610	17	638	nd	nd	nd	nd
Hexazinone	÷	10	253	5	85	nd	nd	nd	nd
Atrazine	÷	5	463	4	12	nd	nd	4	37
Simazine	+	5	1727	4	91	nd	nd	nd	nd
Hydroxysimazine	+	32	1577	16	39	8	8	nd	nd
Isoproturon	+	61	6900	46	1830	5	122	40	154
DNOC	÷	3	271	2	294	1	22	2	8
Diuron	+	27	1632	16	725	nd	nd	nd	nd
Fungicides									
Propiconazole	+	13	251	20	53	3	4	2	2
Fenpropimorph*	+	12	29	2	62	nd	nd	nd	nd
Prochloraz*	+	1	1	15	16	nd	nd	nd	nd
Insecticides									
Dimethoat	+	14	36	1	1	nd	nd	nd	nd
Pirimicarb	+	6	39	6	49	nd	nd	nd	nd
Hydroxycarbofuran	M	nd	nd	nd	nd	1336	1586	nd	nd

* Proposed model pesticides; nd = not determined

More pesticides were measured in concentrations exceeding 100 ng l^{-1} at the upstream station in the Lillebæk catchment (16 pesticides and 4 metabolites) as compared to the downstream main station (8 pesticides), drain 2 (2 pesticides and 1 metabolite) and drain 6 (1 pesticide and 1 metabolite). The 10 pesticides and metabolites with the highest maximum concentrations detected at the upstream culverted station were isoproturon (6900 ng l^{-1}), terbuthylazine (4318 ng l^{-1}), simazine (1727 ng l^{-1}), diuron (1632 ng l^{-1}), MCPA (1610 ng l^{-1}), hydroxysimazine (1577 ng l^{-1}), chlorsulfuron (1422 ng l^{-1}), nitrophenol (744 ng l^{-1}), cyanazin (640 ng l^{-1}) and desethylterbuthylazine (522 ng l^{-1}). Similar findings for the downstream stations were isoproturon (1830 ng l^{-1}), nitrophenol (884 ng l^{-1}), diuron (725 ng l^{-1}), MCPA (638 ng l^{-1}), terbuthylazine (330 ng l^{-1}), DNOC (294 ng l^{-1}), cynanazin (218 ng l^{-1}), lenacil (119 ng l^{-1}), pendimethalin (95 ng l^{-1}) and simazine (91 ng l^{-1}). Seven of the pesticides detected in highest maximum concentrations were similar at the two stream stations, the maximum concentration being highest for all seven pesticides at the upstream culverted station. In tile drainage water at drain 2, the highest maximum concentrations were detected for hydroxycarbofuran (1586 ng l^{-1}), nitrophenol (125 ng l^{-1}) and isoproturon (122 ng l^{-1}), whereas the similar findings at drain 6 were hydroxyatrazine (244 ng l^{-1}), isoproturon (154 ng l^{-1}) and bentazone (76 ng l^{-1}).

Twenty pesticides were detected in more than 25% of the water samples at the upstream station in the Lillebæk catchment (Appendix 6.1). Of these 20 pesticides the substances found most frequently at high concentrations as measured by the median concentration were terbuthylazine (76 ng l^{-1}), isoproturon (61 ng l^{-1}), BAM a metabolite from dichlobenile (45 ng l^{-1}), diuron (27 ng l^{-1}) and hydroxyterbuthylazine (26 ng l^{-1}). Fifteen of the pesticides were detected in more than 25% of the water samples at the downstream station in the Lillebæk catchment (Appendix 6.1). Of these 15 pesticides, the substances found most often at high concentrations as measured by the median concentration were isoproturon (46 ng l^{-1}), BAM (38 ng l^{-1}), MCPA (17 ng l^{-1}), diuron (16 ng l^{-1}) and terbuthylazine (16 ng l^{-1}).

It therefore seems that there is a distinct similarity in the most frequently detected pesticides at high concentrations between the two stream stations in the Lillebæk catchment. This was of course also to be anticipated if the pesticides were only applied in the upstream catchment. However, diuron, terbythylazine, MCPA, and isoproturon were applied in both sub-catchments during at least one of the study years. The reason for finding similar pesticides at both stations may be a result of loss from both sub-catchments to the stream and/or a simple dilution of pesticides lost from only the upstream catchment.

Four of the pesticides were detected in more than 25% of the water samples at drain two as compared to nine pesticides at drain six in the Lillebæk catchment (Appendix 6.1). The four pesticides found most frequently in drain two had all median concentrations below 10 ng l^{-1}. In drain six, isoproturon (40 ng l^{-1}) and the metabolites desethylsatrazine (36 ng l^{-1}), hydroxyterbuthylazine (12 ng l^{-1}) and hydroxyatrazine (14 ng l^{-1}) experienced median concentrations higher than 10 ng l^{-1}.

Five of the pesticides detected in high concentrations in the Lillebæk catchment have been banned for agricultural use for several years in Denmark (Table 6.3). Of these five pesticides, the most commonly detected pestides were atrazine, BAM (a metabolite from dichlobenile), hexazinone, DNOC and nitrophenol, the latter two being emitted from traffic.

6.3 Key pesticides detected in stream and drainage water

A number of key pesticides are selected for a more thorough presentation of their occurrence and concentration in Lillebæk during the study period. The pesticides selected represent six model pesticides chosen at an early stage of the project and other pesticides representing a combination of various active substances (herbicides, fungicides and insecticides) with different physico-chemical properties.

Table 6.4 shows the thirteen pesticides together with information about their physico-chemical properties and use in Danish agriculture.

Table 6.4. The physico-chemical properties of selected key pesticides (Kd=partition coefficient between soil and water; DT50=half-life of the pesticide active ingredient), the amount of pesticides sold (active ingredients) for use in Danish agriculture in 2000 and their use for different crop types.
Tabel 6.4. Udvalgte nøgle pesticiders fysisk-kemiske egenskaber (Kd=sorptionkoefficient mellem jord og vand; DT50=halveringstid for pesticidet), salg af pesticiderne (aktiv stoffer) i dansk landbrug i år 2000 og deres anvendelse.

Compound	Kd	DT ½ (days)	Applied amount of active ingredients in Denmark 2000	Allowed for use in:
Proposed model compounds				
Bentazone	0.32	35	47,773 kg	Undersown spring cereals, peas, grass seed, clover for seed, maize, grass and clover
Pendimethalin	70	127	243,256 kg	Winter cereals, spring cereals, peas, carrots, onion
Fenpropimorph	34.5	16.6	118,649 kg	Cereals, grass seed, barley/pea as green fodder, beets, beetroot, leeks, chives
Diuron	2,8	90-180	30,500 kg	Christmas trees, nurseries, fruit trees,e tc.
Ioxynil	5.6	5.0	39,468 kg	Onion, leeks, cereals (in combination with bromoxynile)
Ethofumesate	12.4	125	15,273 kg	Beets
Prochloraz	94.3	135	1,386 kg	Cereals, grass seed, rape seed
Esfenvalerate	38.8	54	759 kg	Cereals, rape seed, mustard, beets, maize, grass, cereals for green fodder, cabbage, etc.
Other				
2,6-dichlorbenzamid (BAM)			-	Metabolite of TCA banded in 1992 and dichlobenil banded in 1997
Terbuthylazine	2.3	80	32,473 kg	Maize
Propiconazole	12.3	71	21,195 kg	Cereals, beets
Isoproturon	0.83	39	10,275 kg	Dispensation for use in 2000 (banded 1999)
Dimethoate	0.41	2.4	26,610 kg	Cereals, beets, maize

Figure 6.6 shows the median and the range in concentration of terbuthylazine in the different quarters of 1999 and 2000. The herbicide, terbuthylazine, was applied to different crop types within the upstream culverted catchment and within the open channel sub-catchment during the 2nd quarter of 1999 and only in the upstream sub-catchment in 2000.

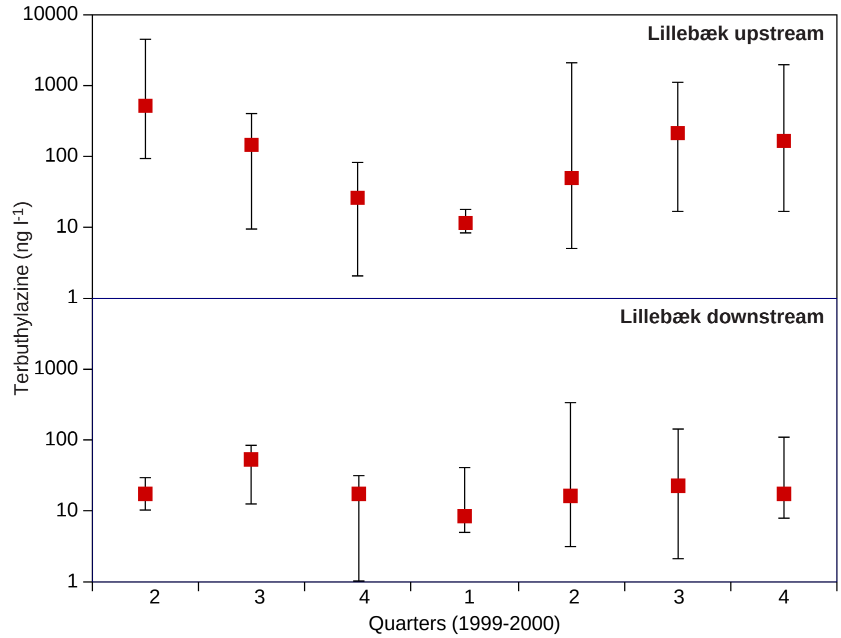


Figure 6.6. Minimum, median and maximum concentrations for the herbicide, terbuthylazine, at the two stream monitoring stations in the Lillebæk catchment during each quarter of the study period (2nd, 3rd, 4th 1999 and 1st, 2nd and 3rd 2000).
Figur 6.6. Minimum, median og maximum koncentrationer af herbicidet terbuthylazine ved de to vandløbsstationer i Lillebæk i hvert kvartal gennem måleperioden (2,3 og 4 kvartal 1999 og 1,2 og 3 kvartal 2000).

A clear seasonal pattern was detected for terbuthylazine at the upstream station, the concentration being lowest during the winter period (4th and 1st quarters) and highest during the 2nd quarter of 1999 and the 2nd and 3rd quarter of 2000 (Fig. 6.6). This seasonal pattern was measured for both the minimum, median and maximum concentration of terbuthylazine at the upstream station. A similar, but much less significant, seasonal pattern was also measured for terbuthylazine at the downstream station (Fig. 6.6). The application of terbuthylazine therefore seems to have an impact on the concentration pattern measured in the stream.

The median and the range in the concentration of isoproturon in the different quarters of 1999 and 2000 are shown in Figure 6.7. The herbicide isoproturon was only applied to different crop types within the upstream culverted catchment and the open channel sub-catchment during the 4th quarter in 1998 and 1999. The largest quantity was however applied in the 4th quarter of 1999.

The application of isoproturon in the 4th quarter of 1999 was followed by an immediate steep rise in the concentration in the same quarter at both stream stations (Fig. 6.7). The concentration of isoproturon increased in the subsequent quarters of 2000 at the upstream station, whereas a decline was measured at the downstream station (Fig. 6.7). The application of isoproturon therefore seems to have an impact on the concentration pattern measured in the stream.

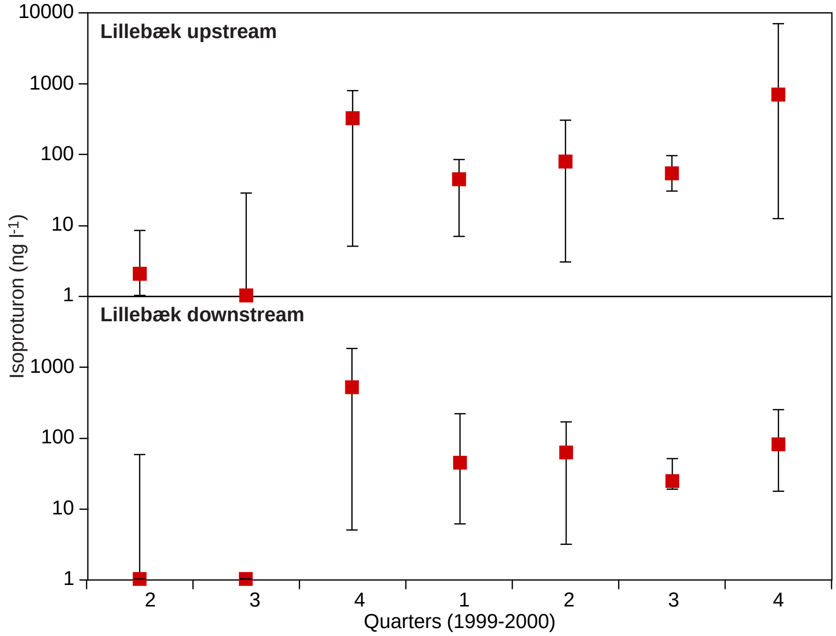


Figure 6.7. Minimum, median and maximum concentrations of the herbicide isoproturon at the two stream monitoring stations in the Lillebæk catchment during each quarter of the study period (2nd, 3rd, 4th 1999 and 1st, 2nd and 3rd 2000).
Figur 6.7. Minimum, median og maximum koncentrationer af herbicidet isoproturon ved de to vandløbsstationer i Lillebæk i hvert af kvartalerne gennem måleperioden (2., 3. og 4. kvartal 1999 og 1., 2. og 3. kvartal 2000).

Figure 6.8 shows the median and the range in the concentration of bentazone in the different quarters of 1999 and 2000. The herbicide bentazone was only applied to different crop types within the upstream culverted catchment and the open channel sub-catchment during the 2nd quarter of 1999 and 2000. The application of bentazone was, however, only 18 g in the upstream culverted sub-catchment in the 2nd quarter of 1999 as compared to 2130 g in the open channel sub-catchment.
Almost similar quantities were applied in the 2nd quarter of 2000.

There was no clear relationship between the measured concentration and application time of bentazone (Fig. 6.8). The concentration of bentazone was highest in the 2nd quarter of 1999 at the upstream station although only a small amount of bentazone was applied. Moreover, the concentration of bentazone remained low during all 2000 regardless of the application during the 2nd quarter of 2000. The concentration of bentazone increased between the 2nd quarter and the 3rd and 4th quarter of 1999 at the downstream station following the application during the 2nd quarter of 1999 (Fig. 6.8). The concentration of bentazone was also slightly higher during the 2nd quarter of 2000 at the downstream station following the application during the same quarter. The concentration pattern for bentazone is therefore not well linked to the timing of bentazone application in the catchment.

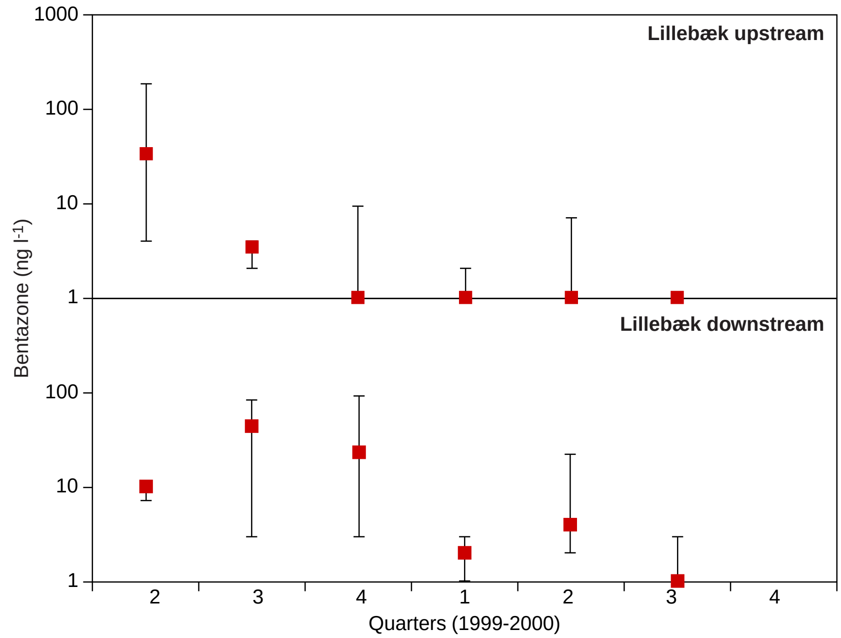


Figure 6.8. Minimum, median and maximum concentrations for the herbicide bentazone at the two stream monitoring stations in the Lillebæk catchment during each quarter of the study period (2nd, 3rd, 4th 1999 and 1st, 2nd and 3rd 2000).
Figur 6.8. Minimum, median og maximum koncentrationer af herbicidet bentazon ved de to vandløbsstationer i Lillebæk i hvert af kvartalerne gennem måleperioden (2., 3. og 4. kvartal 1999 og 1., 2. og 3. kvartal 2000).

The median, 10 and 90 percentiles of the concentration of suspended sediment and key pesticides were calculated for days with more and less than 1 mm of precipitation. In this way the measured concentrations of pesticides were dubdivided into periods with high and steady flow conditions at the two stream stations in the Lillebæk catchment during 2000. The number of water samples in the high-flow and low-flow data sets were 20 and 29, respectively, at the upstream station and 18 and 30, respectively, at the downstream station.

The concentration of suspended sediment on days with high-flow was exceedingly higher than on days with steady flow conditions at both the upstream and downstream station in the Lillebæk (Fig. 6.9). The difference in median concentration of suspended sediment between high-flow and steady-flow conditions was most significant at the upstream station although the maximum concentration (90 percentile) was nearly equally high at the two stream stations (Fig. 6.9). Suspended sediment delivered from the catchment is consequently transported downstream, especially during high-flow periods.

The concentration of terbuthylazine was also higher during high-flow periods than during steady-flow periods at the upstream station in Lillebæk (Fig. 6.10). This was, however, not the case at the downstream station. Terbuthylazíne was applied in both the ustream culverted catchment and the downstream open catchment during the 2nd quarter of 1999, but only in the upstream culverted catchment during the 2nd quarter of 2000. The Kd value of 2.3 for terbuthylazine suggests that it can be transported from the upstream culverted sub-catchment both as dissolved and particulate matter. The small difference in the concentration of terbuthylazine measured during high-flow and steady-flow periods at the downstream station seems to imply that no major source areas deliver terbutylazine to the open stream channel between the upstream and downstream sampling station and hence dilution will occur. Terbuthylazine will also be subjected to sorption, decomposition and/or depositional processes in the open stream channel between the two sampling stations. Another explanation for the significant difference in measured terbuthylazine concentrations between the two sampling stations during rainy periods could be the existence of pesticide-polluted areas (contaminated areas) from where terbuthylazine is lost via tile drains during rainy periods to the culverted stream. Therefore, such contaminated areas linked to the open stream via tile drains do not exist in the downstream sub-catchment.

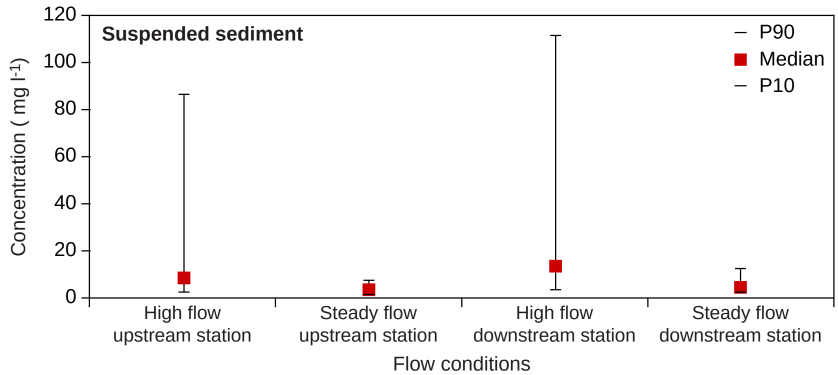


Figure 6.9. The concentration of suspended sediment during high-flow (days > 1 mm precipitation) and steady-flow periods (days < 1 mm precipitation) at the upstream and downstream stream stations in the Lillebæk catchment.
Figur 6.9. Koncentrationen af suspenderet stof på prøvetagningsdage med stigende vandføring (nedbør > 1 mm) og prøvetagningsdage med stabil eller faldende vandføring ved de to vandløbsstationer i Lillbæk oplandet.

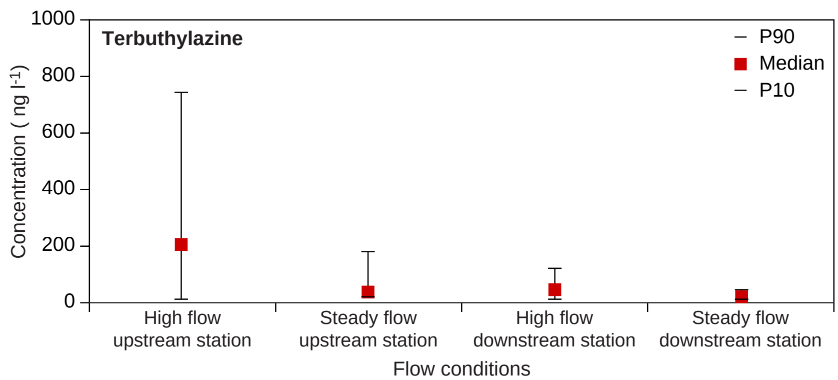


Figure 6.10. The concentration of terbuthylazine during high-flow (days > 1 mm precipitation) and steady-flow periods (days < 1 mm precipitation) at the upstream and downstream stream stations in the Lillebæk catchment.
Figur 6.10. Koncentrationen af terbuthylazin på prøvetagningsdage med stigende vandføring (nedbør > 1 mm) og prøvetagningsdage med stabil eller faldende vandføring ved de to vandløbsstationer i Lillbæk oplandet.

The concentration of propiconazole is also slightly higher at the upstream station during high flow-periods than during periods with steady flow, whereas propiconazole was not detected at the downstream station (Fig. 6.11).

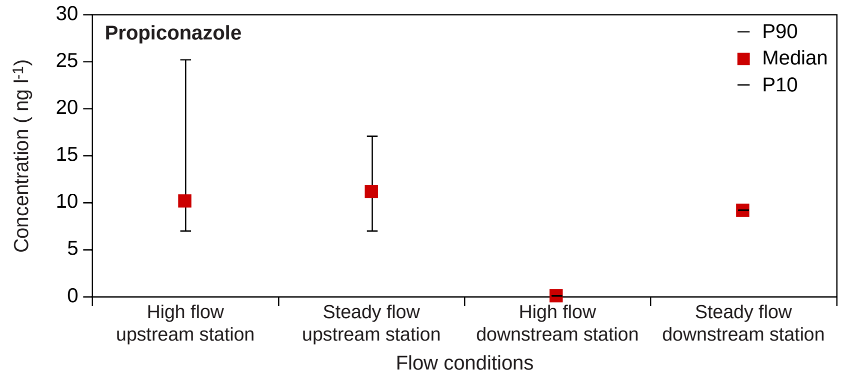


Figure 6.11. The concentration of propiconazole during high-flow (days > 1 mm precipitation) and steady-flow periods (days < 1 mm precipitation) at the upstream and downstream stream station in the Lillebæk catchment.
Figur 6.11. Koncentrationen af propiconazol på prøvetagningsdage med stigende vandføring (nedbør > 1 mm) og prøvetagningsdage med stabil eller faldende vandføring ved de to vandløbsstationer i Lillbæk oplandet.

On the contrary, the concentration of bentazone was slightly higher during periods with steady flow than during high-flow periods (Fig. 6.12). Moreover, the median concentration of bentazone increases from the upstream to the downstream station, the latter being more influenced by discharging groundwater. The observed pattern suggests that bentazone is predominantly delivered to the stream via groundwater. Bentazone has also been detected in concentrations of less than 100 ng l^{-1} in the upper groundwater in the Lillebæk catchment during 1999 and 2000 (Funen County, 2001).

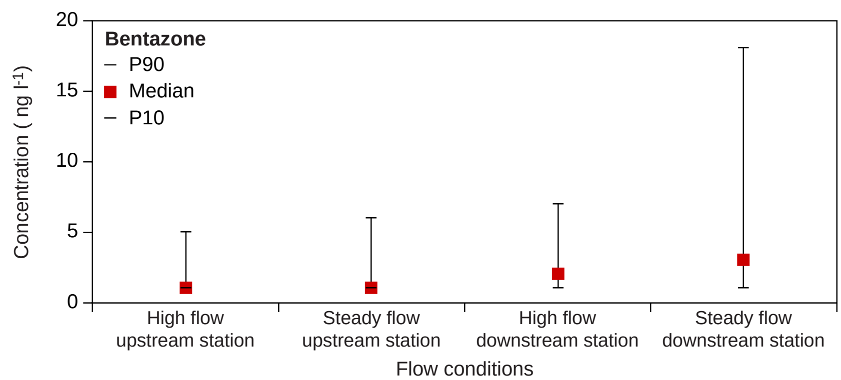


Figure 6.12. The concentration of bentazone during high-flow (days > 1 mm precipitation) and steady-flow periods (days < 1 mm precipitation) at the upstream and downstream stream stations in the Lillebæk catchment.
Figur 6.12. Koncentrationen af bentazon på prøvetagningsdage med stigende vandføring (nedbør > 1 mm) og prøvetagningsdage med stabil eller faldende vandføring ved de to vandløbsstationer i Lillbæk oplandet.

The median concentration of isoproturon is nearly at the same level at the two stations irrespectively of flow conditions (Fig. 6.13). Moreover, the 10 and 90 percentiles did not vary much during high and low-flow conditions at the stream stations. As no dilution or enrichment of the concentration of isoproturon seems to exist at any of the stream stations, isoproturon must be delivered to the stream from both the culverted and the open sub-catchments via groundwater and soil water. Isoproturon has also been detected in concentrations above 200 ng l^{-1} in the upper groundwater in the Lillebæk catchment during 1999 and 2000 (Funen County, 2001).

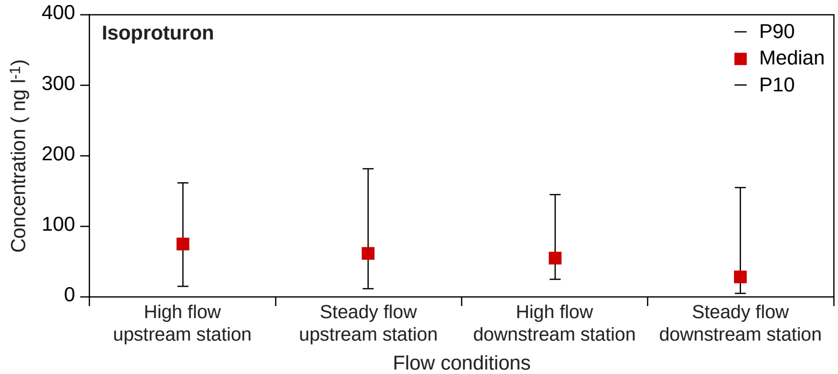


Figure 6.13. The concentration of isoproturon during high-flow (days > 1 mm precipitation) and steady-flow periods (days < 1 mm precipitation) at the upstream and downstream stream stations in the Lillebæk catchment.
Figur 6.13. Koncentrationen af isoproturon på prøvetagningsdage med stigende vandføring (nedbør > 1 mm) og prøvetagningsdage med stabil eller faldende vandføring ved de to vandløbsstationer i Lillbæk oplandet.

The median concentration of the metabolite BAM (from the banned pesticide dichlobenile) is higher at both stream stations during steady-flow conditions than during high-flow conditions (Fig. 6.14). The results show that BAM is delivered both from the sub-catchment via groundwater and soil water. BAM was also detected in upper groundwater in the Lillebæk catchment during 1999, but not in 2000 (Funen County, 2001).

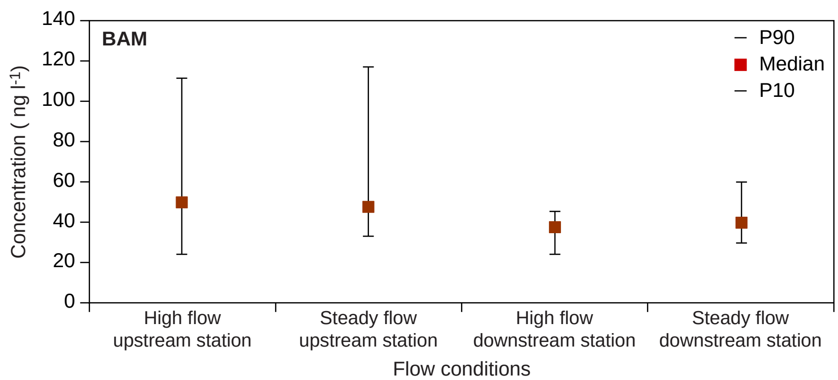


Figure 6.14. concentration of the metabolite BAM during high-flow (days > 1 mm precipitation) and steady-flow periods (days < 1 mm precipitation) at the upstream and downstream stream stations in the Lillebæk catchment.
Figur 6.14. Koncentrationen af nedbrydningsproduktet BAM på prøvetagningsdage med stigende vandføring (nedbør > 1 mm) og prøvetagningsdage med stabil eller faldende vandføring ved de to vandløbsstationer i Lillbæk oplandet.

6.4 Pesticides in suspended sediment

Composite suspended sediment samples were collected on a near monthly basis at the two stream stations in Lillebæk with the ***in situ*** SubMarie suspended sediment sampler (see chapter 4). The number of pesticides detected in suspended sediment increases from March to May 2000 and again from winter to spring in 2001 at the upstream station in the Lillebæk catchment. Nearly the same pattern, but with fewer detected pesticides is found at the downstream station although a sharp decline was found from April to May/June 2000 (Fig. 6.15).

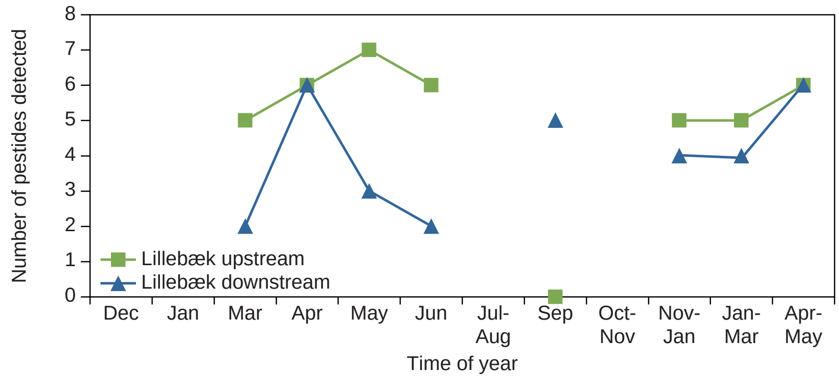


Figure 6.15. Number of pesticides detected in suspended sediment from the upstream and downstream stations in the Lillebæk catchment during March 2000 to May 2001.
Figur 6.15. Antallet af pesticider konstateret i suspenderet stof fra de to målestationer i Lillebæk gennem perioden marts 2000 til maj 2001.

The most significant difference in the number of pesticides detected in suspended sediment between the two stations was in the sample from September 2000 where no pesticides were detected at the upstream station while five pesticides were found at the downstream station.

The sum-concentration of pesticides in suspended sediment was consistently low at both stream stations during the sampled winter months (March 2000, November-January 2000/2001 and January-March 2001 (Fig. 6.16). During these periods the highest amount of suspended sediment is delivered to the streams from their catchments and transported downstream. The content of pesticides in suspended sediment during these periods can therefore be anticipated to be a reference level for the external delivery of pesticides in suspended sediment. The average sum-concentration of pesticides in suspended sediment was nearly three times higher at the upstream station (98 ng g^{-1} DW) than at the downstream station (38 ng g^{-1} DW) during the three sampled winter months.

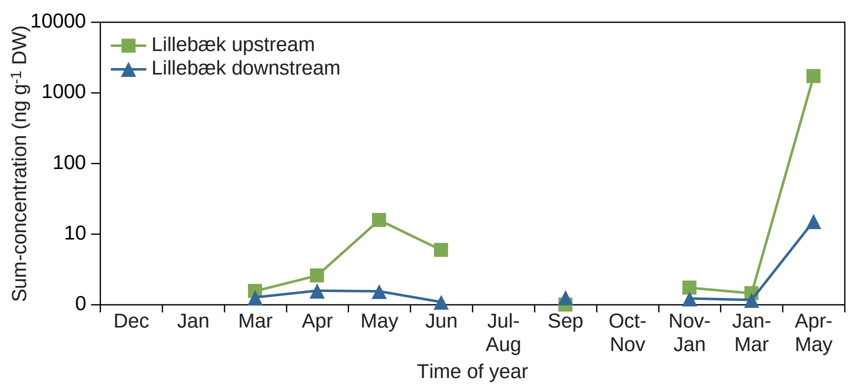


Figure 6.16. Sum-concentration of pesticides measured in suspended sediment from the two stream stations in Lillebæk.
Figur 6.16. Sum-koncentration af pesticider målt i suspenderet stof fra de to vandløbsstationer i Lillebæk gennem perioden marts 2000 til maj 2001.

The sum-concentration of pesticides in suspended sediment increased at both stream stations during the spring application season (April and May 2000 and 2001) (Fig. 6.16). The enrichment of suspended sediment with pesticides was, however, much higher during the spring period at the upstream station than at the downstream station. The highest sum-concentration of pesticides in suspended sediment measured at the upstream station was 597 ng g^{-1} DW in May 2000 and 1617 ng g^{-1} DW during the period April-May 2001 (Fig. 6.16). This shows that pesticides from the water phase must be sorbed to the suspended sediment collected in the sampler during the spring period. Other factors that may influence the pesticide content of suspended sediment are differences in grain size distribution and organic carbon content factors that were not analysed for in the sediment samples.

The maximum concentration of pesticides recovered above the detection limit in suspended sediment at the two stream stations is shown in Figure 6.17. The pesticides measured in the highest concentrations were diuron (400 ng g^{-1} DW) in the sample of May 2000 from the upstream station and pendimethalin (1300 ng g^{-1} DW) and isoproturon (190 ng g^{-1} DW) in the sample from April/May 2001 from the upstream station. Esfenvalerate was measured in the suspended sediment sample from May 2000 at the upstream station at a concentration of 20 ng g^{-1} DW.

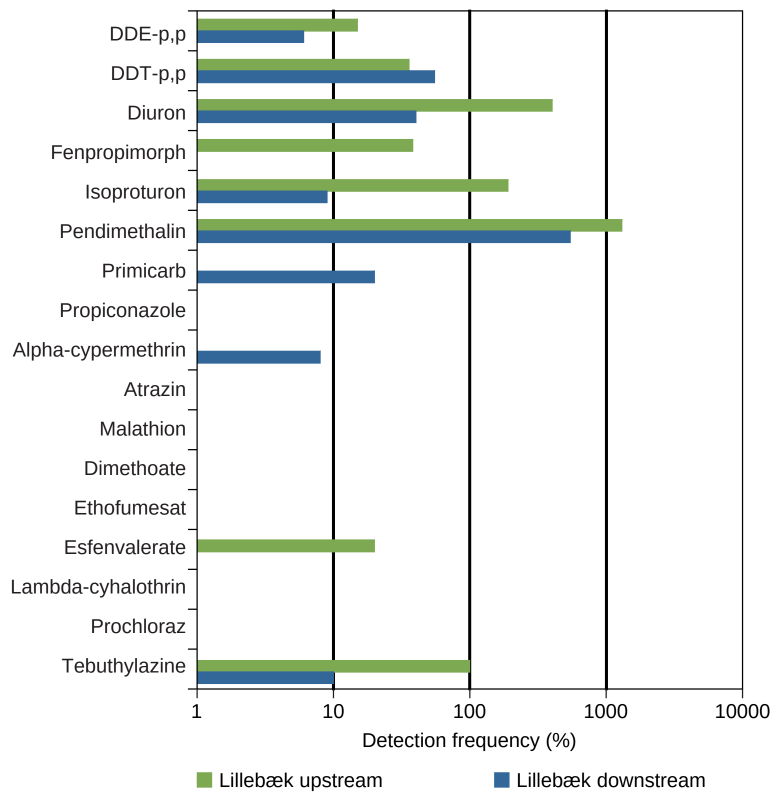


Figure 6.17. Maximum concentration of pesticides measured in 8 suspended sediment samples collected from the upstream station and 8 suspended sediment samples from the downstream station in the Lillebæk catchment from March 2000 to May 2001.
Figur 6.17. Maximum koncentrationer af pesticider i suspenderet stof fra 8 prøver udtaget ved den opstrøms vandløbsstation og 8 prøver udtaget ved den nedstrøms station i Lillebæk oplandet i perioden Marts 2000 til maj 2001.

6.5 Pesticides in streambed sediment

The number of pesticides detected in streambed sediment generally increased from early spring to autumn (1999) or from early May to June (2000). This was, however, most pronounched for the upstream station in the Lillebæk draining the culverted catchment. The highest number of pesticides detected at the upstream station was seven in June 2000, including DDT-p,p and the metabolite DDE-p,p, but also insecticides, such as esfenvalerate, alpha-cypermethrin and pirimicarb were found (Table 6.5). The highest concentration was detected for diuron at the upstream station in June 2000. The number of pesticides detected and the pesticide concentration were considerably lower at the downstream station than at the upstream station in the Lillebæk. Many of the same pesticides were, however, detected in the bed sediment at both stream stations (Table 6.5).

Table 6.5. concentration of pesticides measured in streambed sediment from the upstream and downstream station in the Lillebæk catchment during 1999 and 2000.
Table 6.5. Koncentration af pesticider målt i bundsediment fra de to vandløbsstationer i Lillebæk gennem 1999 og 2000.

	Lillebæk Topenden (upstream)						Lillebæk Fredskovvej (downstream)					
Pesticides	Mar 17 1999	Jun 24 1999	Aug 24 1999	May 2 2000	May 17 2000	June 6 2000	Mar 17 1999	June 24 1999	Aug 24 1999	May 2 2000	May 17 2000	June 6 2000
	Concentration (ng g^{-1} DW)											
Herbicides												
Atrazin	nd	Nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	Nd
Diuron	nd	Nd	10	20	40	100	nd	nd	nd	30	20	20
Ethofumesat	nd	Nd	nd	nd	nd	20	nd	nd	nd	nd	nd	nd
Isoproturon	nd	nd	nd	nd	9	40	nd	nd	nd	6	nd	nd
Pendimethalin	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Terbuthylazin	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Fungicides												
Fenpropimorph	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Prochloraz	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Propiconazol	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Insecticides												
Alpha-cypermethrin	nd	nd	nd	nd	3	3	nd	nd	nd	6	nd	nd
DDE-p,p	4	4	2	nd	5	8	4	nd	2	2	2	2
DDT-p,p	nd	4	10	nd	2	4	nd	nd	4	2	2	nd
Dimethoate	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Esfenvalerate	nd	nd	nd	nd	nd	10	nd	nd	nd	nd	nd	nd
Lambda-cyhalotrin	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Malathion	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Pirimicarb	nd	nd	nd	nd	nd	20	nd	nd	nd	nd	nd	nd

Nd = not determined

7 Pesticide occurrence and concentration in stream and drains in the Odderbæk catchment

7.1 Water and sediment samples collected from the monitoring stations in the Odderbæk catchment

Table 7.1 shows the number of days with water sampling and number of water samples analysed for pesticides in the Odderbæk catchment. Water samples were collected from the two monitoring stations during both sampling years on sampling dates shown in Figure 7.1. A total of 68 water samples were collected from the stream station and 49 water samples from the drain station. A total of 24 water samples were collected during storm events, whereas 13 water samples were collected during periods with steady or decreasing discharge conditions at the Odderbæk stream station (Fig. 7.1).

Table 7.1. Number of water samples and number of days with water sampling on a quarterly basis during the two study years from the 2 monitoring stations in the Odderbæk catchment.
Tabel 7.1. Antallet af vandprøver og antal måledage i parentes vist kvartalsvis gennem de to måleår 1999 og 2000 for de to målestationer i Odderbæk.

	1 Q	2 Q	3 Q	4 Q	1 Q	2 Q	3 Q	Total
	1999				2000			
Stream station (130011)	2 (2)	23 (8)	3 (3)	12 (6)	11 (6)	14 (9)	7 (3)	68 (35)
Drain station (130013)	2 (2)	9 (6)	3 (3)	12 (7)	6 (4)	6 (5)	7 (3)	49 (32)

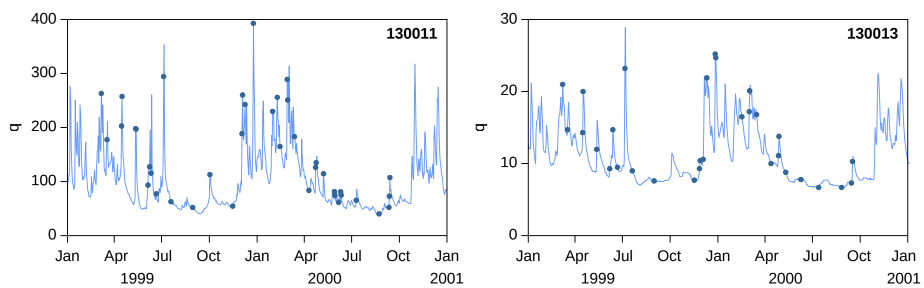


Figure 7.1. Days with water samples collected from the two monitoring stations. On sampling days with storm events (spates) several samples were often collected with the automatic sampling equipment.
Figur 7.1. Tidsplot af døgnmiddel vandføring ved de to målestationer i Odderbæk sammen med en angivelse af de dage hvor vandprøver er blevet udtaget. På måledage med stigende vandføring (flom) er der blevet udtaget vandprøver hver time med det automatiske prøvetagningsudstyr.

Suspended sediment was collected with an ***in situ*** sampler (SubMarie) from the stream stations during the second study year. A total of nine suspended sediment samples were collected from the stream station during the period December 1999 - November 2000. Three streambed sediment samples were collected during three surveys in the first study year (March, June and May 1999) and another three sediment samples were collected during three surveys in the second study year (May and June 2000).

7.2 Detection of pesticides in stream and subsurface tile drainage water

Forty-nine different pesticides and metabolites were analysed in the water samples collected from stream and subsurface tile drainage water. In total, 39 different pesticides were detected at the stream station and 27 at the drain station in the Odderbæk during the 2-year study period. The number of pesticides detected in subsurface drainage water was somewhat lower than from the catchment as a whole (Table 7.2). The number of pesticides detected varied between the different seasons of the study years but were in general higher during the quarters with pesticide application 2nd, 3rd and 4th quarter (Table 7.2). However, part of this variation can possibly be explained by a varying number of water samples being collected during each quarter (Table 7.1).

Table 7.2. Number of pesticides (active substances and metabolites) detected in water samples collected at a quarterly basis during the two study years from the two monitoring stations in the Odderbæk catchment.
Tabel 7.2. Antal pesticider (aktiv stoffer og metaboliter) fundet i de indsamlede vandprøver fra de 2 målestationer i Odderbæk oplandet vist kvartalsvis for de to måleår 1999 og 2000.

	1 Q	2 Q	3 Q	4 Q	1 Q	2 Q	3 Q	4 Q
	1999				2000			
Stream station (130011)	2	16	26	22	9	18	17	-
Drain station (130013)	2	10	4	11	3	4	3	-

A descriptive statistics for the number of pesticides detected per water sample in each quarter of the two study years is shown in Figure 7.2. The number of pesticides in water samples generally increases throughout the seasons of the year, being on average highest in the 4th quarter and lowest in the 1st quarter at the stream and drain station (Fig. 7.2). Moreover, the number of pesticides detected in water samples was generally higher in the wet year of 1999 than in the drier year of 2000.

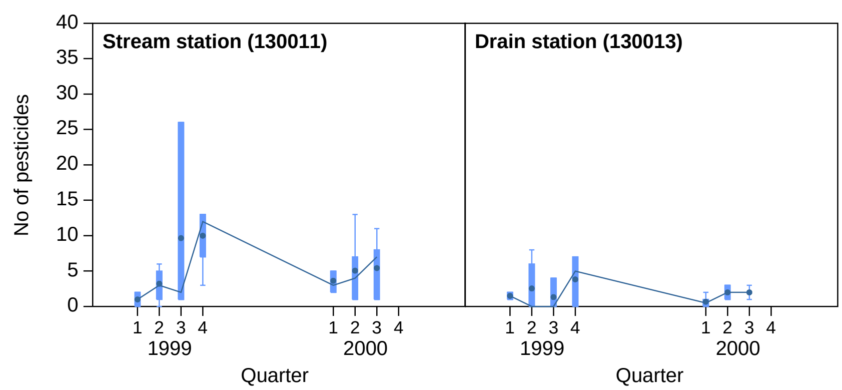


Figure 7.2. Descriptive statistics for the number of pesticides per water sample recovered during each quarter of the two study years at the two stations in the Odderbæk catchment.
Figur 7.2. Deskriptiv statistik vist i et box-plot for antallet af pesticider pr. analyseret vandprøve udtaget ved de 2 målestationer i Odderbæk i de enkelte kvartaler af de to måleår 1999 og 2000.

The detection frequency for herbicides recovered at the two stations in the Odderbæk catchment is shown in Figure 7.3. The highest detection frequencies were generally found at the stream monitoring station as compared to the drain station. In many cases the herbicides were found in both stream and subsurface drainage water and for some herbicides also at comparable detection frequencies (isoproturon, bentazone).

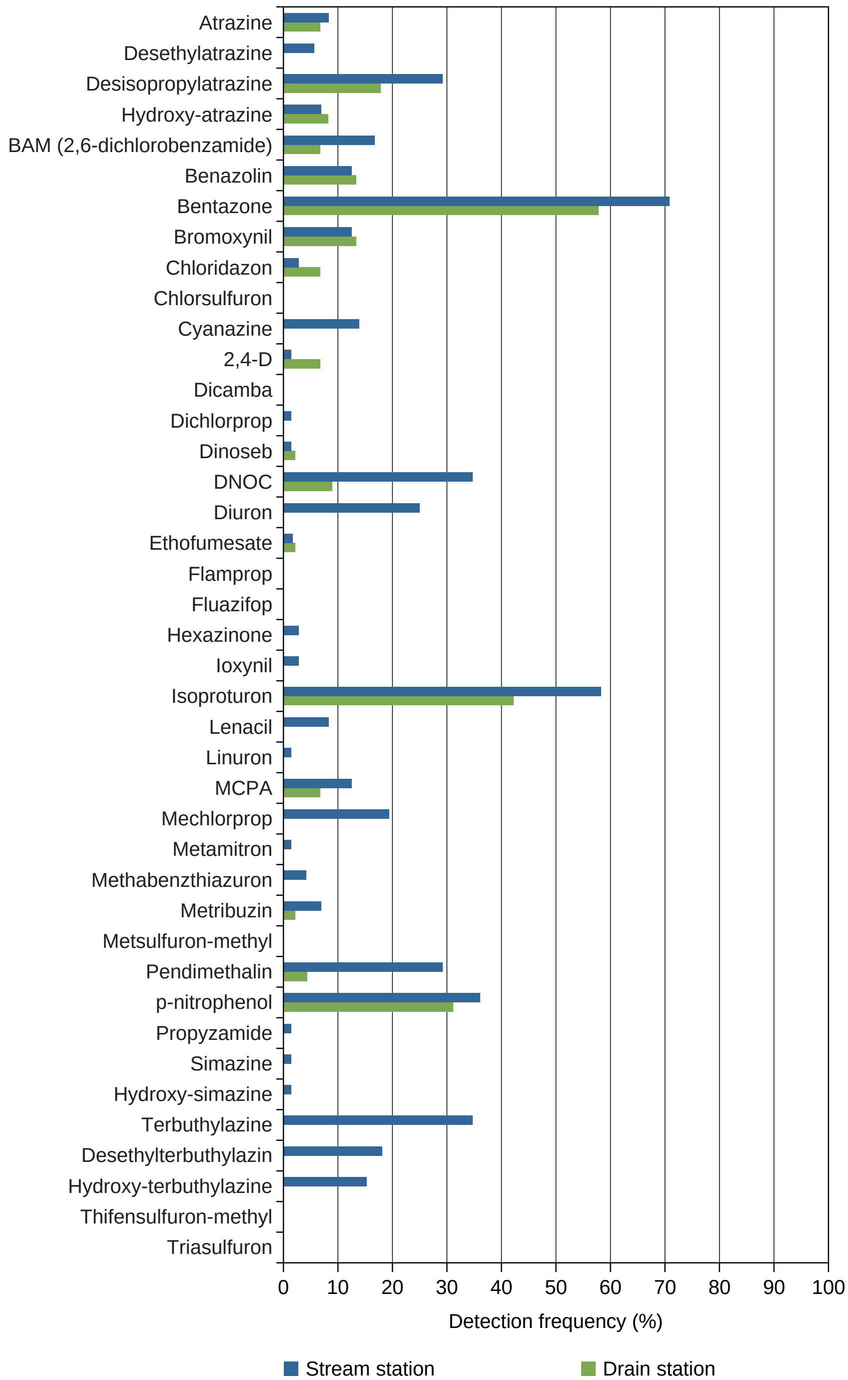


Figure 7.3. Detection frequency for herbicides and metabolites recovered in water samples from the Odderbæk catchment.
Figur 6.3. Fundhyppighed for herbicider og metabolitter analyseret i vandprøver fra de 2 målestationer i Odderbæk gennem de 2 måleår 1999 og 2000.

The ten most common herbicides detected in the samples from the stream station were bentazone (70.8%), isoproturon (58.3%), nitrophenol (36.1%), DNOC (34.7%), terbuthylazin (34.7%) and metabolites (15.3-18.1%), pendimethalin (29.2%), desisopropylatrazine (29.2%), diuron (25%) and mechorprop (19.4%) (Fig. 7.2). In comparison, the ten herbicides with highest detection frequencies in drainage water were bentazone (57.8%), isoproturon (42.2%), nitrophenol (31.1%), desisopropylatrazine (17.8%), benazolin (13.3%), bromoxynil (13.3%), hydroxyatrazin (8.2%), BAM (6.7%), mechlorprop (6.7%) and pendimethalin (4.4%), (Fig. 7.3).

Four of the five fungicides analysed for in water samples were detected in stream water and only one in subsurface drainage water (Fig. 7.4). The detection frequency was, however, considerably lower than for many of the herbicides (Fig. 7.4). The detection frequency was nearly equally low in stream and drainage water, being below 10% for all fungicides (Fig. 7.4).

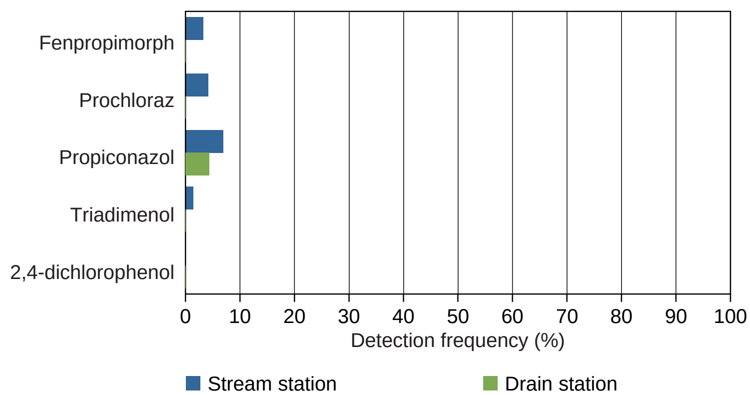


Figure 7.4. Detection frequency for fungicides recovered in water samples from the two stations in the Odderbæk catchment.
Figur 7.4. Fundhyppighed af fungicider i vandprøver udtaget ved de 2 målestationer i oplandet til Odderbæk.

Two of the three insecticides analysed for in water samples were detected in stream water and two insecticides in drainage water (Fig. 7.5). The detection frequency for insecticides was lower than for most of the herbicides and fungicides analysed for in the same water samples, being below 5% in all cases (Fig. 7.5).

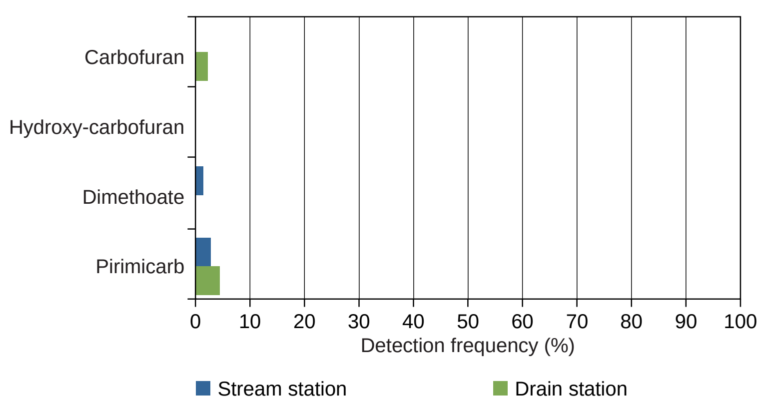


Figure 7.5. Detection frequency for insecticides in water samples from the two stations in the Odderbæk catchment.
Figur 7.5. Fundhyppighed af insekticider i vandprøver udtaget ved de 2 målestationer i oplandet til Odderbæk.

Nineteen pesticides and five metabolites were detected at both monitoring stations and of these ten pesticides were applied in the catchment during the two study years. Pesticides not applied during the two study years were atrazine, 2,4-D, diuron, dinoseb, mechlorprop, DNOC and nitrophenol, many of them being banned in Denmark for several years. The somewhat high detection frequency of DNOC and nitrophenol at both sampling stations can, however, be attributable to emissions from traffic.

The median and maximum pesticide concentrations measured at the stream and drain station in the Odderbæk catchment are shown in Table 7.3 for selected key pesticides from the three groups of herbicides, fungicides and insecticides. The median and maximum concentrations for all pesticides analysed for in water samples from the stream and drain station can be found in Appendix 7.1.

Table 7.3. Median and maximum concentrations of selected key pesticides among herbicides, fungicides and insecticides in water samples from the stream station and the drain station in the Odderbæk catchment.
Tabel 7.3. Median og maximum koncentrationer af udvalgte pesticider (herbicider, fungicider og insekticider) konstateret i vandprøver fra vandløbsstationen og drænstationen i Odderbæk oplandet.

Pesticides	Approved (1999)	Stream station		Drain station	
		Med	Max	Med	Max
Herbicides		Concentration (ng l^{-1})			
Terbuthylazine	+	4	136	1	1
Desethylterbuthylazine	M	3	28	nd	nd
Hydroxyterbuthylazine	M	2	8	1	1
Bentazone*	+	3	2910	4	17
Bromoxynil	+	14	162	12	37
Pendimethalin*	+	14	195	14	26
BAM	M	3	20	1	1
Ioxynil*	+	4	4	nd	nd
Ethofumesate*	+	6	6	112	112
Nitrophenol	M	7	104	4	37
MCPA	+	6	21	8	11
Hexazinone	÷	35	68	nd	nd
Atrazine	÷	1	2	3	4
Simazine	+	1	1	nd	nd
Hydroxysimazine	M	8	8	nd	nd
Isoproturon	+	59	129	71	129
DNOC	÷	4	72	3	4
Diuron	+	7	140	nd	nd
Fungicides					
Propiconazole	+	7	44	2	3
Fenpropimorph*	+	21	42	nd	nd
Prochloraz*	+	1	19	nd	nd
Insecticides					
Dimethoat	+	2	2	nd	nd
Pirimicarb	+	8	14	nd	nd
Hydroxycarbofuran	M	nd	nd	nd	nd

* Proposed model pesticides; nd = not determined; M = metabolite

The number of pesticides measured in concentrations exceeding 100 ng l^{-1} at the stream station in the Odderbæk catchment (seven pesticides) was higher as compared to the drain station (two pesticides). The 10 pesticides and metabolites detected in highest maximum concentrations at the stream station were bentazone (2910 ng l^{-1}), pendimethalin (195 ng l^{-1}), bromoxynil (162 ng l^{-1}), diuron (140 ng l^{-1}), terbuthylazine (136 ng l^{-1}), isoproturon (129 ng l^{-1}), nitrophenol (104 ng l^{-1}), DNOC (72 ng l^{-1}), cyanazin (68 ng l^{-1}) and hexazinon (68 ng l^{-1}). The similar findings for the drain station were isoproturon (129 ng l^{-1}), ethofumesate (112 ng l^{-1}), chloridazone (43 ng l^{-1}), bromoxynil (37 ng l^{-1}), nitrophenol (37 ng l^{-1}), pendimethalin (26 ng l^{-1}), 2,4-D (26 ng l^{-1}), bentazone (17 ng l^{-1}), metribuzin (12 ng l^{-1}) and MCPA (11 ng l^{-1}). Five of the pesticides detected in highest maximum concentrations were similar at the stream and drain station. However, the maximum concentration of pesticides was exceedingly higher in stream water than in tile drainage water.

Seven of the pesticides were detected in more than 25% of the water samples at the stream station in the Odderbæk catchment (Appendix 7.1). Of these seven pesticides the substances found most often at high concentrations as measured by the median concentration were isoproturon (59 ng l^{-1}), pendimethalin (14 ng l^{-1}), nitrophenol (7 ng l^{-1}), DNOC (4 ng l^{-1}) and terbuthylazine (4 ng l^{-1}). Three of the pesticides were detected in more than 25% of the water samples at the drain station in the Odderbæk catchment (Appendix 7.1). Of these three pesticides the substances found most often at high concentrations as measured by the median concentration were isoproturon (71 ng l^{-1}), bentazone (4 ng l^{-1}) and nitrophenol (4 ng l^{-1}). Isoproturon was the most frequently detected pesticide found at high concentrations at both the stream and drain station in the Odderbæk catchment.

7.3 Key pesticides detected in stream and drainage water

A number of key pesticides are selected for a more thorough presentation of their occurrence and concentration in Odderbæk during the study period. The selected pesticides represent six model pesticides chosen at an early stage of the project and other pesticides representing a combination of various active substances (herbicides, fungicides and insecticides) with different physico-chemical properties (see Table 6.4 in chapter 6).

The median and the range in the concentration of isoproturon in the different quarters of 1999 and 2000 are shown in Figure 7.6 for the stream station in Odderbæk catchment. The herbicide isoproturon was applied to different crop types within the catchment during the 4th quarter of 1998, 2nd and 4th quarters of 1999 and 3rd quarter of 2000, always in the highest quantities in the autumn.

No clear seasonal trends in the concentration of isoproturon could be detected (Fig. 7.6). Moreover, no major impacts on the concentration of isoproturon in stream water during the periods with application could be seen. However, the median concentration of isoproturon was generally lowest in the 1st quarter of 2000, which was without application and experienced the highest discharge and hence dilution effects.

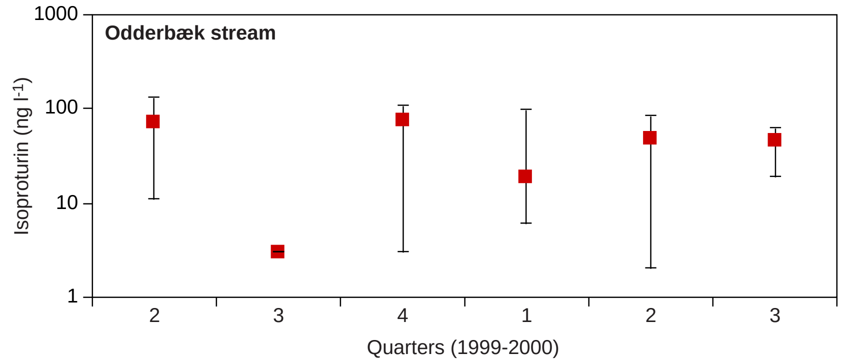


Figure 7.6. Minimum, median and maximum concentrations for the herbicide isoproturon at the stream monitoring station in the Odderbæk catchment during each quarter of the study period (2nd, 3rd, 4th 1999 and 1st, 2nd and 3rd 2000).
Figur 7.6. Minimum, median og maximum koncentrationer af herbicidet isoproturon ved vandløbsstationen i Odderbæk i hvert af kvartalerne gennem måleperioden (2,3 og 4 kvartal 1999 og 1,2 og 3 kvartal 2000).

The median and the range in the concentration of bentazone in the different quarters of 1999 and 2000 are shown in Figure 7.7 for the stream station in the Odderbæk catchment. The herbicide bentazone was only applied to different crop types within the catchment during the 2nd quarters of 1999 and 2000. A clear seasonal trend was obeserved with the highest median and maximum concentrations of bentazone during the 2nd quarters of 1999 and 2000 and the 3rd quarter of 1999. The median and the range in the concentration of bentazone were lowest in the 1st quarter of 2000. The seasonal trend in the concentration of bentazone thus followed the trend in applications in the catchment.

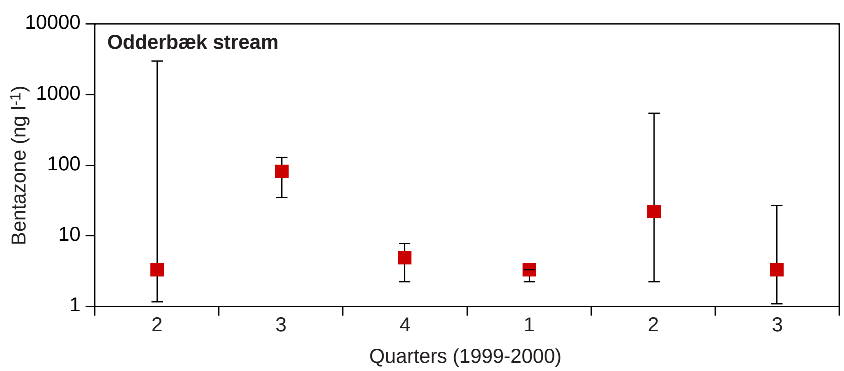


Figure 7.7. Minimum, median and maximum concentrations for the herbicide bentazone at the stream monitoring station in the Odderbæk catchment during each quarter of the study period (2nd, 3rd, 4th 1999 and 1st, 2nd and 3rd 2000).
Figur 7.7. Minimum, median og maximum koncentrationer af herbicidet bentazon ved vandløbsstationen i Odderbæk i hvert af kvartalerne gennem måleperioden (2,3 og 4 kvartal 1999 og 1,2 og 3 kvartal 2000).

The median and the range in the concentration of terbuthylazine in the different quarters of 1999 and 2000 are shown in Figure 7.8. The herbicide terbuthylazine was applied to different crop types within the catchment during the 2nd quarters of 1999 and 2000. No seasonal pattern was detected for terbuthylazine (Fig. 7.8). The median concentration of terbuthylazine was always very low. High maximum concentrations of terbuthylazine were, however, measured in the 2nd and 3rd quarters of 2000 (Fig. 7.8).

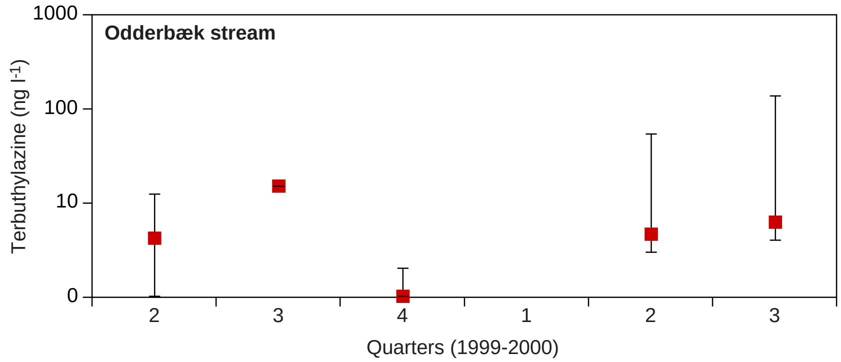


Figure 7.8. Minimum, median and maximum concentrations for the herbicide terbuthylazine at the stream monitoring station in the Odderbæk catchment during each quarter of the study period (2nd, 3rd, 4th 1999 and 1st, 2nd and 3rd 2000).
Figur 7.8. Minimum, median og maximum koncentrationer af herbicidet terbuthylazine ved vandløbsstationen i Odderbæk i hvert kvartal gennem måleperioden (2,3 og 4 kvartal 1999 og 1,2 og 3 kvartal 2000).

The median, 10 and 90 percentiles of the concentration of suspended sediment and key pesticides were calculated for days with more and less than 1 mm of precipitation. In this way, the measured concentrations of pesticides were dub-divided into periods with high and steady flow conditions at the stream station in the Odderbæk catchment during 2000. The number of water samples in the high-flow and low-flow data sets were 24 and 13, respectively.

The concentration of suspended sediment was marginally higher during days with high-flow than during days with steady-flow conditions at the stream station in the Odderbæk catchment (Fig. 7.9). Relatively high suspended sediment concentrations prevailed, however, during steady or decreasing flow conditions.

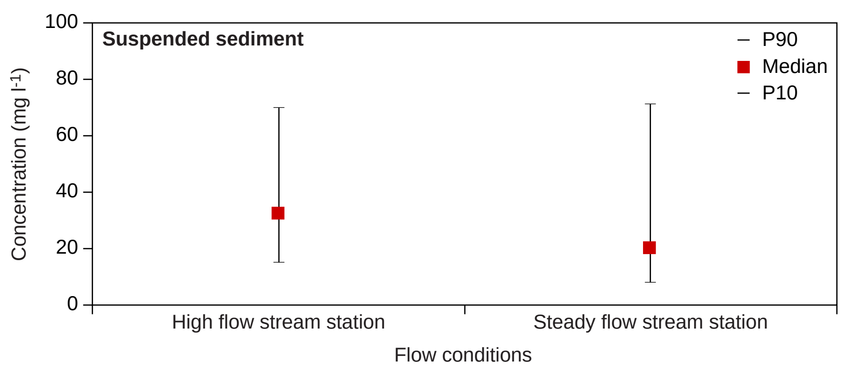


Figure 7.9. The concentration of suspended sediment during high flow (days > 1 mm precipitation) and steady flow periods (days < 1 mm precipitation) at stream station in the Odderbæk catchment.
Figur 7.9. Koncentrationen af suspenderet stof på prøvetagningsdage med stigende vandføring (nedbør > 1 mm) og prøvetagningsdage med stabil eller faldende vandføring ved vandløbsstationen i Odderbæk oplandet.

The concentration of isoproturon revealed a higher median and maximum concentration during high-flow periods than during steady-flow periods at the stream station in the Odderbæk catchment (Fig. 7.10). This pattern proposes that isoproturone must be readily available in source areas for being delivered to stream water during the rainy periods. One possibility is leaching from the soil column to upper groundwater and hence also subsurface drainage water in the tile drained parts of the catchment. High concentrations of bentazone were, however, measured in the Odderbæk during steady-flow periods (Fig. 7.10). Such a pattern could indicate that the herbicide was lost to the stream channel via wind drift during application in the catchment. In the case of terbythylazine, no large differences could be seen as the concentration range during either flow pattern was very narrow (Fig. 7.10).

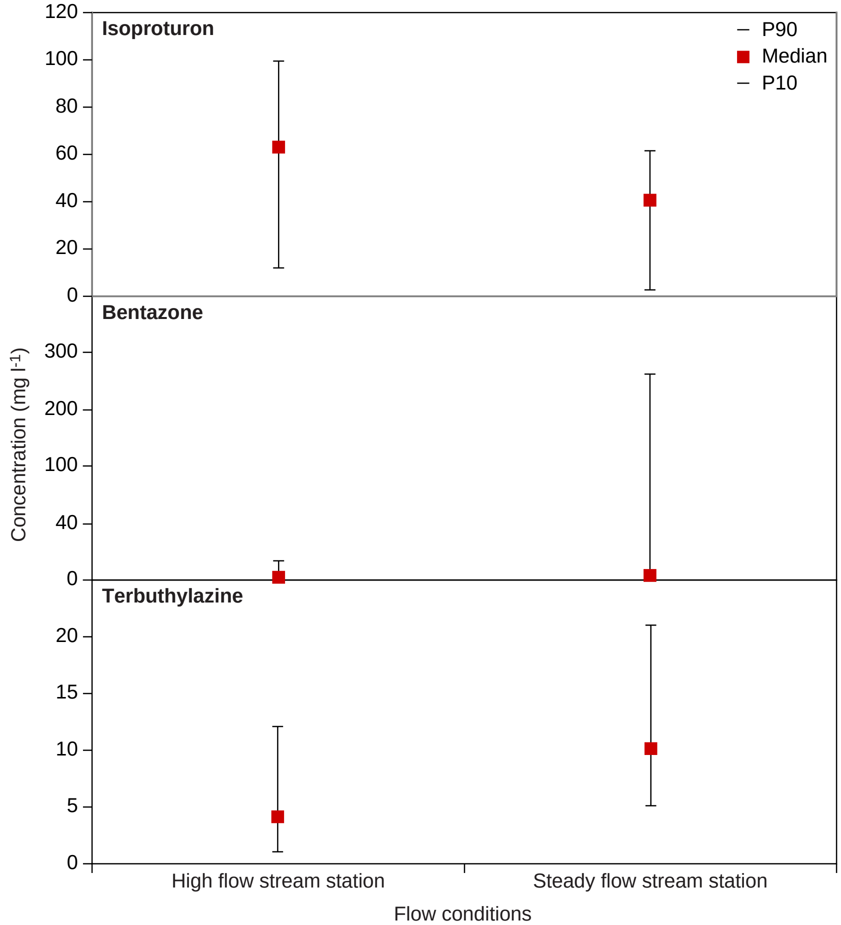


Figure 7.10. concentration of isoproturon, bentazone and terbuthylazine during high-flow (days > 1 mm precipitation) and steady-flow periods (days < 1 mm precipitation) at the stream station in the Odderbæk catchment.
Figur 7.10. Koncentrationen af isoproturon, bentazon og terbuthylazin på prøvetagningsdage med stigende vandføring (nedbør > 1 mm) og prøvetagningsdage med stabil eller faldende vandføring ved vandløbsstationen i Odderbæk oplandet.

The opposite pattern can be seen for pendimethaline, which experiences the highest concentrations during rainy periods (Fig. 7.11). The sorption coefficient for pendimethalin is high (Kd=70) and hence pendimethaline is readily sorbed and delivered and transported with particulate matter.

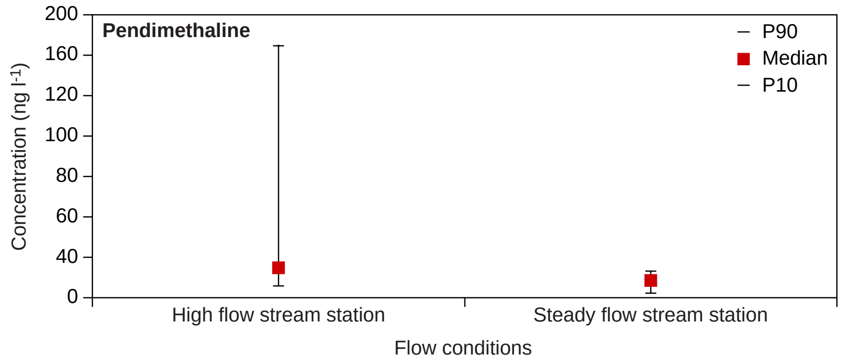


Figure 7.11. concentration of pendimethaline during high-flow (days > 1 mm precipitation) and steady-flow periods (days < 1 mm precipitation) at the stream station in the Odderbæk catchment.
Figur 7.11. Koncentrationen af pendimethalin på prøvetagningsdage med stigende vandføring (nedbør > 1 mm) og prøvetagningsdage med stabil eller faldende vandføring ved vandløbsstationen i Odderbæk oplandet.

7.4 Pesticides in suspended sediment

Composite suspended sediment samples were collected at a near monthly basis at the stream stations in Odderbæk with the SubMarie sampler (see chapter 4). The number of pesticides detected was one in two samples from December 1999 and January 2000 (Fig. 7.12). No pesticides were detected in suspended sediment sampled during March, April, July/August, October/November 2000 and November/January 2001, whereas three pesticides were detected in the sample from May 2000 and two pesticides in September 2000 (Fig. 7.12).

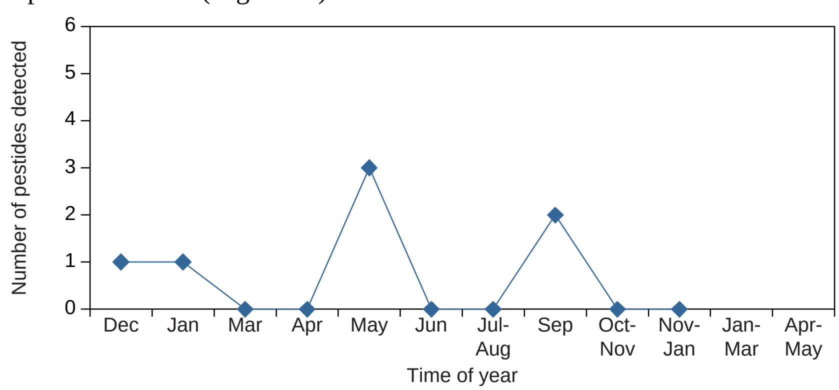


Figure 7.12. Number of pesticides detected in suspended sediment from the stream station in the Odderbæk catchment from December 1999 to January 2001.
Figur 7.12. Antallet af pesticider konstateret i suspenderet stof fra målestationen i Odderbæk gennem perioden marts 2000 til maj 2001.

The sum-concentration of pesticides in suspended sediment was highest in the suspended sediment sampled during May 2000 and September 2000 (Fig. 7.13). The sum-concentration in the sediment sample from May 2000 was 132 ng g^{-1} DW and 77 ng g^{-1} DW in September 2000. Pendimethalin was measured at the highest concentration of 100 ng g^{-1} DW in suspended sediment from May 2000, followed by diuron (40 ng g^{-1} DW) in the suspended sediment sample from September. Pendimethalin was detected in three of the nine suspended sediment samples, whereas diuron was detected in two samples and terbuthylazine in one sample. Pesticides recovered above the detection limit in suspended sediment at the stream station in Odderbæk were DDE-p,p, diuron, pendimethalin and terbuthylazine.

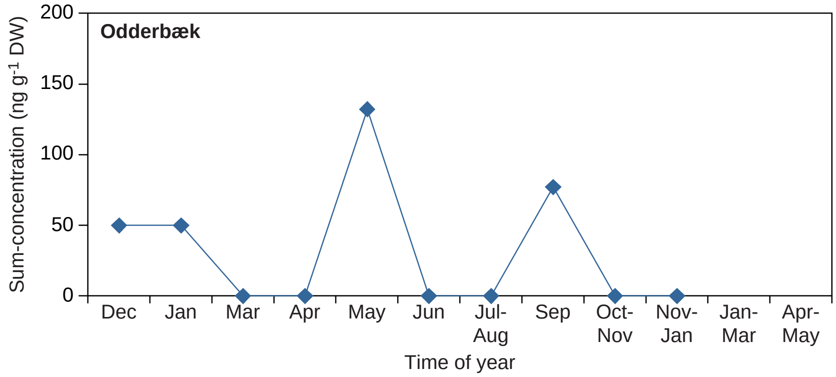


Figure 7.13. Sum-concentration of pesticides detected in suspended sediment from the stream station in Odderbæk catchment from December 1999 to January 2001.
Figur 7.13. Sum-koncentrationen af pesticider fundet i suspenderet stof fra vandløbs-stationen i Odderbæk oplandet fra december 1999 til januar 2001.

7.5 Pesticides in streambed sediment

None of the 17 pesticides analysed for in the five streambed sediment samples taken from the Odderbæk stream was measured above the detection limit. Sediment sampling was undertaken in April, June and August 1999 and May 15th and 29th 2000.

8 Application and loss of pesticides in the Lillebæk catchment

The transport of pesticides was calculated for the two stream stations during the periods with water sampling. The calculated transport of pesticides at the two stream stations is therefore a minimum estimate of the pesticides actually exported from the catchments. Moreover, the number of hours sampled varied between each quarter of the study period (Table 8.1). The second study year (2000) had nearly the same number of hours covered by sampling at the two stream stations and hence the transport estimate between the two stations can be compared. A relatively large number of hours were covered by water samples during the 2nd quarter of 2000 because a composite daily sampling was conducted during May and early June at both stations.

Table 8.1. Number of hours when water samples were taken and the percentage of time sampled at both stream stations in the Lillebæk catchment, and the mean daily discharge during each quarter at the downstream station (Fredsskovvej) in the Lillebæk catchment.
Tabel 8.1. Antallet af timer i de enkelte kvartalerne hvor der er udtaget vandprøver og beregnet transport af pesticider. Endvidere er tidsrummet dækket med prøvetagninger vist relativt sammen med den gennemsnitlige vandføring ved den nedstrøms station i Lillebæk oplandet.

Quarters	2nd	3rd	4th	1999	1st	2nd	3rd	4th	2000
Total hours sampled at the upstream station (Topenden)	122.0	81.5	130.5	334.0	34.0	877.0	82.0	77.0	1070.0
Percentage of time sampled	5.6%	3.7%	5.9%	5.1%	1.6%	40.2%	3.7%	3.5%	12.2%
Total hours sampled at the downstream station (Fredskovvej)	57.5	28.0	40.0	125.5	76.0	825.0	92.0	56.0	1049.0
Percentage of time sampled	2.6%	1.3%	1.8%	1.9%	3.5%	37.8%	4.2%	2.5%	12.0%
Mean discharge at the downstream station (Fredskovvej)	31 l/s	16 l/s	57 l/s	-	83 l/s	26 l/s	7 l/s	24 l/s	-

8.1 Application and loss of pesticides in the upstream culverted sub-catchment

8.1.1 Application and loss of pesticides in the upstream sub-catchment

A total of 18 different pesticides were applied during the investigated period, which was 2nd quarter of 1999 to 3rd quarter 2000 (see appendix 8.1). Although sampling initially started during the 2nd quarter of 1999, the application in the previous autumn is also included in Appendix 8.1. The total consumption of the 18 pesticides constituted approx. 171.0 kg active substances in the upstream sub-catchment of Lillebæk (Table 8.2).

The corresponding pesticide loss constituted approx. 33.6 g during the six quarters covered by water sampling (Table 8.2). The calculated pesticide loss is clearly a minimum estimate because of the low percentage of time covered by water sampling. A maximum estimate of pesticide loss can be obtained by a simple extrapolation of the measured loss to the total time within each quarter of the year. In this case, the pesticide loss constituted 516 g during the study period, which is believed to be a clear overestimate due to the focus on sampling during storm events. The minimum loss:applied ratio was 0.0196% and the maximum loss:applied ratio 0.302% for the 18 applied pesticides in the sub-catchment over the entire study period. Moreover, a minimum of approx. 3.4 g was calculated to be lost as metabolites from terbuthylazine and 8.0 g was lost from 30 pesticides and metabolites that were not applied during the study period.

Table 8.2. Applied pesticide quantity, loss of applied pesticides and their metabolites, and loss of 'old' pesticides in the upstream sub-catchment (Topenden) of the Lillebæk catchment.
Tabel 8.2. Udsprøjtede mængder af pesticider, beregnet minimumtab af de samme pesticider og deres metaboliter og det beregnede tab af 'gamle' pesticider i det opstrøms delopland i Lillebæk oplandet hvor vandløbet er rørlagt.

Quarters	2nd	3rd	4th	1999	1st	2nd	3rd	2000
Pesticides			Grammes active ingredients					
Applied quantity	47558	3964	55704	106956	112	61184	2270	63566
Loss of applied pesticides	5.46	1.264	15.337	22.061	0.494	11.641	0.372	12.507
Loss of metabolites to applied pesticides	0.645	0.311	1.111	2.067	0.169	0.778	0.148	1.095
Loss of old pesticides and metabolites	0.544	1.276	1.857	3.677	0.729	3.42	0.169	4.318

Table 8.2 shows the applied amount of 18 pesticides and the loss of these pesticides and their metabolites, together with the quarterly loss of other non-applied pesticides and their metabolites. Pesticide application was highest in the 2nd quarter of 2000 followed by the 4th quarter of 1999 and 2nd quarter of 1999. The estimated minimum loss of the applied pesticides was generally highest in the quarters of the years with high pesticide application irrespective of the runoff conditions (Table 8.1 and 8.2). In contrast, the loss of non-applied pesticides and metabolites in the upstream sub-catchment was almost equallly high in 1999 and 2000 (Table 8.2).

8.1.2 Total application, loss and loss ratio of the 18 pesticides applied in the upstream sub-catchment

Figure 8.1 shows the amount of the 18 different pesticides applied during the study period (2nd quarter 1999 to 3rd quarter 2000). The five pesticides with the largest application within the upstream sub-catchment were pendimethalin, fenpropimorph, metamitron, isoproturon and MCPA (Fig. 8.1).

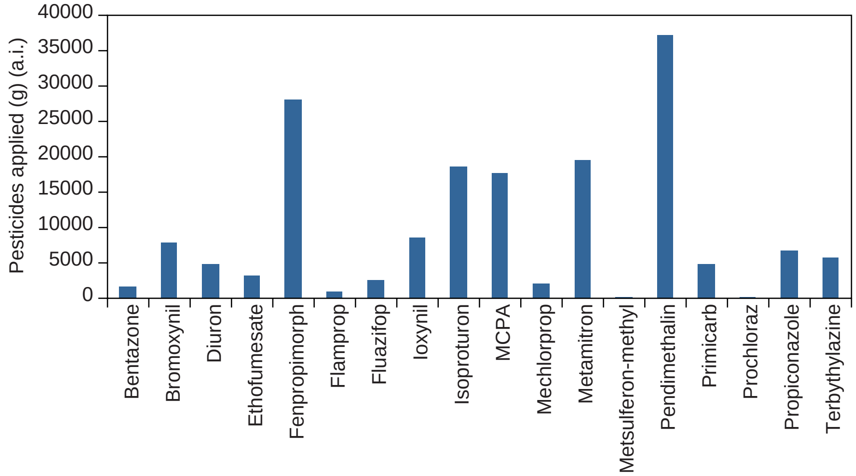


Figure 8.1. Pesticides applied in the upstream culverted sub-catchment of the Lillebæk during the study period (2nd quarter 1999 to 3rd quarter 2000).
Figur 8.1. Udsprøjtede mængder af pesticider i det opstrøms delopland i Lillebæk hvor vandløbet er rørlagt gennem måleperioden (2 kvartal 1999 til 3 kvartal 2000).

The calculated minimum loss of pesticides applied within the sub-catchment during the study period was highest for isoproturon followed by terbuthylazine, diuron, MCPA and pendimethalin (Fig. 8.2). All of these pesticides, except pendimethalin, have low sorption coefficients (K_d). The calculated loss of the other pesticides applied in the sub-catchment was low (Fig. 8.2).

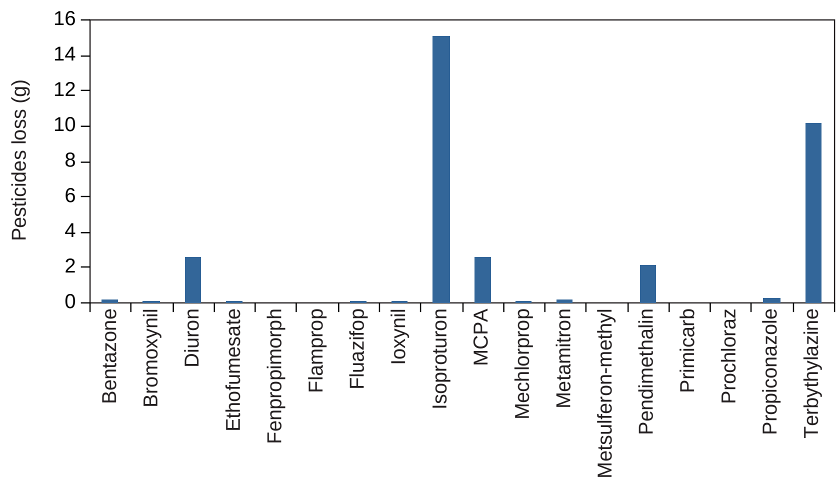


Figure 8.2. Calculated minimum loss of pesticides applied within the upstream culverted sub-catchment during the study period (2nd quarter 1999 to 3rd quarter 2000).
Figur 8.2. Beregnet minimum tab af pesticider som er anvendt i deloplandet gennem måleperioden (2 kvartal 1999 til 3 kvartal 2000).

The loss:applied ratio of pesticides was less than 1% for all of the 18 pesticides applied in the sub-catchment during the study period. The highest loss ratio was calculated for terbuthylazine (0.173%) followed by isoproturon (0.081%), diuron (0.053%), MCPA (0.015%) and bentazone (0.012%) (Fig. 8.3). The other 13 pesticides had a loss:applied ratio less than 0.01% (Fig. 8.3).

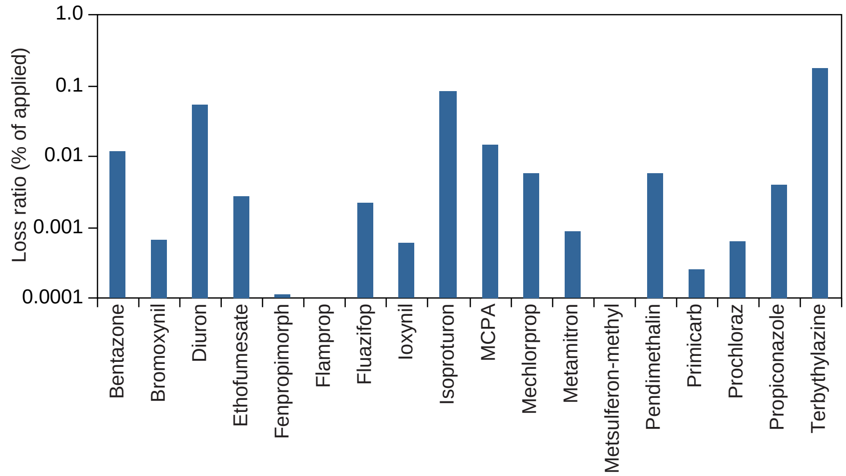


Figure 8.3. Loss ratio (calculated minimum loss/applied amount) of 18 pesticides used in the upstream culverted sub-catchment during the study period (2nd quarter 1999 to 3rd quarter 2000).
Figur 8.3. Beregnet minimums tabsrate (tab:anvendte mængder) af pesticider som er anvendt i deloplandet gennem måleperioden (2 kvartal 1999 til 3 kvartal 2000).

8.1.3 Loss of 'old' pesticides not applied within the upstream sub-catchment

The loss of several pesticides that were not registered as having been applied within the upstream sub-catchment of the Lillebæk has been calculated (Table 8.3 and appendix 8.2).

Table 8.3. Calculated minimum loss of pesticides (shown as total amount and per sampled hour), that were not registered as having been applied during the study period 1999-2000 in the upstream sub-catchment of the Lillebæk.
Tabel 8.3. Beregnet minimums tab af pesticider som ikke er registreret som udbragt I deloplande til Lillebæk gennem måleperioden. Det beregnede tab er vist som total mængde og som mængde pr. time dækket af prøvetagningen.

	1999	2000	1999	2000
	Grammes		mg/hour	
Atrazine	0.260	0.130	0.78	0.13
Atrazine (two metabolites)	0.396	0.271	1.19	0.27
BAM	0.189	1.051	0.57	1.06
Chlorsulfuron	1.087	0	3.25	0
Cyanazine	0.446	0.092	1.34	0.09
Dichlorprop	0.007	0	0.02	0
Dimethoate	0.008	0.022	0.02	0.02
DNOC	0.029	0.257	0.09	0.26
Hexazinone	0.490	0.381	1.47	0.38
Lenacil	0	0.156	0	0.16
Nitrophenol	0.144	1.540	0.43	1.55
Propyzamide	0.001	0.246	0.002	0.25
Simazine	0.648	0.053	1.94	0.05
Simazine (one metabolite)	0.091	0.002	0.27	0.002

Many of these pesticides have been banned for several years (see chapter 6). Consequently, these pesticides are more or less persistent and are still carried to the culverted stream with soil water or groundwater. For some of these 'old' pesticides, the calculated loss is comparable to the loss of the pesticides currently applied. A wind drift of these formerly applied pesticides can be ruled out. Therefore, a relationship to runoff conditions could be expected. However, the calculated loss of these 'old' pesticides experienced no consistent relationship to discharge conditions during the two study years. Mean daily discharge was higher in 1999 than in 2000, but the the most significant loss of six of the 'old' pesticides was calculated during 2000. This could, however, simply be explained by the higher number of hours sampled during 2000 than 1999. A comparison of the loss per sampled hour during the two years does, however, improve the relationship to runoff conditions (Table 8.3). The loss of pesticides with high sorption coefficients, such as atrazine, simazine and their metabolites was, however, exceedingly higher in the wet 1999 than in the dryer 2000.

8.1.4 Application and loss of key pesticides in the upstream sub-catchment during each quarter of the study period

Isoproturon was applied in the upstream sub-catchment of the Lillebæk in autumn 1998 before the measurements started during the 1st quarter of 1999 (Table 8.4). A new application of isoproturon took place in the 4th quarter of 1999. The calculated loss of isoproturon was nearly zero during the first three quarters of 1999 even though the period was wet and despite the application in the preceding autumn (Table 8.4). A major loss of isoproturon was calculated during the 4th quarter of 1999 following a high application in the sub-catchment (Table 8.4). Thereafter, the loss of isoproturon declined, except for the 2nd quarter of 2000. The increase in the loss of isoproturon during the 2nd quarter of 2000 is probably linked to the high percentage of sampling time (see Table 8.1). The loss of isoproturon to the culverted stream is therefore generally strongly linked to the application in the catchment.

Diuron was applied within the sub-catchment during the 2nd quarter of 1999 and 2000 (Table 8.4). Again, the calculated loss was highest during these two quarters with very small losses during the other quarters of the study period (Table 8.4).

Table 8.4. Application and calculated minimum loss of five selected key pesticides during each quarter of the study period, including the application in autumn 1998.
Tabel 8.4. Udsprøjtede mængder og beregnet minimum tab af fem udvalgte pesticider for hvert kvartal I perioden efterår 1998 til 3 kvartal 2000.

Quarters/ pesticides	3rd and 4th 1998	1st 1999	2nd 1999	3rd 1999	4th 1999	1st 2000	2nd 2000	3rd 2000
	Grammes active ingredients							
Isoproturon								
Applied	1550	0	0	0	18500	0	0	0
Loss	nd	nd	0.005	0.007	12.392	0.332	2.289	0.033
Terbuthylazine	34	1	2	3	4	1	2	3
Applied	0	0	2400	0	0	0	3500	0
Loss	nd	nd	3.524	0.411	0.854	0.123	5.075	0.217
Diuron	34	1	2	3	4	1	2	3
Applied	0	0	960	0	0	0	3840	0
Loss	nd	nd	1.000	0.037	0.008	0.005	2.472	0.036
Pendimethalin	34	1	2	3	4	1	2	3
Applied	4343	0	28	540	36470	0	120	0
Loss	nd	nd	0.011	0.039	2.018	0.021	0.072	0.004
MCPA	34	1	2	3	4	1	2	3
Applied	0	0	2205	0	0	0	15373	0
Loss	nd	nd	0.430	0.711	0.003	0	1.335	0.074

nd = not determined

Terbuthylazine was only applied in the 2nd quarter of 1999 and 2000 (Table 8.4). Accordingly, the calculated loss of terbuthylazine was highest during these two quarters with low losses during the other quarters of the study period (Table 8.4).

Pendimethalin was applied in the preceding autumn of the study period, a major application in the 4th quarter of 1999 and small applications in the 2nd quarter of 1999 and 2000 and the 3rd quarter of 1999. The calculated loss of pendimethalin was closely linked to the amount being applied during the study period, whereas no impact of the application in autumn 1998 could be seen on the loss during the first quarters of 1999 (Table 8.4).

MCPA was applied during the 2nd quarter of 1999 and 2000, the major application being in the 2nd quarter of 2000 (Table 8.4). The highest loss of MCPA was also calculated for the 2nd quarter of 2000, whereas the second highest loss was calculated for the 3rd quarter of 1999 (Table 8.4).

A consistent relationship seems to exist between the time of application and the calculated loss of the five key pesticides from the upstream culverted sub-catchment of Lillebæk. This relationship can only be explained by a loss of the applied pesticides through the soil column (presumably via tile drainage water), as losses via wind drift to the culverted stream can be excluded.

8.1.5 Modeling pesticide loss from the upstream sub-catchment

No significant relationship can be developed between the total consumption of the 18 pesticides used in the upstream culverted catchment and the total loss from the sub-catchment during the study period (2nd quarter of 1999 to 3rd quarter of 2000) (Fig. 8.4). Similarly, no significant relationship exists between the total loss of pesticides and the sorption coefficient measured as the median K_d value for each of the pesticides (Fig. 8.5).

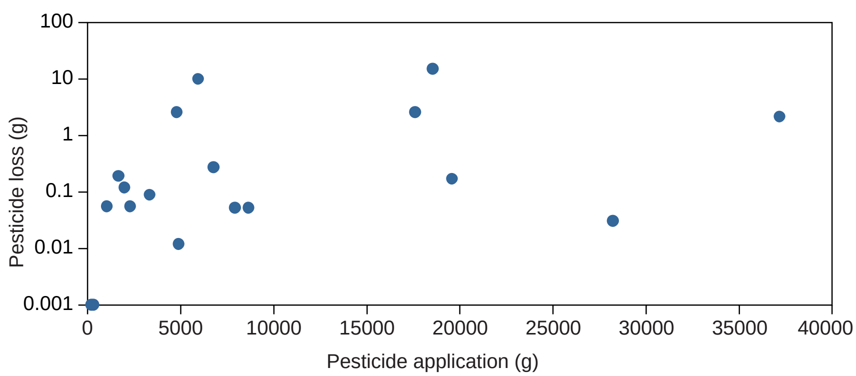


Figure 8.4. Relationship between calculated loss of 18 pesticides and the amount of pesticides applied in the upstream culverted sub-catchment of the Lillebæk during the study period.
Figur 8.4. Samplot mellem beregnet tab af 18 pesticider og de anvendte mængder af pesticider gennem måleperioden i det øvre delopland til Lillebæk.

A stepwise regression analysis revealed, however, that a relationship could be established between the pesticide loss (in grammes) and the application of pesticides in the catchment (in grammes), the sorption coefficient (K_d) and halflife of the pesticides in soil (DT_{50}). The equation is shown in (1):

$$\ln(P_{loss}) = -4.09 + 0.000213 \bullet P_{applied} + 0,0292 \bullet DT_{50} - 0.114 \bullet K_d \quad (1)$$

A total of 16 pesticides were included in the analysis as two pesticides were rejected from the analysis because of no loss, R^2 was 0.40 and $p = 0.12$.

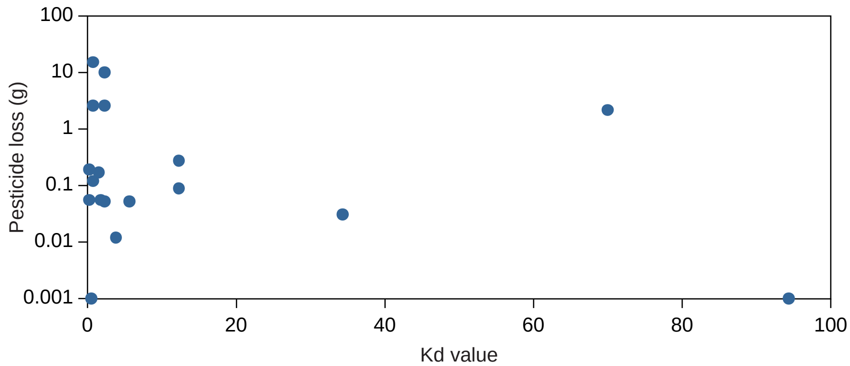


Figure 8.5. Relationship between pesticide loss and the sorption coefficient for each pesticide measured as the median K_d value.
Figur 8.5. Samplot mellem beregnet pesticidtab og sorptions koefficienten for hvert pesticide målt som median af K_d-værdier.

The established relationship links pesticide loss with pesticide application and the physico-chemical properties of each pesticide in spite of the variation in the number of water samples from the stream and hence variation in the time period covered within a quarter. One reason for the somewhat poor empirical relationship that was established could be the influence of point sources (pesticide-contaminated areas) in the upstream sub-catchment. Another reason could be that the chosen sampling strategy focused on sampling mainly during days with rain and high flows in the stream with the purpose of obtaining data for the dynamic model validation - a strategy, which may not be optimal for empirical modeling.

8.2 Application and loss of pesticides in the Lillebæk catchment as a whole

8.2.1 Overall application of pesticides and total loss of pesticides

The total applied amount of 18 pesticides in the entire 465 ha catchment of the Lillebæk was approx. 275.2 kg active ingredients from the 2nd quarter of 1999 to the 3rd quarter of 2000 (Table 8.5). A total of 21.1 g of the 18 pesticides applied in the catchment was as a minimum estimate lost from the entire catchment during the study period. The calculated pesticide loss is clearly a minimum estimate because of the low percentage of time covered by water sampling. A maximum estimate of pesticide loss can be obtained by a simple extrapolation of the measured loss to the total time within each quarter of the year. In this case, the pesticide loss constituted 286 g during the study period, which is believed to be a clear overestimate due to the focus on sampling during storm events. Moreover, 0.09 g simazine was lost from the catchment. Simazine was not applied in the upstream catchment but in the 1st quarter of 2000 in the downstream catchment. The minimum loss:applied ratio constituted 0.0074% and the maximum loss:applied ratio constituted 0,103% for all 18 pesticides in the Lillebæk catchment over the entire study period. Moreover, a minimum of 1.5 g of metabolites from terbuthylazine and

9.3 g of 28 pesticides and metabolites not applied were lost during the study period.

The applied amount of 18 pesticides and the loss of these pesticides, their metabolites and pesticides not applied during the study period are shown for each quarter in Table 8.5. The application was highest in the 2nd quarter of 1999 followed by the 2nd quarter of 2000 and 4th quarter of 1999. Simazine was also applied in the downstream sub-catchment with a total application of 800 g in the 3rd quarter of 1999 and 24,583 g in the 1st quarter of 2000. The estimated minimum loss of the 18 applied pesticides was generally highest in the quarters with the highest application, irrespectively of the runoff conditions (Table 8.1 and 8.5). An exception was the 2nd quarter of 1999 that had a large application of pesticides but a very small loss. The reason for this is possibly the very low number of hours covered by sampling (Table 8.1). The loss of pesticides and metabolites not applied within the catchment showed no relationships to runoff during the study period (Table 8.5).

Table 8.5. Applied amount of pesticides, loss of applied pesticides and their metabolites and loss of 'old' pesticides in the entire Lillebæk catchment of 465 ha.
Tabel 8.5. Udsprøjtede mængder af pesticider, beregnet minimum tab af de samme pesticider og deres metaboliter og det beregnede tab af 'gamle' pesticider i hele Lillebæk oplandet.

Quarters	2nd	3rd	4th	1999	1st	2nd	3rd	2000
Pesticides	Grammes active ingredients							
Applied amount of pesticides	91336	4219	84280	179835	6934	85988	2445	95367
Loss of applied pesticides	0.201	1.291	1.696	3.188	4.422	12.638	0.750	17.810
Loss of metabolites to applied pesticides	0.011	0.166	0.195	0.372	0.457	0.552	0.118	1.127
Loss of old pesticides and metabolites	0.081	0.427	1.305	1.813	3.397	3.913	0.419	7.729

8.2.2 Application, loss and loss ratio of 18 pesticides applied in the Lillebæk catchment as a whole

The 18 different pesticides applied in the entire Lillebæk catchment during the study period (2nd quarter 1999 to 3rd quarter 2000) are shown in Figure 8.6.

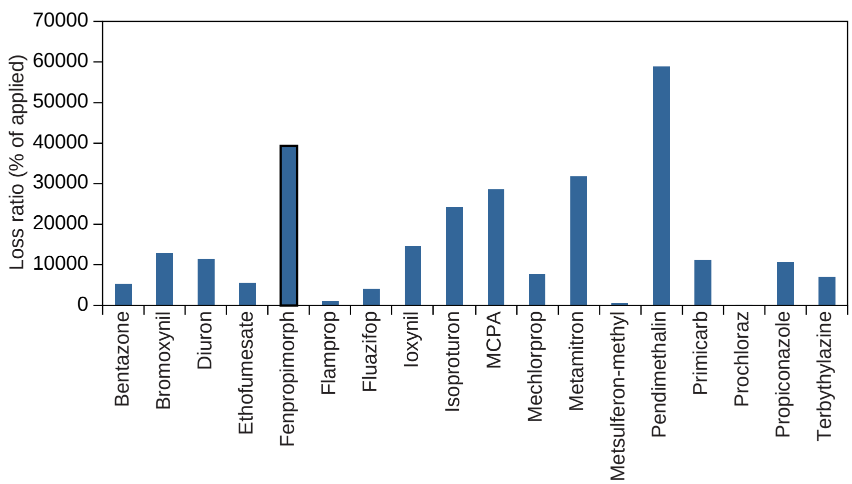


Figure 8.6. Pesticides applied in the entire Lillebæk catchment during the study period (2nd quarter 1999 to 3rd quarter 2000.
Figur 8.6. Udsprøjtede mængder af pesticider i hele Lillebæk oplandet gennem måleperioden (2 kvartal 1999 til 3 kvartal 2000).

The highest pesticide application within the catchment was reported for pendimethalin, fenpropimorph, metamitron, MCPA, isoproturon and ioxynil. Moreover, a considerable amount of simazine was applied (25.4 kg). The calculated minimum loss of pesticides applied within the sub-catchment during the study period was highest for isoproturon, MCPA, diuron, terbuthylazin and bentazone (Fig. 8.7). All of these pesticides have low sorption coefficients (K_d). The calculated loss of the other pesticides applied in the sub-catchment was generally low (Fig. 8.7).

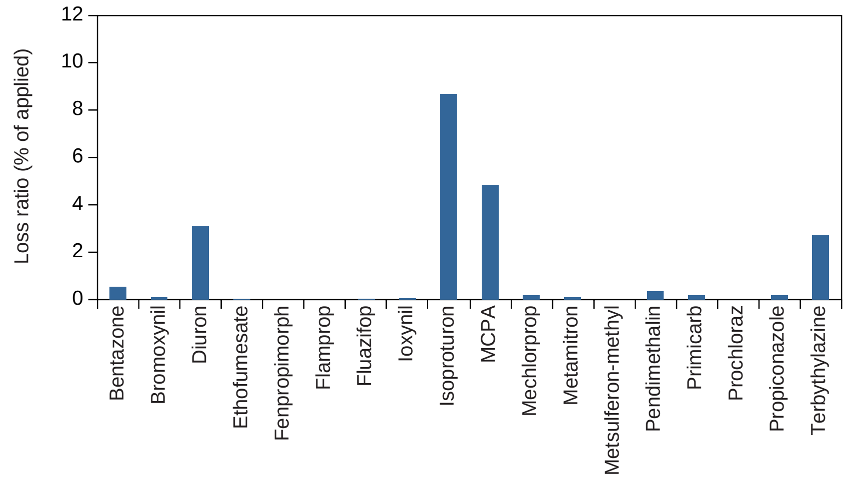


Figure 8.7. Calculated minimum loss of pesticides applied within the entire Lillebæk catchment during the study period (2nd quarter 1999 to 3rd quarter 2000).
Figur 8.7. Beregnet tab af pesticider som er anvendt I hele Lillebæk oplandet gennem måleperioden.

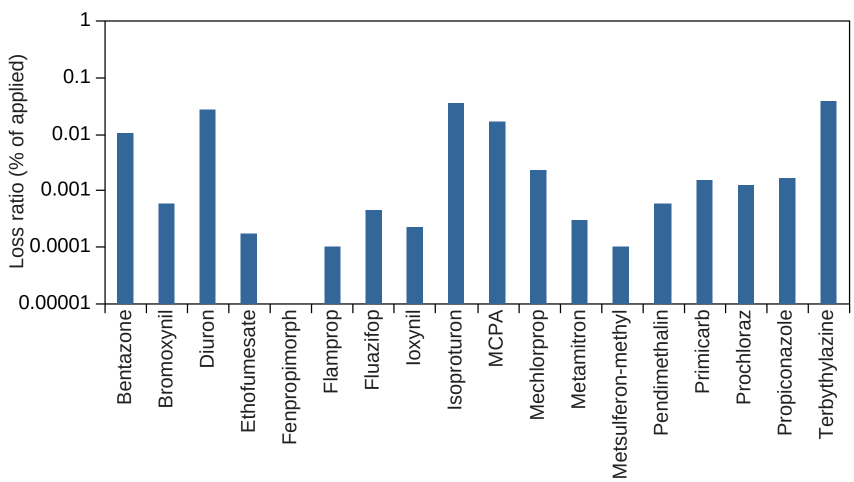


Figure 8.8. Loss ratio (calculated minimum loss/applied amount) of 18 pesticides used in the entire Lillebæk catchment during the study period (2nd quarter 1999 to 3rd quarter 2000).
Figur 8.8. Beregnet minimums tabsrate (tab:anvendte mængder) af pesticider som er anvendt i hele Lillebæk oplandet gennem måleperioden (2 kvartal 1999 til 3 kvartal 2000).

The loss:applied ratio of pesticides was less than 0.1% for all of the 18 compounds applied in the Lillebæk catchment during the study period. The highest loss:applied ratio was calculated for isoproturon (0.042%), tebuthylazine (0.027), diuron (0.027%), MCPA (0.018%) and bentazone

(0.0093%) (Fig. 8.8). The other 13 pesticides had a ratio less than 0.01% and in the case of simazine, the loss ratio was as low as 0.00043% (Fig. 8.8).

8.2.3 Loss of 'old' pesticides not applied within the Lillebæk catchment

A loss of several pesticides not registered as having been applied within the Lillebæk catchment has been calculated (Table 8.6 and appendix 8.4).

Table 8.6. Calculated minimum loss of pesticides that were not registered as being applied during the study period 1999-2000 in the entire Lillebæk catchment.
Tabel 8.6. Beregnet minimumstab af pesticider som ikke er registreret som udbragt I oplandet til Lillebæk gennem måleperioden..

	1999	2000
	Grammes	
Atrazine	0.020	0.285
Atrazine (two metabolites)	0.030	0.724
BAM	0.024	2.655
Chlorsulfuron	0	0
Cyanazine	0.255	0.095
Dichlorprop	0.001	0.064
Dimethoate	0	0
DNOC	0.315	0.225
Hexazinone	0.243	0.485
Lenacil	0	0.412
Nitrophenol	1.156	1.168
Propyzamide	0	1.122

Many of these pesticides have been banned for several years (see chapter 6). These pesticides are therefore more or less persistent and are still delivered to the culverted or open stream channel with soil water, groundwater or surface runoff. The calculated loss of some of the 'old' pesticides is comparable to the loss of the pesticides currently applied. However, in the case of chlorsulfuron and dimethoate, a loss was calculated from the upstream sub-catchment (see Table 8.3), whereas no loss was calculated from the catchment as a whole. This may indicate the importance of dilution of the pesticide concentration from the upstream station to the downstream station. Along this short distance the discharge increases more than does the catchment area, the increase being dependent on the season of the year. The increase in discharge will dilute the concentration measured at the upstream station and if the pesticides are not being delivered to the stream from the downstream catchment, it may actually fall below the detection limit. Another important factor could also be that pesticides are transformed during the passage through the stream channel.

8.2.4 Application and loss of key pesticides during each quarter of the study period in the Lillebæk catchment as a whole

Isoproturon was applied in the Lillebæk catchment in autumn 1998 before measuring started in the 1st quarter of 1999 (Table 8.7). Another application of isoproturon took place in the 4th quarter of 1999. The calculated loss of isoproturon was nearly zero during the first three quarters of 1999, irrespective of the period being wet and in spite of the application in the preceding autumn (Table 8.4). A major loss of isoproturon was calculated during the 4th quarter of 1999 following a high application in the sub-catchment (Table 8.4). Thereafter, the loss of isoproturon was high in the 1st and 2nd quarter of 2000 and declined again in the 3rd quarter. The increase in the loss of isoproturon during the 2nd quarter of 2000 can possibly be linked to the high percentage of the period of time that sampling was conducted (see Table 8.1). The loss of isoproturon to the stream is therefore generally linked to the application in the catchment.

Terbuthylazine was applied in the 2nd quarter of 1999 and 2000 (Table 8.7). The calculated loss of terbuthylazine was low in 1999, possibly because of the low number of sampling hours. The more thorough sampling conducted in 2000 revealed the highest loss of terbuthylazine in the 2nd quarter where the herbicide was applied in the catchment (Table 8.7).

Diuron was applied within the sub-catchment during the 2nd quarter of 1999 and the 1st and 2nd quarter of 2000 (Table 8.7). As for terbuthylazine, no relationship to application could be seen in 1999, whereas the calculated loss was highest during the 2nd quarter of 2000 (Table 8.7).

Pendimethalin was applied in the preceding autumn of the study period, a major application in the 4th quarter of 1999 and small applications in the 2nd quarter of 1999 and 2000 and the 3rd quarter of 1999. The calculated loss of pendimethalin was high in the 1st quarter of 2000 following the largest application in the 4th quarter of 1999 (Table 8.7). The loss of pendimethalin was very low in all other quarters.

MCPA was applied during the 2nd quarter of 1999 and 2000, the major application being in the 2nd quarter of 2000 (Table 8.7). The highest loss by far of MCPA was also calculated for the 2nd quarter of 2000 where sampling was also most frequent (Table 8.7).

A relationship seems to exist between the time of application and the calculated loss of the five key pesticides from the entire catchment in the Lillebæk, especially during 2000. The relationship is generally poorer than the relationship found for the upstream culverted part of the catchment. The main reason is possibly the few number of storm events sampled in 1999 due to malfunction of the automatic sampler. Sampling in 2000 was undisturbed and more reliable transport estimates were therefore obtained. The application and loss of pesticides from the upstream culverted sub-catchment and the downstream sub-catchment with an open stream channel can therefore be inter-compared in 2000.

Table 8.7. Application and calculated minimum loss of five selected key pesticides during each quarters of the study period, including the application in the autumn of 1998 for the entire Lillebæk catchment.
Tabel 8.7. Udsprøjtede mængder og beregnet minimum tab af fem udvalgte pesticider for hvert kvartal I hele Lillebæk oplandet for perioden efterår 1998 til 3 kvartal 2000.

Quarter/ pesticides	3rd and 4th 1998	1st 1999	2nd 1999	3rd 1999	4th 1999	1st 2000	2nd 2000	3rd 2000
Isoproturon								
Applied	2200	0	0	0	24300	0	0	0
Loss	nd	nd	0.001	0	1,318	3,397	3,760	0,204
Terbuthylazine								
Applied	0	0	3525	0	0	0	3500	0
Loss	nd	nd	0,073	0,153	0,014	0,481	1,583	0,406
Diuron								
Applied	0	0	960	0	0	6720	3840	0
Loss	nd	nd	0,004	0,787	0,001	0,037	2,225	0,049
Pendimethalin								
Applied	7260	0	1012	540	56420	0	880	0
Loss	nd	nd	0	0	0,036	0,309	0,014	0,007
MCPA								
Applied	0	0	6871	0	0	0	21748	0
Loss	nd	nd	0,003	0,173	0,220	0	4,420	0,023

nd = not determined

8.2.5 Modeling pesticide loss from the entire Lillebæk catchment

A relationship exists between the total applied amount of the 18 pesticides used in the entire catchment and the total loss from the catchment during the study period (2nd quarter of 1999 to 3rd quarter of 2000) (Fig. 8.9).

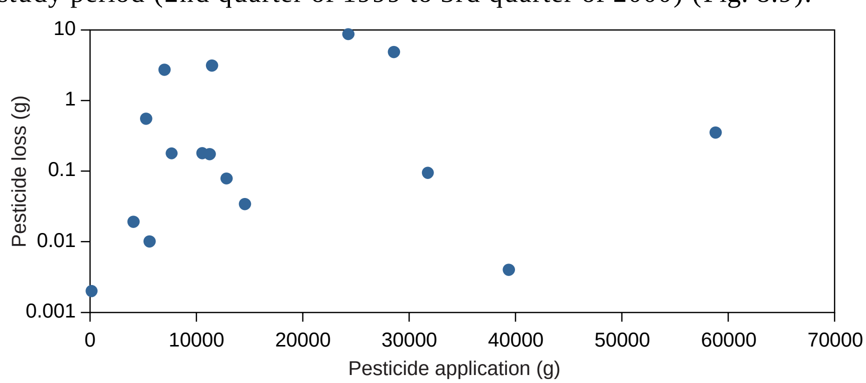


Figure 8.9. Relationship between calculated loss of 18 pesticides and the amount of pesticides applied in the entire Lillebæk catchment during the study period.
Figur 8.9. Samplot mellem beregnet tab af 18 pesticider og de anvendte mængder af pesticider gennem måleperioden i hele Lillebæk oplandet.

A weak relationship seems to exist also between the total loss of pesticides and the sorption coefficient measured as the median K_d value for each of the pesticides (Fig. 8.10).

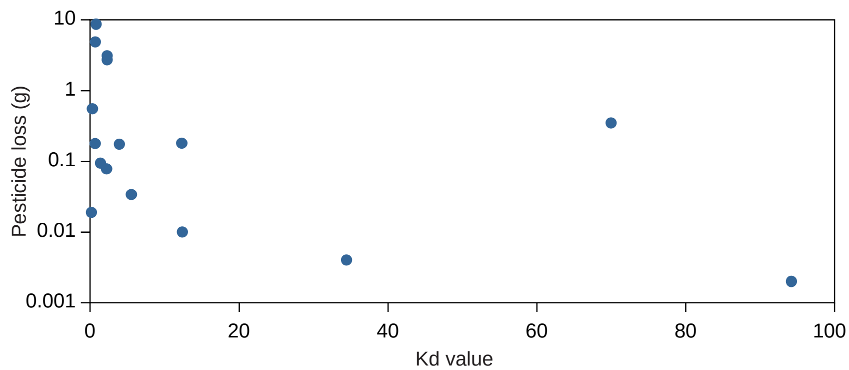


Figure 8.10. Relationship between pesticide loss and the sorption coefficient for each pesticide measured as the median K_d value for the entire Lillebæk catchment.
Figur 8.10. Samplot mellem beregnet pesticidtab og sorptionskoefficienten for hvert pesticide målt som median af K_d-værdier.

A stepwise regression analysis revealed that a significant relationship could be established between the pesticide loss (in grammes) and the application of pesticides in the catchment (in grammes), the sorption coefficient (K_d) and the half-life of the pesticide (DT_{50}), respectively. The equation is shown in (2):

$$\ln(P_{loss}) = -2.39 + 0.000079 \bullet P_{applied} - 0.0450 \bullet K_d \qquad (2)$$

A total of 16 pesticides were included in the analysis because two pesticides experienced no loss, R^2 is 0.45 and P = 0.037.

The established relationship links pesticide loss with pesticide application and the physico-chemical properties of each pesticide in spite of the variation in the number of water samples from the stream and hence variation in the period of time covered within a quarter. Another weakness in the sampling strategy for the purpose of establishing empirical relationships is the decision to take samples mainly on days with rain and high flows in the stream (especially during the first study year). A more consistent sampling strategy also covering the entire period might have improved the empirical relationship.

8.3 Comparison of pesticide application and loss from the two sub-catchments in the Lillebæk catchment

The application of 18 different pesticides from the 4th quarter of 1999 to the 3rd quarter of 2000 was calculated for the upstream culverted sub-catchment and the downstream open channel sub-catchment. The two sub-catchments are almost similar in catchment area, the upstream sub-catchment being 229 ha and the downstream sub-catchment 236 ha. The application, loss and loss ratio of the 18 pesticides are shown in Table 8.8 for the two sub-catchments and the entire Lillebæk catchment.

The application of pesticides was 1.5 times higher within the upstream culverted sub-catchment than in the downstream sub-catchment (Table 8.8). Fifteen pesticides were applied in the upstream sub-catchment as compared to 13 in the downstream sub-catchment (Fig. 8.11).

Table 8.8. Application, calculated loss and loss:applied ratio for two sub-catchments in the Lillebæk catchment: the upstream culverted and the downstream open channel during the year covering the 4th quarter of 1999 to the 3rd quarter of 2000.
Tabel 8.8. Udsprøjtede mængder af pesticider, beregnet tab og tabsrate for de to deloplande I Lillebæk oplandet, det opstrøms rørlagte og det nedstrøms med et åbent vandløbsforløb.

	Application	Loss	Loss ratio (loss/applied)
	Grammes active ingredients		
Upstream sub-catchment (culverted) (229 hectares)	119,270	27.844	0.0233%
Downstream sub-catchment (open channel) (236 hectares)	60,377	8.338	0.0138%
Entire Lillebæk catchment (465 hectares)	179,647	19.506	0.0109%

The calculated minimum loss of pesticides from the two sub-catchments was quite different, as it was more than 3 times higher from the upstream culverted sub-catchment than from the downstream open channel sub-catchment (Table 8.8). The loss ratio was therefore also almost two times higher for the upstream culverted sub-catchment than for the downstream open channel sub-catchment (Table 8.8).

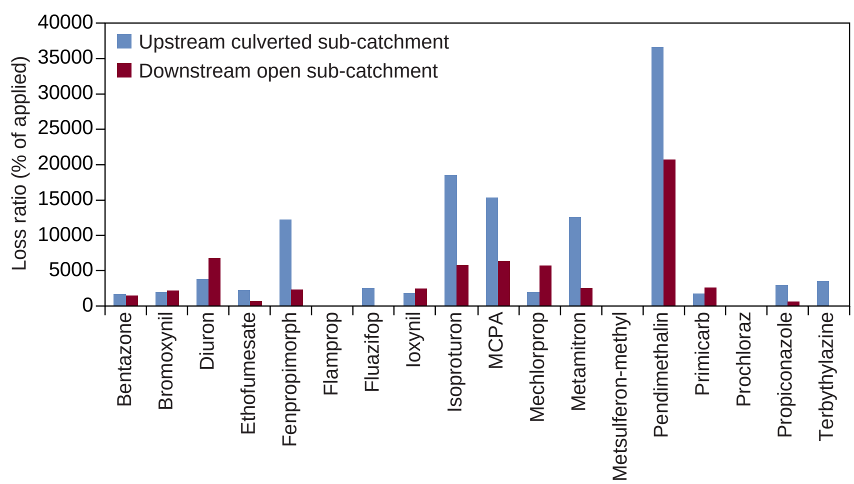


Figure 8.11. Pesticides applied in the upstream culverted sub-catchment and the downstream open channel sub-catchment of the Lillebæk during the year covering the 4th quarter of 1999 to the 3rd quarter of 2000.
Figur 8.11. Anvendte mængder af pesticider I de to deloplande af Lillebæk gennem et år fra 4 kvartal 1999 til 3 kvartal 2000.

The loss ratio of the different pesticides in the two sub-catchments is shown in Figure 8.12. Six pesticides were only lost from the upstream culverted sub-catchment although five of these were applied in both sub-catchments (Fig. 8.12). Four of these pesticides were, however, applied in a lower quantity in the downstream sub-catchment than in the upstream sub-catchment. As the applied amount seems to be exponentially related to the loss ratio (see section 8.1.5), this could explain the missing loss of these pesticides in the downstream sub-catchment. On the other hand, a higher amount of diuron was applied in the downstream sub-catchment than in the upstream sub-catchment and still no loss was calculated from the downstream sub-catchment (Fig. 8.12). The reason could be that diuron and maybe other of the pesticides are sorbed to particulate matter or taken up by biota in the open channel. This is supported by the findings of a strong increase in the diuron content in suspended sediment and streambed sediment at the upstream station during the spring spraying season April-June 2000 (see section 6.4 and 6.5).

Eight pesticides were lost from both sub-catchments (Fig. 8.12). The loss:applied ratio was higher for seven of these pesticides from the downstream sub-catchment than from the upstream sub-catchment. All of these pesticides, except pendimethalin, are very soluble and could be delivered to the downstream part of Lillebæk by groundwater which discharges more in the downstream sub-catchment than in the upstream sub-catchment (see chapter 5). Another explanation could be a higher application within the downstream sub-catchment than in the upstream sub-catchment. This was, however, only the case for four of the seven pesticides (see Fig. 8.11). Another explanation could be a loss of pesticides to the open channel via wind drift, a pathway that can be neglected in the upstream culverted sub-catchment.

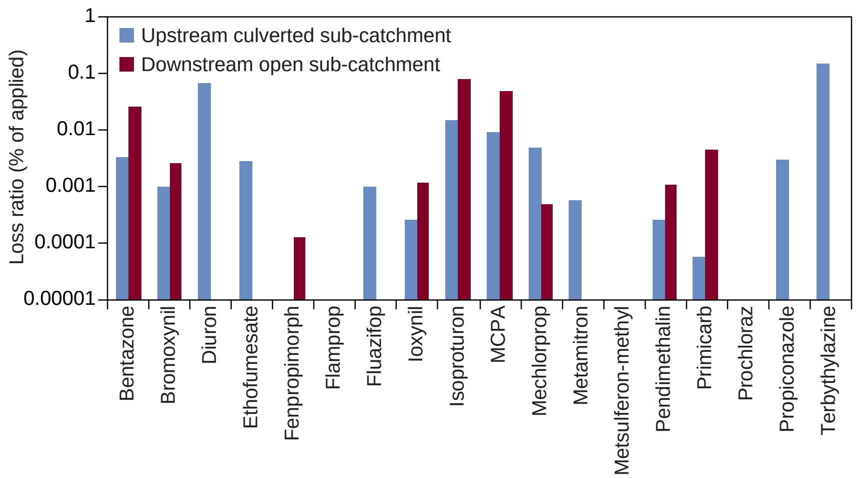


Figure 8.12. Loss:applied ratio for the upstream culverted sub-catchment and the downstream and open channel sub-catchment in the Lillebæk catchment during the year covering the 4th quarter of 1999 and the 3rd quarter of 2000.
Figur 8.12. Tabsrate (tab divideret med anvendt mængde) i det opstrøms rørlagte delopland og det åbne nedstrøms delopland iLillebæk gennem måleåret 4 kvartal 1999 til 3 kvartal 2000.

8.4 Pesticide loss in the 4th quarter 2000

The pesticide loss was also calculated for the 4th quarter of 2000 based on sampling of a few storm events (see Table 8.1). The loss of 18 applied pesticides per sampled hour was nearly as high in the 4th quarter of 2000 (0.081 g/h) as in the 4th quarter of 1999 (0.117 g/h) in the upstream culverted catchment. The 4th quarter of 1999 and 2000 experienced the highest loss per sampled hour than all other quarters of the year. The loss of 18 applied pesticides in the entire Lillebæk catchment were higher per sampled hour in 4th quarter 2000 (0.077 g/h) than in the 4th quarter 1999 (0.042 g/h). Nearly two thirds of the pesticide loss could be ascribed to the herbicide isoproturon, which possible also was applied in both catchments during the 4th quarter 2000.

The loss of old pesticides and metabolites was not very different from observations in the other quarters of the study period (Table 8.2, 8.5 and 8.9). The loss of metabolites to applied pesticides was, however, relatively high in the 4th quarter 2000 especially from the entire Lillebæk catchment.

Table 8.9. Applied amount of pesticides, loss of applied pesticides and their metabolites and loss of 'old' pesticides in the upstream culverted and entire Lillebæk catchment during 4th quarter 2000.
Tabel 8.9. Udsprøjtede mængder af pesticider, beregnet minimum tab af de samme pesticider og deres metaboliter og det beregnede tab af 'gamle' pesticider idet rørlagte opstrøms opland og hele Lillebæk oplandet.

4th quarter 2000	Lillebæk upstream culverted catchment	Lillebæk entire catchment
Monitoring time	77 hours	56 hours
Applied amount of pesticides	41,768 g	64,266 g
Loss of applied pesticides	6.301 g	4.302 g
Loss of metabolites to applied pesticides	0.811 g	0.767 g
Loss of old pesticides and metabolites	0.817 g	1.197 g

9 Application and loss of pesticides in the Odderbæk catchment

The transport of pesticides was calculated for the stream station during the periods with water sampling. The calculated transport of pesticides at the stream stations is therefore a minimum estimate of the pesticides actually exported from the catchment. Moreover, the estimate of pesticide transport does not reflect the same number of hours within each quarter of the two study years (Table 8.1).

9.1 Application and loss of pesticides in the catchment

9.1.1 Applied amount and loss of pesticides

A total of 18 different pesticides were applied during the investigated period, which was the 2nd quarter of 1999 to 3rd quarter 2000 (see appendix 9.1). Although sampling initially started in the 2nd quarter of 1999, the application in the previous autumn is also included in Appendix 8.1. The total applied amount of the 18 pesticides amounted to approx. 980.4 kg active ingredients in the Odderbæk catchment (Table 8.2). The corresponding pesticide loss constituted approx. 97.4 g for the six quarters covered by water sampling (Table 8.2). The calculated pesticide loss is a clear minimum estimate because of the low percentage of time covered by water sampling. A maximum estimate of pesticide loss can be obtained by a simple extrapolation of the measured loss to the total time within each quarter of the year. In this case, the pesticide loss amounted to 2295 g during the study period, which is clearly believed to be an overestimate due to the focus on sampling during storm events. The minimum loss:applied ratio was 0.0099% and the maximum loss:applied ratio 0.233% for the 18 applied pesticides in the catchment over the entire study period. Moreover, a minimum of approx. 0.6 g was calculated as being lost as metabolites from terbuthylazine, and 5.8 g was lost from 30 pesticides and metabolites that were not applied during the study period.

The applied amount of 18 pesticides and the loss of these pesticides and their metabolites, together with the loss of other non-applied pesticides and their metabolites are shown on at quarterly basis in Table 9.2. Pesticide application was highest in the 2nd quarter of 2000 followed by the 2nd quarter of 1999 and the 4th quarter of 1999. The estimated minimum loss of the applied pesticides was higher in the wet year of 1999 than in the somewhat dryer year of 2000 (Table 9.1 and 9.2). This pattern was not so evident for the loss of pesticides and metabolites that were not applied in the catchment during the study period (Table 8.2).

Table 9.1. Number of hours when water samples were taken and the percentage of time sampled at the stream station in the Odderbæk catchment. The table also shows mean daily discharge during each quarter.
Tabel 9.1. Antallet af timer i de enkelte kvartalerne hvor der er udtaget vandprøver og beregnet transport af pesticider. Endvidere er tidsrummet dækket med prøvetagninger vist relativt sammen med den gennemsnitlige vandføring ved den vandløbsstationen i Odderbæk oplandet.

Quarter	2nd	3rd	4th	1999	1st	2nd	3rd	2000
Total hours sampled at the stream station	122.0	28.0	98.0	248.0	76.0	78.0	30.0	184.0
Percentage of time sampled	5.6%	1.3%	4.4%	3.8%	3.5%	3.5%	1.4%	2.8%
Mean discharge at the stream station	94 l/s	65 l/s	103 l/s	-	165 l/s	78 l/s	55 l/s	-

Table 9.2. Applied amount of pesticides, loss of applied pesticides and their metabolites and loss of 'old' pesticides in the Odderbæk catchment.
Tabel 9.2. Udsprøjtede mængder af pesticider, beregnet minimum tab af de samme pesticider og deres metaboliter og det beregnede tab af 'gamle' pesticider i Odderbæk.

Quarters	2nd	3rd	4th	1999	1st	2nd	3rd	2000
Pesticides	Grammes active ingredients							
Applied amount of pesticides	306,740	4951	201,515	513,206	0	396,125	71,082	467,207
Loss of applied pesticides	72.158	6.314	9.768	88.240	3.285	4.954	0.885	9.124
Loss of metabolites to applied pesticides	0.053	0.348	0.120	0.521	0	0.070	0.066	0.136
Loss of old pesticides and metabolites	0.708	2.285	1.218	4.121	0.128	0.943	0.586	1.657

9.1.2 Total application, loss and loss ratio of the 18 pesticides applied in the sub-catchment

The 18 different pesticides applied during the study period (2nd quarter 1999 to 3rd quarter 2000) are shown in Figure 8.1. The five pesticides with the highest application within the catchment were pendimethalin, isoproturon, bentazone, terbuthylazine and fenpropimorph (Fig. 9.1).

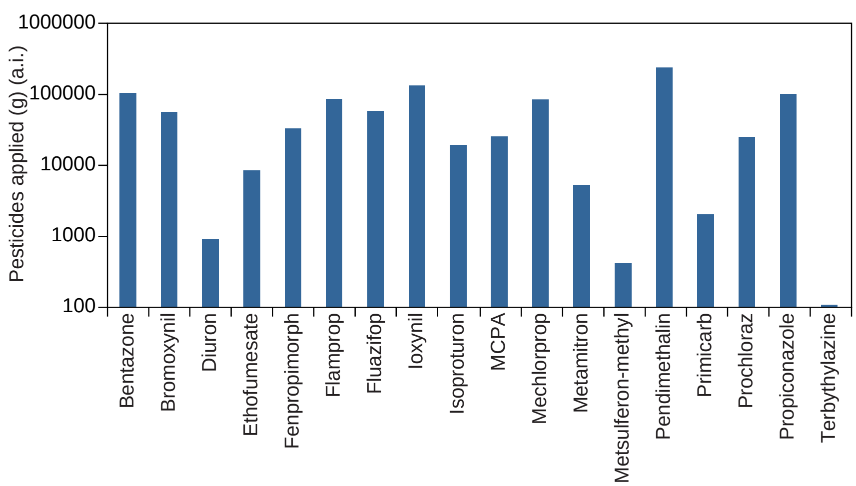


Figure 9.1. Pesticides applied in the Odderbæk catchment during the study period (2nd quarter 1999 to 3rd quarter 2000.
Figur 9.1. Udsprøjtede mængder af pesticider i Odderbæk oplandet gennem måleperioden (2 kvartal 1999 til 3 kvartal 2000).

The calculated minimum loss of pesticides applied within the catchment during the study period was highest for bentazone followed by isoproturon, pendimethalin, terbuthylazine and propiconazole (Fig. 9.2). Bentazone and isoproturon both have low sorption coefficients (K_d). The calculated loss of the other pesticides applied in the catchment was low (Fig. 9.2).

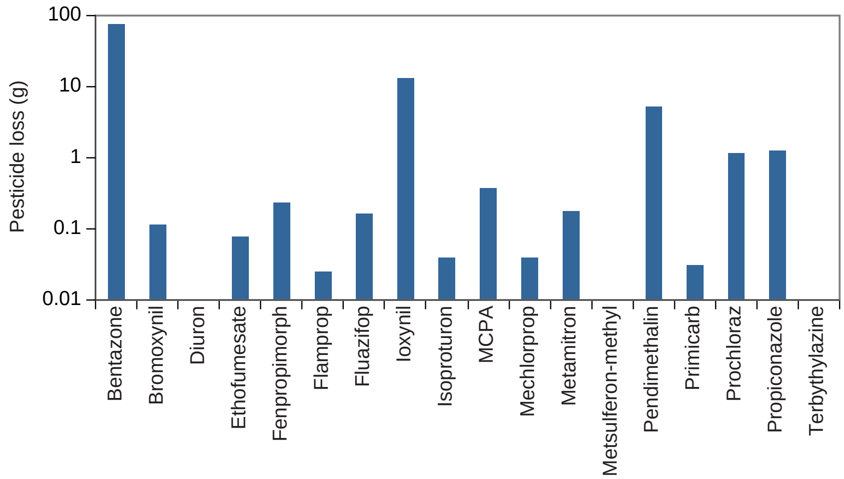


Figure 9.2. Calculated minimum loss of pesticides applied within the Odderbæk catchment during the study period (2nd quarter 1999 to 3rd quarter 2000).
Figur 9.2. Beregnet minimum tab af pesticider som er anvendt i deloplandet gennem måleperioden (2 kvartal 1999 til 3 kvartal 2000).

The loss:applied ratio of pesticides was less than 1% for all of the 18 pesticides applied in the sub-catchment during the study period. The highest loss ratio was calculated for bnetazone (0.072%) followed by isoproturon (0.0098%), propiconazole (0.0046%), metribuzin (0.0033%) and metsulfuron (0.0024%) (Fig. 9.3).

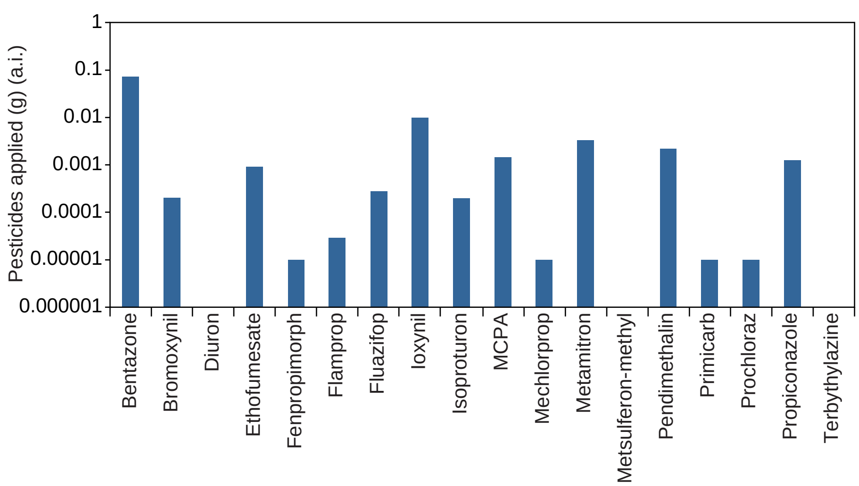


Figure 9.3. Loss ratio (calculated minimum loss/applied amount) of 18 pesticides used in the Odderbæk catchmen during the study period (2nd quarter 1999 to 3rd quarter 2000).
Figur 9.3. Beregnet minimums tabsrate (tab:anvendte mængder) af pesticider som er anvendt i Odderbæk oplandet gennem måleperioden (2 kvartal 1999 til 3 kvartal 2000).

9.1.3 Loss of 'old' pesticides not applied within the sub-catchment

A loss of several pesticides not registered as having been applied in the Odderbæk catchment has been calculated (Table 9.3 and appendix 9.2). Many of these pesticides have been banned for several years (see chapter 6). These pesticides are therefore more or less persistent and are still carried to the stream with soil water or groundwater. For some of these 'old' pesticides, the calculated loss is comparable to the loss of the pesticides currently being applied. A wind drift of these previously applied pesticides can be ruled out. A relationship with runoff conditions could therefore be expected. The calculated loss of these 'old' pesticides experienced a relationship with discharge conditions during the two study years. Mean daily discharge was higher in 1999 than in 2000 and the pesticide loss was also generally higher in 1999 than in 2000 (Table 9.3).

Table 9.3. Calculated minimum loss of pesticides (shown as total amount and per sampled hour) that were registered as not having been applied during the study period 1999-2000 in the Odderbæk catchment.
Tabel 9.3. Beregnet minimums tab af pesticider som ikke er registreret som udbragt I oplandet til Odderbæk gennem måleperioden. Det beregnede tab er vist som total mængde og som mængde pr. time dækket af prøvetagningen.

	1999	2000
	Grammes	
Atrazine	0.039	0.013
Atrazine (three metabolites)	0.174	0.091
BAM	0.163	0.082
Chlorsulfuron	0	0
Cyanazine	0	0.055
Dichlorprop	0.039	0
Diuron	1.265	0.555
DNOC	0.268	0.424
Hexazinone	0.709	0.381
Lenacil	0	0
Nitrophenol	0.829	0.211
Propyzamide	0.006	0
Simazine	0.039	0
Simazine (one metabolite)	0.309	0

9.1.4 Application and loss of key pesticides in each quarter of the study period

Isoproturon was applied during several quarters of the study period in the Odderbæk catchment (Table 9.4). The loss of isoproturon is generally linked to the application in the catchment, as the loss of isoproturon increases in quarters with application and decreases in quarters with no application (Table 9.4).

Table 9.4. Application and calculated minimum loss of five selected key pesticides in each quarter of the study period including the application in autumn 1998.
Tabel 9.4. Udsprøjtede mængder og beregnet minimum tab af fem udvalgte pesticider for hvert kvartal i perioden efterår 1998 til 3 kvartal 2000.

Quarter/ Pesticides	3rd and 4th 1998	1st 1999	2nd 1999	3rd 1999	4th 1999	1st 2000	2nd 2000	3rd 2000
	Grammes active ingredients							
Isoproturon								
Applied	31,928	0	8250	0	92,795	0	0	32,310
Loss	nd	1.479	2.135	0.116	6.791	2.944	0.817	0.399
Terbuthylazine								
Applied	0	0	41186	0	0	0	598838	0
Loss	nd	0	0.126	0.580	0.051	0	0.186	0.320
Bentazone								
Applied	0	0	42942	0	0	0	61799	0
Loss	nd	0.049	66.965	4.613	0.274	0.184	3.146	0.096
Pendimethalin								
Applied	87916	0	47412	0	105568	0	44990	38772
Loss	nd	0	1.908	0.116	2.494	0.054	0.639	0.052
MCPA								
Applied	0	0	15267	0	0	0	10073	0
Loss	nd	0	0	0.193	0	0	0.147	0.029

nd = not determined

Bentazone was applied within the catchment during the 2nd quarter of 1999 and 2000 (Table 9.4). The calculated loss was high during these two quarters and the highest bentazone loss was calculated in the wet 2nd quarter of 1999, followed by the 3rd quarter of 1999 and 2nd quarter of 2000 (Table 9.4). In all other quarters the loss of bentazone was very low.

Pendimethalin was applied in several quarters of the year and was always followed by an increase in the loss (Table 9.4). The calculated loss of pendimethalin was therefore closely linked to the amount applied during the study period, although the application in autumn 1998 was not reflected in the loss during the first quarters of 1999 (Table 9.4).

Terbuthylazine was only applied in the 2nd quarter of 1999 and 2000 (Table 9.4). The calculated loss of terbuthylazine was, however, highest during the 3rd quarter (Table 9.4).

MCPA was applied during the 2nd quarter of 1999 and 2000 (Table 9.4). The highest loss of MCPA was calculated for the 3rd quarter of 1999 and the second highest loss was calculated for the 2nd quarter of 2000 (Table 9.4).

On a quarterly basis, there seems to be a general relationship between the time of application and the calculated loss of the five key pesticides from the catchment of Odderbæk. This relationship can be explained by a loss of the applied pesticides through the soil column. Wind drift could also be a possible source of pesticides to surface water, but in the case of MCPA and terbuthylazine, the major pesticide loss was calculated for the quarter following the actual pesticide application.

9.1.5 Modeling pesticide loss from the catchment

A relationship seems to exist between the total applied amount of the 18 pesticides used in the Odderbæk catchment and the total loss from the catchment during the study period (2nd quarter of 1999 to 3rd quarter of 2000) (Fig. 9.4). Thus, the pesticide loss generally increases with increased application. A somewhat weaker inverse relationship seems to exist between the total loss of pesticides and the sorption coefficient measured as the median K_d value for each of the pesticides (Fig. 9.5).

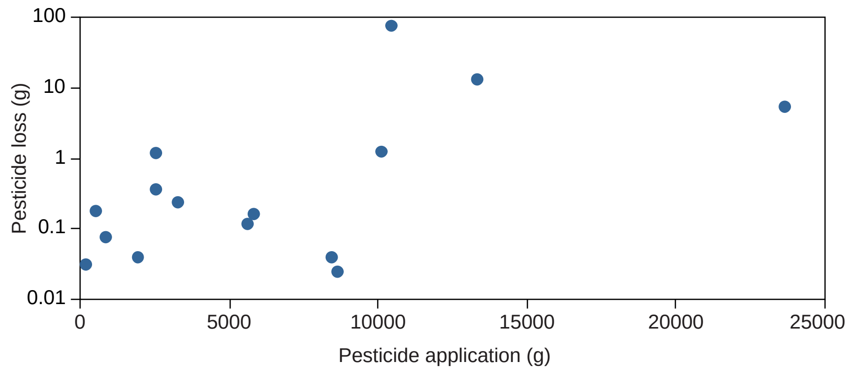


Figure 9.4. Relationship between calculated loss of 18 pesticides and the amount of pesticides applied in the Odderbæk catchment during the study period.
Figur 9.4. Samplot mellem beregnet tab af 18 pesticider og de anvendte mængder af pesticider gennem måleperioden i Odderbæk oplandet.

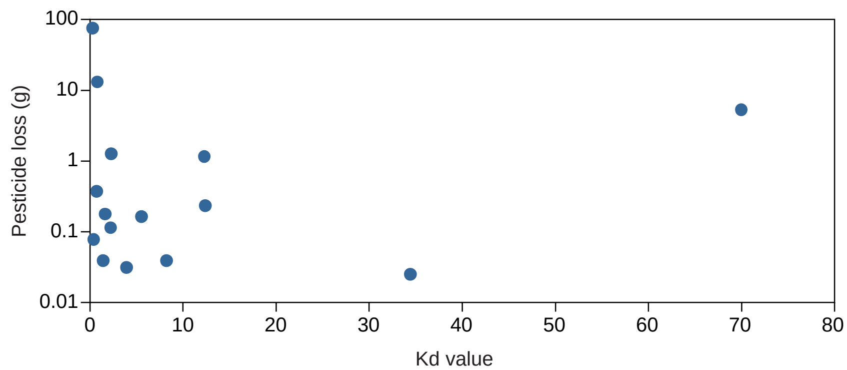


Figure 9.5. Relationship between pesticide loss and the sorption coefficient for each pesticide measured as the median K_d value.
Figur 9.5. Samplot mellem beregnet pesticidtab og sorptions koefficienten for hvert pesticide målt som median af K_d-værdier.

A stepwise regression analysis revealed that a significant relationship could be established between the pesticide loss (in grammes) and the application of pesticides in the catchment (in grammes), the sorption coefficient (K_d) and the halflife (DT_{50}). The equation is shown in (1):

$$\ln(P_{loss}) = -3.57 + 0.000038 \bullet P_{applied} + 0.0221 \bullet DT_{50} - 0.0501 \bullet K_d \qquad (1)$$

The number of pesticides in the analysis is 16, R^2 is 0.60 and $p = 0.014$.

The established relationship links pesticide loss with pesticide application and the physico-chemical properties of each pesticide in spite of the variation in the number of water samples from the stream and hence variation in the period of time covered within a quarter.

10 Linking application and hydrology in the catchment to pesticide concentration in stream water

This chapter describes the results of an intensive, composite daily sampling (hourly water samples) conducted at the two stream stations in Lillebæk from 2-3 May to 6-7 June 2000. The aim of this intensive sampling survey was to investigate more closely the concentration of pesticides in stream water during the main spraying season (spring) and the pathways for pesticides in the two sub-catchments. Morever, the chapter includes an analysis of pesticide concentration response to rain in the Lillebæk and Odderbæk streams. The intensive sampling period in May/June 2000 comprised 36 consecutive days of sampling. At the downstream station, only two days were missing in the time series due to a failure in the pesticide analysis process.

10.1 Application of pesticides in the Lillebæk catchment in May/June 2000

Table 10.1 shows the application date and the amount of isoproturon, MCPA, diuron, bentazone, propiconazole, pirimicarb and fenpropimorph applied onto the fields within the two sub-catchments during the investigated period.

Table 10.1. Date and amount of selected pesticides applied in the upstream and downstream sub-catchments in the Lillebæk catchment during the investigated period 2nd May to 7th June 2000.
Tabel 10.1. Dato og mængden af udbragte pesticider i de to deloplande i Lillebæk oplandet igennem perioden 2 maj til 7 juni 2000.

Date of application	Upstream culverted sub-catchment	Date of application	Downstream open channel sub-catchment
25st April	0.6 ha with 1200 g Terbuthylazine		
25st April	0.6 ha with 640 g Diuron		
2nd May	0.3 ha with 37.5 g Bentazone	12th May	0.8 ha with 750 g MCPA
17th May	2.2 ha with 1584 g Bentazone	5th June	3.7 ha with 2775 g MCPA
2nd May	0.3 ha with 11.25 g MCPA	12th May	11.4 ha with 1500.24 g Pirimicarb
12th May	11.9 ha with 8925 g MCPA	5th June	3.7 ha with 185 g Pirimicarb
2nd May	2.7 ha with 101.25 g Propiconazol	5th May	1.6 ha with 80 g Propiconazol
4th May	7.7 ha with 673.9 g Propiconazol	17th May	3.7 ha with 138.75 g Propiconazol
5th May	12.0 ha with 450 g Propiconazol	22nd May	1.3 ha with 65 g Propiconazol
17th May	10.5 ha with 364.38 g Propiconazol	5th May	1.6 ha with 240 g Fenpropimorph
1st May	2.0 ha with 2300 g Terbuthylazine	12th May	2.8 ha with 189 g Fenpropimorph
1st May	2.0 ha with 3200 g Diuron	15th May	6.7 ha with 445.5 g Fenpropimorph
2nd May	2.7 ha with 243 g Fenpropimorph	17th May	3.7 ha with 416.25 g Fenpropimorph
4th May	17.8 ha with 3226 g Fenpropimorph	22nd May	1.3 ha with 156 g Fenpropimorph
10th May	8.6 ha with 258 g Fenpropimorph		
12th May	30.9 ha with 1593 g Fenpropimorph		
15th May	4.6 ha with 310.5 g Fenpropimorph		
17th May	10.5 ha with 901.5 g Fenpropimorph		

10.2 Precipitation and discharge in Lillebæk during the investigated period

Total precipitation constituted 60.2 mm during the 37-day investigation period from 2 May to 7 June 2000. The first two weeks were dry followed by several days with precipitation at the end of May and in early June (Fig. 10.1).

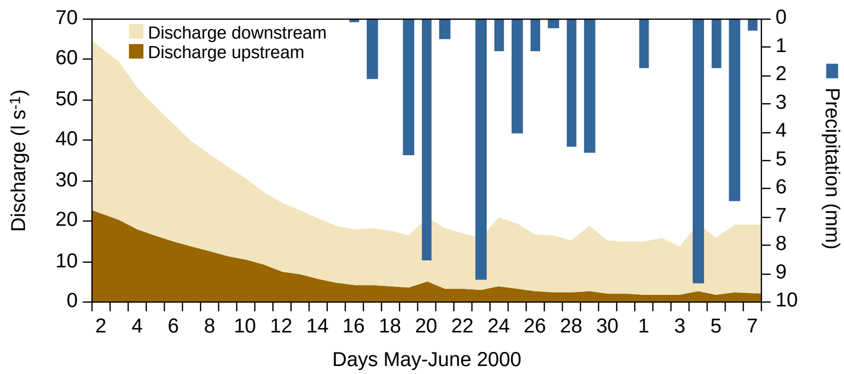


Figure 10.1 Daily precipitation and daily mean discharge at the upstream and downstream station in the Lillebæk catchment during the investigated period in May and early June 2000. Note that precipitation is plotted as a diurnal sum from 8 a.m. to 8 a.m the following day.
Figur 10.1 Daglig nedbør og afstrømning ved de to målestationer i Lillebæk oplandet gennem perioden 2 maj til 7 juni 2000. Bemærk af nedbør er målt fra kl. 08.00 til 08.00 den følgende dag.

The average discharge was 6.5 l/s at the upstream station and 18.4 l/s at the downstream station during the 36-day investigation period. The changes in daily mean discharge reflected the precipitation pattern during the period. Daily mean discharge experienced a general decrease at both the upstream and downstream monitoring station during the investigated period (Fig. 10.1). Precipitation events on the 19-21 May, 23-24 May, 28 May, 3 June and 5-6 June were followed by small increases in discharge (Fig. 10.1).

10.3 Concentration of the herbicide isoproturon at the two stream stations in Lillebæk

Isoproturon was not applied during the 2nd Quarter of 2000 and hence not in the period investigated. The latest application of isoproturon took place in October 1999. The average concentration of isoproturon was 85 ng/l at the upstream station and 69 ng/l at the downstream station during the 36-day study period. The concentration of isoproturon revealed no clear relationship to discharge when considering the hydrograph and the chemograph at the upstream and downstream stations (Fig. 10.2).

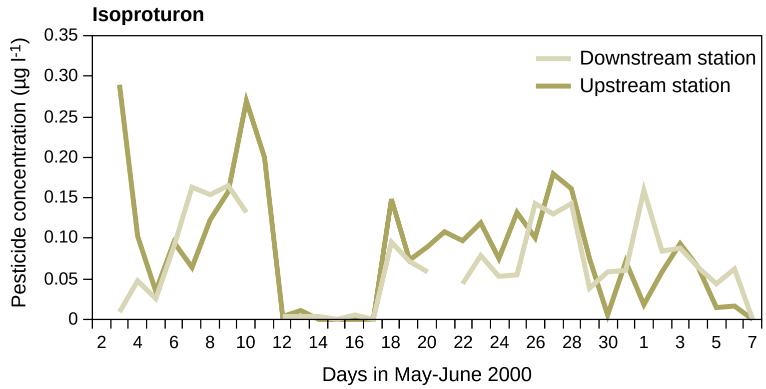


Figure 10.2 The daily mean concentration of the herbicide isoproturon and daily mean discharge at the upstream and downstream monitoring station in Lillebæk during a 36-day period in May and June 2000. Note that the concentration of pesticides were measured in a composite water sample from 16.00 p.m. to 15.00 p.m. on the following day. In this and the following figures the concentration is shown on the day with the longest time of sampling.
Figur 10.2 Døgnmiddel koncentration af herbicidet isoproturon og døgnmiddel vandføring ved de to målestationer i Lillebæk oplandet gennem perioden 2 maj til 6 juni 2000. Bemærk at koncentrationen af pesticider er bestemt over tidsrummet 16.00 til 15.00, men i figuren vist for døgnet med flest prøvetagningstimer.

The concentration of isoproturon decreased, however, at the end of the investigated period following increases in discharge on 28-29 May and in early June. Such a pattern could be typical when the soil water content decreases and the upper groundwater loses contact with tile drainage systems in the two sub-catchments.

10.4 Concentration of the metabolite BAM at the two stream stations in Lillebæk

BAM is a metabolite from the herbicide dichlobenil that has not been applied in the Lillebæk catchment since 1997. The average concentration of BAM was 38 ng/l at the upstream station and 31 ng/l at the downstream station during the 36-day study period (Fig. 10.3). The concentration of BAM revealed no clear pattern during the study period although there was a tendency for an increase in the BAM concentration from early May to mid-May when discharge decreased rapidly at both sampling stations (Fig. 10.1 and 10.3). Thus, stream hydrology is in a transition period changing from being dominated by tile drainage water to a dominance of groundwater. Moreover, BAM has been detected (detection frequency=15%) in the upper groundwater (< 5 m) in the Lillebæk catchment (Funen County, 2001).

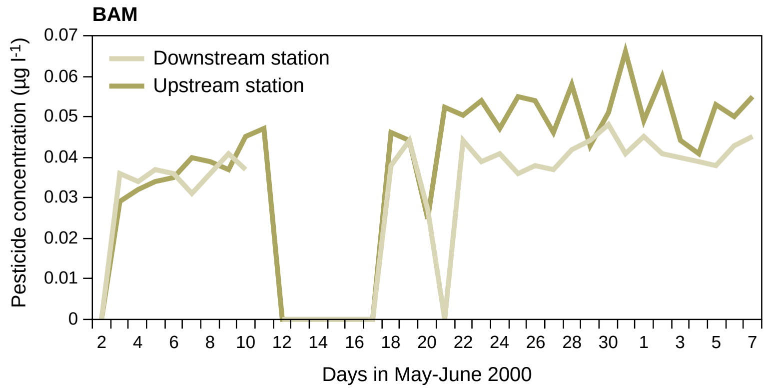


Figure 10.3 daily mean concentration of the metabolite BAM and daily mean discharge at the upstream and downstream monitoring stations in Lillebæk during a 36-day period in May and June 2000.
Figur 10.3 Døgnmiddel koncentration af metaboliten BAM og døgnmiddel vandføring ved de to målestationer i Lillebæk oplandet gennem perioden 2 maj til 6 juni 2000.

10.5 Concentration of the herbicide MCPA at the two stream stations in Lillebæk

The average concentration of MCPA was 71 ng/l at the upstream station and 95 ng/l at the downstream station during the 36-day study period. The herbicide MCPA was applied on two dates in both sub-catchments during the study period (Table 10.1). MCPA was applied on a small field and in small amounts on the 2 May in the upstream sub-catchment. This application had no influence on the concentration of MCPA measured in stream water (Fig. 10.4). The second application was on the 12 May in both sub-catchments. The application of MCPA in the downstream open channel sub-catchment was followed by a rapid increase in the concentration of MCPA at the downstream station, whereas nearly no increase was measured at the upstream station (Fig. 10.4).

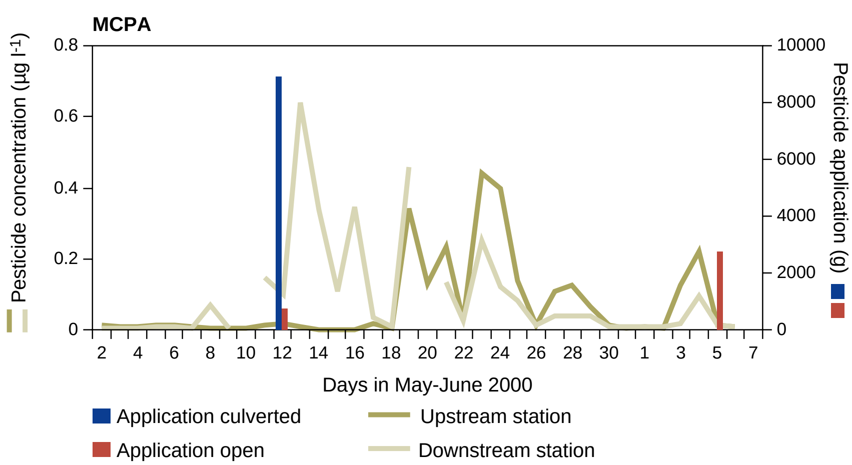


Figure 10.4 daily mean concentration of the herbicide MCPA and daily mean discharge at the upstream and downstream monitoring station in Lillebæk during a 36-day period in May and June 2000.
Figur 10.4 Døgnmiddel koncentration af herbicidet MCPA og døgnmiddel vandføring ved de to målestationer i Lillebæk oplandet gennem perioden 2 maj til 6 juni 2000.

This pattern cannot be related directly to wind drift of MCPA to the open stream channel as the application took place two days before the rise in MCPA concentration to a maximum of more than 600 ng/l at the downstream station (Fig. 10.4). Another explanation could be related to the cleaning of spraying equipment or percolation of MCPA through the soil from wet areas close to the stream channel. The concentration of MCPA increased during the periods with increasing discharge at both stream stations during the remaining part of the study period (Fig. 10.4). The increase in the concentration of MCPA with increasing discharge was, however, more evident during the first two storm events on the 19-21 May and 23-24 May than during the two events on 27-28 May and 3-4 June (Fig. 10.4). This pattern show that part of the MCPA applied was available for leaching with soil water via tile drains to the stream but that the availability declined with time after application.

10.6 Concentration of the herbicide Diuron at the two stream stations in Lillebæk

The average concentration of diuron was 79 ng/l at the upstream station and 44 ng/l at the downstream station during the 36 days study period. Diuron was applied on the 25th April and the first May in the upstream catchment and on the 15th March in the downstream sub-catchment.

Water samples analysed on the 13th March and 10th April taken during steady flow conditions at both stations had diuron concentrations below the detection limit. On contrary, diuron was measured in water samples taken from the upstream station during a rain event on the 22nd and 23th April in concentrations uo to 780 ng l^{-1} even though diuron had not been applied in the catchment since 2nd quarter of 1999. The very high concentration of 780 ng l-1 was measured in a water sample having very high particulate matter thus pointing at a delivery of diuron with soil lost via tile drains presumable from macropore flow. A diuron concentration of 135 ng l-1 was also measured on the 25th April at the downstream station. This relatively high concentration could be due to the application of diuron in the downstream sub-catchment on the 15th March.

The concentration of diuron was low at both stations during May/June except during storm events where the concentration increased to a maximum of 760 ng/l during the storm event on the 23rd May at the upstream station (Fig. 10.5). The chemograph for diuron clearly shows that the substance is delivered to the stream with soil water presumably through tile drains. The higher concentration detected during the early storm events (20-22nd May and 24th May) at the upstream station than at the downstream station could reflect the recent application in the upstream sub-catchment. The lower concentration at the downstream station can merely be explained by a dilution as discharge was 4 times higher at the downstream station and the concentration of diuron nearly 4 times lower. Another possibility is that diuron is lost to the stream from point source polluted areas in the upstream sub-catchment.

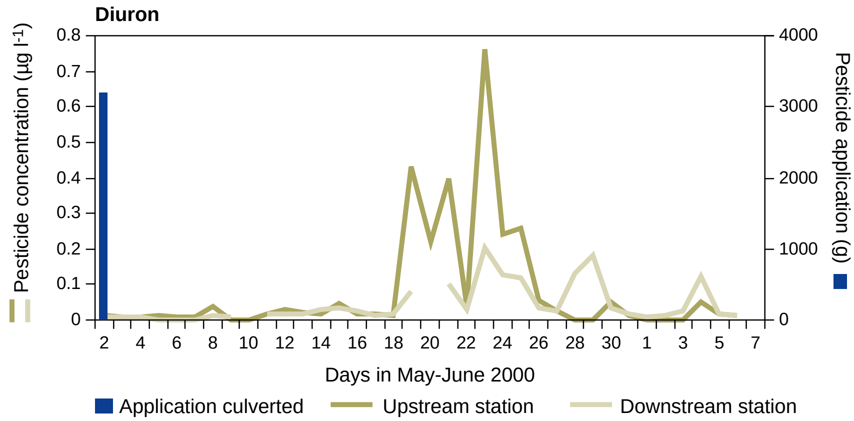


Figure 10.5 The daily mean concentration of the herbicide diuron and daily mean discharge at the upstream and downstream monitoring station in Lillebæk during a 36 day period in May and June 2000.
Figur 10.5 Døgnmiddel koncentration af herbicidet diuron og døgnmiddel vandføring ved de to målestationer i Lillebæk oplandet gennem perioden 2 maj til 6 juni 2000.

10.7 Concentration of the herbicide Terbuthylazine at the two stream stations

The average concentration of terbuthylazine was much higher (147 ng/l) at the upstream station than at the downstream station (23 ng/l) during the 36 days study period (Fig. 10.6).

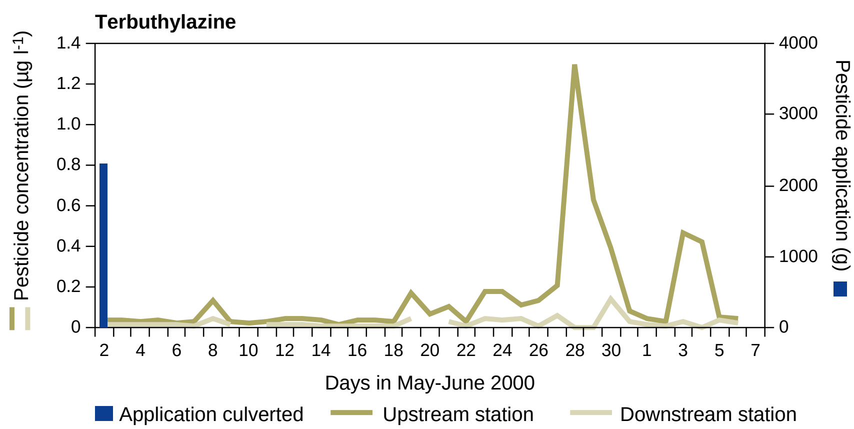


Figure 10.6. The daily mean concentration of the herbicide terbuthylazine and daily mean discharge at the upstream and downstream monitoring station in Lillebæk during a 36 day period in May and June 2000.
Figur 10.6. Døgnmiddel koncentration af herbicidet terbuthylazin og døgnmiddel vandføring ved de to målestationer i Lillebæk oplandet gennem perioden 2 maj til 6 juni 2000.

Terbuthylazine was applied in the upstream sub-catchment on the 1st May but not in the downstream sub-catchment. This could explain the large difference in concentration of terbuthylazine between the two stations. The concentration of terbuthylazine increased during storm events at the upstream station especially the late storm events on the 28-29th May and 3-4th June (Fig. 10.6). Terbuthylazine is either lost to tile drainage water from the two fields being sprayed in the upstream catchment during the rain periods or lost from a point source in the catchment.

10.8 Concentration of the fungicide Fenpropimorph at the two stream stations

Fenpropimorph was the pesticide applied most widely and in the greatest quantity during the 36-day investigation period (see Table 10.1). Never the less, fenpropimorph was not measured at any of the two stream stations. Accordingly, neither wind drift nor leaching through the soil of fenpropimorph to the stream seems to have occurred despite the high application of fenpropimorph both in terms of area and amount of active substance (see Table 10.1). The fact that fenpropimorph was not lost through the soil column to tile drainage water during the storm events in May can be explained by the large sorption coefficient of fenpropimorph (K_d value of 34.5).

10.9 Concentration of the insecticide pirimicarb at the two stream stations

Pirimicarb was applied in the downstream sub-catchment on the 12th May and the 5th June during the investigated period. Pirimicarb was only measured during the storm event on the 23th May and only at the downstream station (Fig. 10.7).

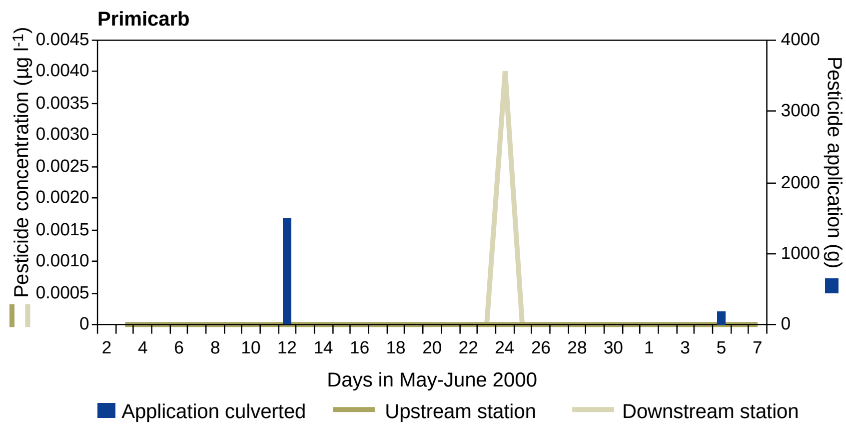


Figure 10.7. The daily mean concentration of the insecticide pirimicarb and daily mean discharge at the upstream and downstream monitoring station in Lillebæk during a 36 day period in May and June 2000.
Figur 10.8. Døgnmiddel koncentration af insekticidet pirimicarb og døgnmiddel vandføring ved de to målestationer i Lillebæk oplandet gennem perioden 2 maj til 6 juni 2000.

10.10 Mass-balance for pesticides in the two sub-catchments in Lillebæk

A pesticide mass-balance was calculated for a 34 days period of composite daily sampling at the two stations in the Lillebæk catchment (Table 10.2). The mass-balance covered all the diurnal samples from the two stations during the period 3rd May to 7th June except two days where samples were missing (11th May and 21st May).

Table 10.2 Mass-balances for five different pesticides in the Lillebæk catchment during a 34 days period with composite daily sampling from the 3 May to 7 June 2000.
Tabel 10.2 Massebalance for 5 forskellige pesticider i Lillebæk oplandet på baggrund af puljede døgnprøver udtaget gennem perioden 3 maj til 7 juni 2000.

		Upstream culverted sub-catchment (229 ha)		Entire catchment (465 ha)		Downstream open sub-catchment (236 ha)	
Pesticides	K_d	Loss (mg)	Loss (mg/mm)	Loss (mg)	Loss (mg/mm)	Loss (mg)	Loss (mg/mm)
MCPA	0.75	789	101	4268	381	3479	237
Bentazone	0.32	32.7	4,2	336	30	303	21
Isoproturon	0.83	1860	239	3583	320	1723	117
Diuron	2.30	936	120	1995	178	1059	72
Terbuthylazine	2.31	1596	205	1163	104	-433	-29

The mass-balance shows that the very soluble pesticides MCPA and bentazone experienced a much higher loss from the open sub-catchment than from the culverted sub-catchment both in absolute amounts and calculated as a loss per mm runoff (Table 10.2). MCPA was applied in both sub-catchments during the intensive study period, whereas bentazone only was applied in the upstream culverted sub-catchment (Table 10.1). The higher loss of MCPA and bentazone from the downstream catchment indicates that groundwater must be an important pathway for these two pesticides in this catchment.

Isoproturon and diuron being also soluble pesticides (low K_d) had a higher loss per mm runoff from the upstream culverted sub-catchment than the downstream open catchment (Table 10.2). Isoproturon has not been used in both sub-catchments since the 4th quarter 1999 and diuron was only applied in the culverted catchment during the intensive sampling period (Table 10.1). In the case of terbuthylazine the loss was high from the upstream sub-catchment, whereas a negative loss (storage or transformation) seems to occur during the transfer of terbuthylazine through the open channel reach (Table 10.2). Isoproturon and diuron was detected in both suspended sediment and streambed sediment during May to June 2000 and in the streambed sediment in increasing concentrations during May. Terbuthylazine was detected in suspended sediment but not in streambed sediment. The only possibly explanation is that terbuthylazine undergoes rapid transformations when exposed in streambed sediments.

10.11 Concentration of pesticides during single storm events in the Lillebæk catchment

The concentration of pesticides seems to rise especially during storm events for several of the compounds presented in the previous sections. Examples of the pesticide behaviour in streams during four storm events are shown in Figure 10.8. The concentration of terbuthylazine and diuron increases at the onset of the storm events and peaks together or near with the peak in maximum discharge (Fig. 10.8). However, the concentration of terbuthylazine and diuron was much higher during the storm event in May than in the other 3 storm events (Fig. 10.8). Both pesticides were also applied during the 2nd quarter of 1999. Terbuthylazine was detected during all four storm events, whereas diuron was not detected during the storm event in December 1999 experiencing highest discharge values and only as trace amounts during the storm event in February 2000 (Fig. 10.8).

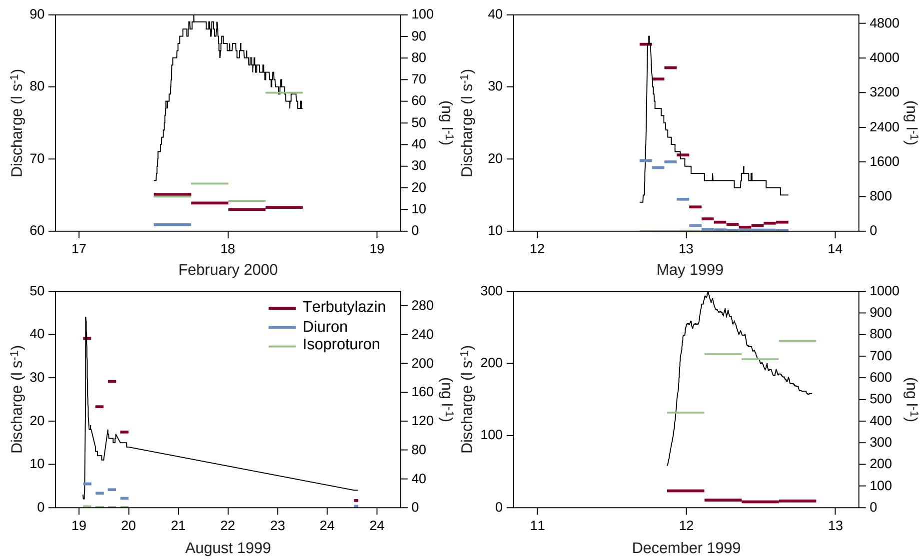
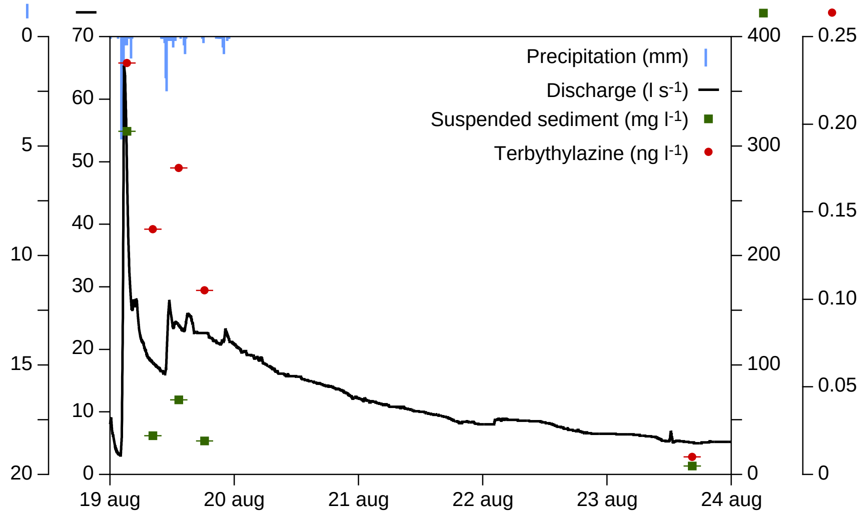


Figure 10.8. The concentration of terbuthylazine, diuron and isoproturon together with the instantaneous discharge at the upstream sampling station in the Lillebæk catchment during four storm events on different seasons of the year (May 1999, August 1999, December 1999 and February 2000).
Figur 10.8. Koncentrationen af terbuthylazin, diuron og isoproturon sammen med øjebliksvandføringen ved den opstrøms målestation i Lillebæk ved fire afstrømningshændelser igennem et år (maj 1999, august 1999, december 1999 og februar 2000).

Isoproturon revealed another pattern than terbuthylazine and diuron during storm events, the maximum concentration lagging peak discharge. Such a delayed pattern is typical for substances being leached through the soil column to tile drainage water and further to the stream channel. Moreover, isoproturon had the far highest concentrations during the December 1999 and February 2000 storm events, whereas showed very low concentrations during the May and August storm events (Fig. 10.8). The reason for this seasonal pattern is explained to the application of isoproturon, which happened in the upstream sub-catchment during the 4th quarter of 1999.

Both terbuthylazine, diuron and other pesticides with Kd values above 1-2 revealed relationships to the concentration of suspended sediment in the water samples during storm events, whereas no relationships could be established in the case of the more soluble pesticides isoproturon and bentazone (Fig. 10.9).



	no.	Kd, mean	Kd, median
Correlation to suspended sediment	4	5.3	3.31
No correlation	6	0.85	0.72

Figure 10.9. The relationship between the pesticide concentration and suspended sediment concentration at the upstream sampling station in the Lillebæk catchment.
Figur 10.9. Sammenhængen mellem pesticidkoncentrationen og koncentrationen af suspenderet stof ved den opstrøms station i Lillebæk oplandet.

One main reason for the high concentrations of terbuthylazine and diuron during extremely flashy storm events in May 1999 must be one or a combination of two mechanisms: (1) Terbuthylazine and diuron are delivered to the stream via tile drainage water from the fields where the pesticides were recently applied during the intensive and heavy rainfall; (2) terbuthylazine and diuron from the water phase were sorbed to sediment stored in the culverted stream during the period between application and the storm event and then flushed out during the storm event.

The reason for the much lower concentrations of terbuthylazine and diuron during the storm event in August 1999 must be that the pesticides were not applied during the 3rd quarter of 1999 and hence concentrations in the water or sediment phase were reduced due to less sorption and transformation of initial substances. The somewhat lower concentration of terbuthylazine and missing detections of diuron during the storm event in December 1999 and February 2000 must be due to the same reason as explained above for the August storm event, except that the longer time period since last application has given more time to transformation of the pesticides. The storm event in December 1999 reached higher maximum discharges than the other storm events in May, August and February and with nearly the same maximum concentration of suspended sediment as at least the August storm event.

10.12 Concentration of pesticides during single storm events in the Odderbæk catchment

The concentration of isoproturon was high during the storm events in December 1999 and February 2000, whereas only trace amounts of bentazone was detected (Fig. 10.10). The reason for this is clearly that isoproturon was applied in the Odderbæk catchment during the 4th quarter 1999, whereas bentazone only was applied in the 2nd quarter 1999. The concentration of isoproturon more or less followed the variation in discharge during the storm events showing that it is rapidly carried from the soil to surface water.

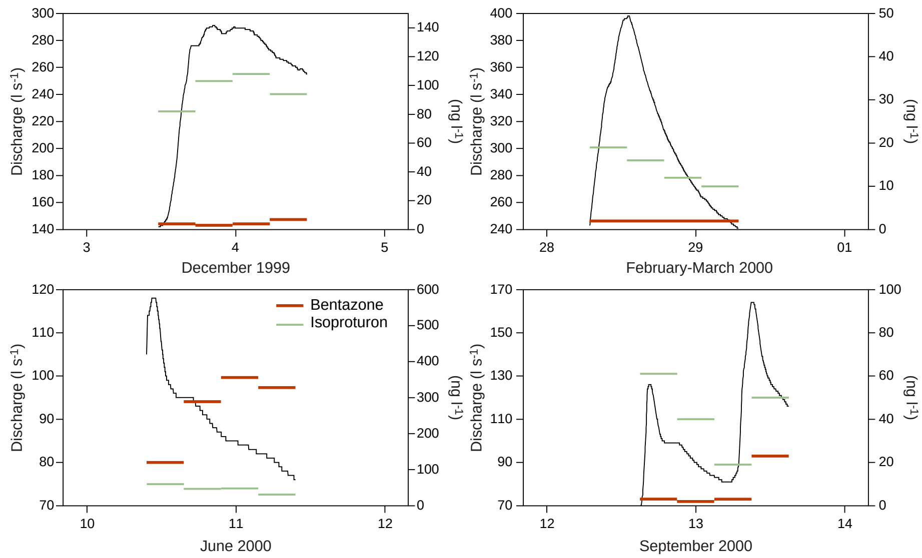


Figure 10.10 The concentration of bentazone and isoproturon together with the instantaneous discharge at the stream station in the Odderbæk catchment during four storm events on different seasons of the year (December 1999, February 2000, June 2000 and September 2000).
Figur 10.10 Koncentrationen af bentazon og isoproturon sammen med øjebliks vandføringen ved vandløbsmålestationen i Odderbæk ved fire afstrømningshændelser igennem et år (december 1999, februar 2000, juni 2000 og september 2000).

The concentration of bentazone was higher than isoproturon during the storm event in June 2000 and bentazone concentration clearly lagged the peak discharge (Fig. 10.10). Bentazone was also applied in the catchment during the 2nd quarter of 2000, whereas this was not the case for isoproturon. The concentration of bentazone was the highest observed and higher than reached for isoproturon. This shows the impact of pesticide application and subsequent loss during the relatively low flow period of the autumn spraying season. Wind drift or bentazone being washed out of stream bank vegetation can not cause the concentration pattern observed in the stream as this would have caused a rapid increase in bentazone concentration peaking before maximum discharge (Fig. 10.10). During the storm event in September 2000 the concentration of isoproturon is again higher than for bentazone (Fig. 10.10). The explanation is simply that isoproturon was applied in the catchment during the 3rd quarter of 2000.

11 Comparison of pesticide fate in the two catchments and prediction of recurrence intervals for pesticide concentrations

11.1 Pesticide application

The amount of pesticides applied per hectare to the ten dominant crop types did not differ much between the Lillebæk catchment (1998/1999: 0.918 kg/ha and 1999/2000: 1.163 kg/ha) and the Odderbæk catchment (1998/1999: 1.013 kg/ha and 1999/2000: 1.042 kg/ha). Herbicides were, however, applied in much greater quantities in the Odderbæk catchment than in the two sub-catchments of the Lillebæk during the two study periods (Table 11.1). On the contrary, more fungicides and insecticides were applied in the Lillebæk catchment than in the Odderbæk catchment (Table 11.1).

Table 11.1. Application of herbicides, fungicides and insecticides in the two sub-catchments in the Lillebæk catchment and in the Odderbæk catchment during two years.
Tabel 11.1. Forbrug af herbicider, fungicider og insekticider i de to deloplande af Lillebæk og i Odderbæk oplandet gennem to år.

	Herbicides	Fungicides	Insecticides	Total
	Pesticide use (kg active substances)			
Upstream culverted sub-catchment in the Lillebæk (229 ha)				
October 1998 to September 1999	66.1	54.8	4.42	125.3
October 1999 to September 2000	108.2	63.5	2.25	174.0
Downstream open sub-catchment in the Lillebæk (235 ha)				
October 1998 to September 1999	74.0	92.4	4.78	171.2
October 1999 to September 2000	141.9	120.5	3.85	266.3
Odderbæk catchment (1143 ha)				
October 1998 to September 1999	1041	69.2	4.35	1115
October 1999 to September 2000	732.4	207.9	12.0	952.3

11.2 Pesticide detection and concentration in stream and tile drainage water

More pesticides and metabolited were detected in stream water than in tile drainage water within the two catchments during the study period. Of the total of 49 pesticides and metabolites analysed for in water samples nearly the same number of pesticides and metabolites was detected at the three stream stations. This amounted to 42 pesticides at the upstream station in the Lillebæk, 40 pesticides at the downstream station in the Lillebæk and 39 pesticides at the stream station in the Odderbæk catchment. The number of different pesticides detected at the two drain stations in the Lillebæk catchment amounted to 17 and 16, whereas 27 different pesticides were detected at the drain station in the Odderbæk catchment.

The detection frequency for 12 selected key pesticides or metabolites varied, however, considerably between the two stream stations in the Lillebæk catchment and the stream station in the Odderbæk catchment (Table 11.2). Herbicides, fungicides and insecticides have a much higher detection frequency at the stream stations in the dominantly loamy and tile drained Lillebæk catchment than at the stream station in the dominantly sandy Odderbæk catchment. Exceptions are the widely used and very soluble herbicides bentazone and isoproturon that are found nearly with the same frequency in the two catchments. The herbicide pendimethalin that has a high sorption potential was, however, also found at a nearly similar frequency in the two catchments. No major differences were observed in the detection frequencies in the tile drains monitored in the Lillebæk and Odderbæk catchment. The only exception being BAM which was recovered more often in drain water from the station in the Odderbæk catchment. This could be explained with the much greater dominance of deeper groundwater in the large drain monitored in the Odderbæk catchment as opposed to the upper groundwater dominated drains in the Lillebæk catchment.

Table 11.2. Detection frequencies for 12 pesticides at the 3 stream stations and 3 drain stations in the two studied catchments during the two study years.
Tabel 11.2. Fundhyppighed for 12 pesticider ved de 3 vandløbsstationer og de 3 drænstationer i de to oplande gennem de to måleår.

Pesticide	Upstream Lillebæk	Downstream Lillebæk	Odderbæk	Drain 2 Lillebæk	Drain 6 Lillebæk	Drain Odderbæk
	Stream stations			Drain stations		
Herbicides						
BAM (metabolite)	75%	70%	12%	3.6%	0%	14%
Bentazone	62%	87%	69%	57%	67%	61%
Ethofumesate	24%	1.0%	1.8%	0%	0%	2.0%
Ioxynil	17%	7.3%	2.9%	7.1%	0%	0%
Isoproturon	76%	84%	56%	54%	46%	47%
Pendimethalin	34%	26%	25%	0%	13%	12%
Terbuthylazine	97%	87%	32%	7.1%	21%	6.1%
Fungicides						
Fenpropimorph	20%	4.8%	1.8%	0%	0%	2.9%
Prochloraz	3.5%	3.1%	1.5%	0%	0%	4.1%
Propiconazole	55%	18%	5.9%	7.1%	4.2%	6.1%
Insecticides						
Dimethoate	12%	3.1%	1.5%	0%	0%	0%
Pirimicarb	12%	9.4%	2.9%	0%	0%	0%

Table 11.3. Median and maximum concentrations of 12 pesticides at the three stream stations in the two catchments.
Tabel 11.3. Median og maximum koncentrationer af 12 pesticider ved de tre vandløbsstationer i de to oplande.

Pesticide	Upstream Lillebæk	Downstream Lillebæk	Odderbæk	Upstream Lillebæk	Downstream Lillebæk	Odderbæk
	Median concentration (ng/l)			Maximum concentration (ng/l)		
Herbicides						
BAM (metabolite)	44	37	4	127	66	20
Bentazone	2	3	3	180	89	2910
Ethofumesate	3	1	6	39	1	6
Ioxynil	5	2	4	98	14	4
Isoproturon	42	49	57	771	1830	129
Pendimethalin	14	11	24	168	95	195
Terbuthylazine	79	15	4	4318	330	136
Fungicides						
Fenpropimorph	12	2	42	29	62	42
Prochloraz	1	15	19	1	16	19
Propiconazole	13	20	7	251	53	44
Insecticides						
Dimethoate	11	1	2	36	1	2
Pirimicarb	6	8	8	39	49	14

The measured differences in detection frequencies in stream water for many of the key pesticides in the Lillebæk and the Odderbæk catchment suggest that applied pesticides are carried more easily and possibly with a shorter residence time from the field to the stream in the loamy, tile drained Lillebæk catchment than in the sandy and more groundwater dominated Odderbæk catchment. In the case of the metabolite BAM from TCA (banned 1992) and dichlobenile (banned 1997) the reason for the large difference in detection frequency between the two catchments can be that BAM has been detected in upper groundwater in Lillebæk and not in Odderbæk. If BAM only is delivered with deeper groundwater to the Odderbæk stream but both with deeper and upper groundwater to the Lillebæk stream then this can explain the large difference in the measured detection frequency.

The median and maximum concentrations of 12 selected pesticides are shown in Table 11.3. No major differences can be seen between the median pesticide concentrations in stream water in the Lillebæk and Odderbæk catchment. The only exceptions are for the concentration of the metabolite BAM and terbuthylazine being considerably lower in the Odderbæk stream than in the Lillebæk stream.

The maximum pesticide concentrations measured in stream water differed from substance to substance between the two catchments. The maximum concentration s were, however, generally highest in the stream draining the upstream culverted Lillebæk catchment. The maximum concentrations were more comparable between the two stream stations draining the Lillebæk and Odderbæk catchments although substance specific differences occured (Table 11.3). The concentrations of herbicides were, however, in general much higher than for fungicides which in turn was higher than for insecticides in both catchments. This can simply be explained by the large differences in the applied amount of herbicides, fungicides and insecticides, which normally decreases in this order (Table 11.1). The differences in Kd values for the group of pesticides shown in Table 11.3 is of course also an important factor for the differences between herbicides and fungicides.

11.3 Pesticide loss

The pesticide concentration and loss during the four storm events shown in chapter 10 is shown in Table 11.4 and 11.5. Each of the storm events was intensively sampled. We have chosen one storm in each of the quarters to represent the seasonal dynamics of water and pesticides. The loss and discharge weighted concentration of pesticides during the four storm events is highly correlated to the application time of the pesticides. Thus, both the loss and discharge weighted concentration of isoproturon was considerably higher during the storm event in the 4th quarter than in the other quarters in both catchments (Table 11.4 and 11.5). On contrary, diuron and terbuthylazine in the Lillebæk catchment and bentazone in the Odderbæk catchment experienced highest losses and concentrations in the 2nd quarter of the year (Table 11.4 and 11.5). Another marked difference between the fate of pesticides during storm events in the two catchments is that the loss and discharge weighted concentration is more extreme in the Lillebæk catchment than in Odderbæk catchment.

Table 11.4. Loss and discharge weighted concentration of 3 selected pesticides during one storm event in each quarter of the year for the upstream station in the Lillebæk catchment. The loss is calculated based on sampling during a period of 24 hour during each storm event.

Tabel 11.4. Tab og vandføringsvægtet koncentration af 3 pesticider gennem en afstrømningshændelse i hvert kvartal for den opstrøms vandløbsmålestation i Lillebæk. Tabet af pesticider er beregnet på baggrund af flere puljede enkeltprøver udtaget over en 24 timers periode.

Lillebæk upstream	Quarter of year	Runoff	Diuron	Terbuthy-lazine	Isoproturon	Diuron	Terbuthy-lazine	Isoproturon
		(mm)		Loss (mg)		Discharge weighted concentration (ng/l)		
17-18th February 2000	1	3.1	5.2	91.1	205	0.7	12.7	28.6
12-13th May 1999	2	0.7	981	2543	4.5	592	1534	2.7
19 August 1999	3	0.6	26.7	193	1.3	20	145	1.0
11-12th December 1999	4	8.1	0	775	11944	nd	42	651

Table 11.5. Loss and discharge weighted concentration of 3 selected pesticides during one storm event in each quarter of the year for the stream station in Odderbæk catchment. The loss is calculated based on sampling during a period of 24 hour during each storm event.
Tabel 11.5. Tab og vandføringsvægtet koncentration af 3 pesticider gennem en afstrømningshændelse i hvert kvartal for vandløbsstationen i Odderbæk. Tabet af pesticider er beregnet på baggrund af flere puljede enkeltprøver udtaget over en 24 timers periode.

Odderbæk	Quarter	Runoff	Bentazone	Isoproturon	Bentazone	Isoproturon
		(mm)	Loss (mg)		Discharge weighted concentration (ng/l)	
28-29th February 2000	1	2.3	53.2	390	2.0	14.7
10-11th June 2000	2	0.7	2054	369	264	47.5
12-13th September 2000	3	0.8	83.3	399	9.0	43.2
3-4th December 1999	4	2.0	100.4	2192	4.5	98.0

The average loss of selected pesticides and suspended sediment from the 2 sub-catchments in the Lillebæk and the Odderbæk catchment during the period 3rd quarter 1999 to 3rd quarter 2000 is shown in Figure 11.1. The average loss is calculated per sampling hour and is, therefore, comparable between the catchments. The pesticide and suspended sediment loss is in many cases greater from the Odderbæk catchment than from the two sub-catchments in the Lillebæk (Fig. 11.1).

However, the applied pesticide amount was much greater in the Odderbæk catchment than in the Lillebæk catchment. Consequently, the loss:applied ratio for the Odderbæk catchment was three times lower than for the entire Lillebæk catchment and nearly 8 times lower than for the upstream culverted sub-catchment when considering 18 applied pesticides during the year covered by the 4th quarter of 1999 to the 3rd quarter of 2000 (Table 11.6). Although the loss figures shown is only calculated for the sampling period and therefore is a minimum estimate (see chapter 8) the figures can be used to make comparison between the catchments. The ‘true’ loss:applied ratio for the catchments is, however, higher than the results shown in Table 11.6.

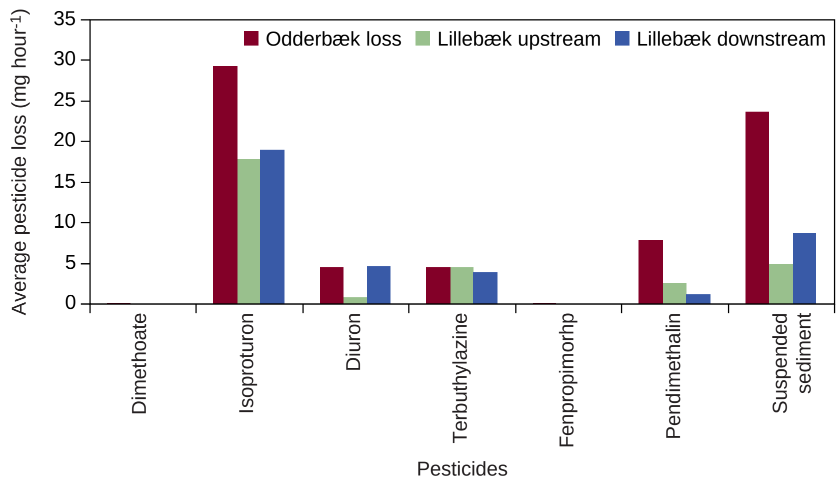


Figure 11.1. Average loss per sampling hour of selected pesticides and suspended sediment during the period 3rd quarter of 1999 to 3rd quarter of 2000 in the two sub-catchments of the Lillebæk and the Odderbæk catchment.
Figur 11.1. Gennemsnitligt tab pr. prøvetagnings time af udvalgte pesticider og suspenderet stof gennem perioden 3 kvartal 1999 til 3 kvartal 2000 fra de to deloplande i Lillebæk og Odderbæk oplandet.

Table 11.6 Application, calculated loss and loss ration for the upstream sub-catchment in the Lillebæk, the entire Lillebæk catchment and the Odderbæk catchment during the year covering 4th quarter of 1999 to 3rd quarter of 2000.
Tabel 11.5 Anvendte pesticidmængder, beregnet tab og tabsraten for det opstrøms rørlagte delopland I Lillebæk, hele Lillebæk oplandet og Odderbæk oplandet for året omfattet af 4 kvartal 1999 til 3 kvartal 2000.

	Pesticide application	Pesticide loss	Loss:applied ratio
	Grammes		
Lillebæk upstream culverted sub-catchment	119,270	27.844	0.0233%
Entire Lillebæk catchment	179,647	19.506	0.0109%
Odderbæk catchment	634,318	19.848	0.0031%

11.4 Prediction of recurrence intervals for different pesticide concentrations

We fitted a generalized extreme-value (GEVD) distribution (Kite, 1978) to the samples of pesticides from the upstream station in the Lillebæk catchment by the maximum likelihood method. The GEVD distribution has three parameters (location, scala and shape) The distribution has been extensively used to fit maximum and minimum discharges in hydrological applications (e.g. Ovesen ***et al.***, 2000). The GEVD distribution is in this report used to calculate the concentration with a 95% confidence interval at different recurrence intervals for the selected pesticides.

The recurrence interval for concentrations of terbuthylazine and diuron at the upstream station in the Lillebæk catchment is shown in Figure 11.2. The statistical analysis for this stream station is based on a total of 97 water samples for the entire study period with 56 being sampled during storm events. The predicted recurrence interval for the concentration of terbuthylazine and diuron shows that extremely high concentrations can occur at the upstream station in the Lillebæk catchment (Fig. 11.2). An intensive sampling effort is, however, needed in order to measure these maxima (Fig. 11.2). Thus, a monthly sampling programme will only discover one tenth of the actual predicted concentration range for terbuthylazine and diuron.

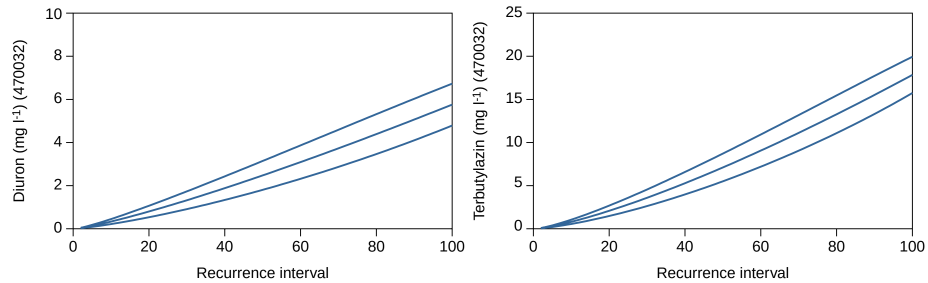


Figure 11.2 Recurrence intervals for the concentration of diuron and terbuthylazine at the upstream station in the Lillebæk catchment.
Figur 11.2 Gentagelses interval for koncentrationen af diuron og terbuthylazin ved den opstrøms vandløbsstation i Lillebæk.

The recurrence interval for concentrations of terbuthylazine, diuron and isoproturon at the downstream station in the Lillebæk catchment is shown in Figure 11.3. The statistical analysis for this stream station is based on a total of 79 water samples for the entire study period with 28 being sampled under storm events. The predicted recurrence interval for the concentration of terbuthylazine and diuron shows that far less extreme concentrations occur at the downstream station in the Lillebæk catchment than at the upstream station (Fig. 11.2 and 11.3). The predicted concentration range for isoproturon is, however, nearly as wide as that predicted at the upstream station (Fig. 11.3). Less sampling effort is needed to describe the actual concentration range and discover maximum concentrations for terbuthylazine and diuron at the downstream station in the Lillebæk. A monthly sampling programme for terbuthylazine and diuron will discover nearly half of the actual predicted concentration range of terbuthylazine and diuron.

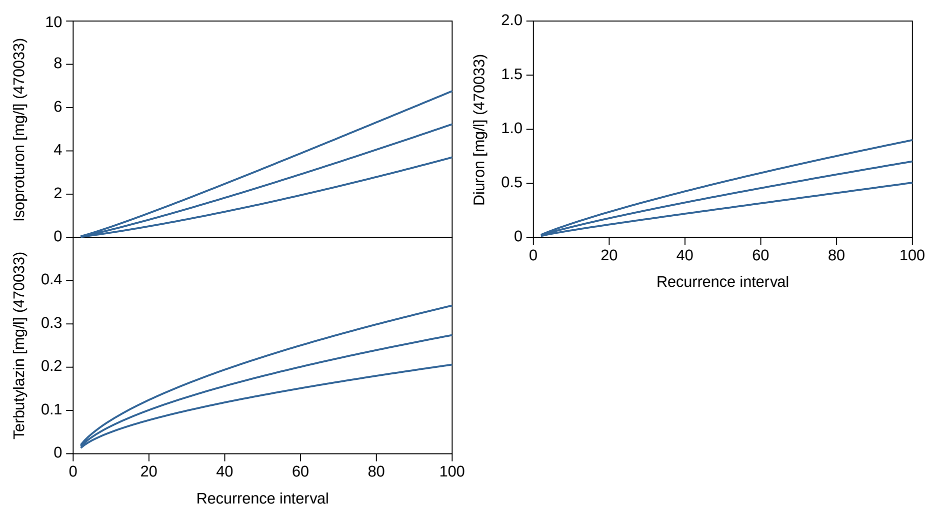


Figure 11.3 Recurrence intervals for the concentration of diuron, terbuthylazine and isoproturon at the downstream station in the Lillebæk catchment.
Figur 11.2 Gentagelses interval for koncentrationen af diuron, terbuthylazin og isoproturon ved den nedstrøms vandløbsstation i Lillebæk.

12 References

Albanis, T.A., Danis, T.G. and Kourgia, M.K. (1994) Transportation of pesticides in estuaries of the Axios, Loudias and Aliakmon rivers, Greece. Sci. Total Environ. 156, 11-22.

Battaglin, W.A., Goolsby, D.A. and Coupe, R.H. (1993) Annual use and transport of agricultural chemicals in the Mississippi River, 1991-1992. Open file Report 93-418, 26-40, US Geological Survey, Denver, CO, USA.

Baym H. og Hansen, H.P.B. (2001) Gårdspladser og vaskepladser forurener grundvandet med pesticider. VANDteknik 1, 12-17.

Belamie, R. & Gouy, V. (1992) Introduction of pollutants into streams and rivers. Impact of rain and runoff. The fate of chemical pollutants: Seminar 13. December 1991, Nival P. and Saliot, A. (Eds.), Institut Oceanographique, Paris, France, 18 (5), 505-521.

Bossi, R., Vejrup, K.V., Mogensen, B.B. & W.A.H. Asman (in prep.) Analysis of Polar Pesticides in Danish Rainwater by Liquid Chromatography Tandem Mass Spectrometry J. Chromatograph, in prep.

Bønding, V. (2001) Pesticides indvirkning på markoinvertebratfaunaen i mindre østdanske vandløb med særligt henblik på Baetis rhodani (in Danish). Specialerapport fra DMU og KU, Ferskvandsbiologisk Laboratorium.

Dobel, S., Mogensen, B.B. & Sørensen, P.B. (2000) Validation of a ranking model in relation to Danish monitoring data. In " P.B. Sørensen, L.Carlsen, B.B. Mogensen, R. Brüggemann, B. Luther, S. Pudenz, U. Simon, E. Halfon, T. Bittner, K. Voigt, G. Welzl, F. Rediske (ed): Order Theoretical Tools in Environmental Sciences. Proceedings of the Second Workshop October 21st, 1999 in Roskilde, Denmark. NERI Technical Report No. 318", pp.145- 161. (2000)

Frank, R., Logan, L. and Clegg, B.S. (1991) Pesticide and polychlorinated biphenyl residues in waters at the mouth of the Grand, Saugeen and Thames Rivers, Ontario, Canada, 1986-1990. Arch. Environ. Contam. Toxicol. 21, 585-595.

Funen County (1997) (Pedersen, S.E og Wiberg-Larsen, P. et. al.) De fynske vandløb. VANDMILJØovervågning. Tema: Ferskvand (in Danish). Fyns amt, Natur- og vandmiljøafdelingen, 210s. + bilag.

Funen County (1999). (Pedersen, S:E:, Schwærter, R.C.) Pesticidundersøgelser i vandløb, kildevæld og dræn. 1994-1997 (in Danish). Fyns Amt, Natur- og Vandmiljøafdelingen – februar 1999.

Funen County (2001): Aquatic Environment of Fyn, Denmark, 1976-2000. Streams and Lakes, Coastal Waters, Groundwater, Environmental Impact of Wastewater and Agriculture. Funen County, Odense, Denmark, PP: 148

Gomme, J.W., Shurvell, S., Hennings, S.M. and Clark, L. (1991) Hydrology of pesticides in a chalk catchment: surface waters. J. Inst. Water Environ. Manag. 5, 546-552.

Harris, G.L., Nicholls, P.H., Bailey, S.W., Howse, H.R. and Mason, D.J. (1994) Factors influencing the loss of pesticides in drainage from a cracking clay soil. J. Hydrol. 159, 235-253.

Holm, J., Petersen, C. and Koch, C.B. (2003) Facilitated transport of pesticides. Pesticides Research No. 67, Danish Environmental Protection Agency, 51 pp.

Iversen, H.L., Laubel, A., Jensen, J.P. & Sørensen, P.B. (2001) Miljøfremmede stoffer og tungmetaller. I: Bøgestrand, J. (red.): Vandløb og kilder 2000. NOVA 2003. Danmarks Miljøundersøgelser. - Faglig rapport fra DMU 378: 45-59.

Kite, G. W. (1978) Frequency and risk analysis in hydrology. Water Resources Publications.

Kladivko, E.J., Van Scoyoc, G.E., Monke, E.J., Oates, K.M. and Pask, W. (1991) Pesticide and nutrient movement into subsurface tile drains on a silt loam soil in Indiana. J. Environ. Qual. 20, 264-270.

Kreuger, J. (1996) Pesticides in stream water within a small catchment in southern Sweden. Report from the 'Vemmehög project' 1990-94 (in Swedish). Swedish University of Agricultural Sciences, Technical Report No. 32, 65

Kreuger, J. (1998) Pesticides in stream water within an agricultural catchment in southern Sweden, 1990-1996. The Science of the Total Environment 216, 227-251.

Kreuger, J. and Törnqvist, L. (1998) Multiple regression analysis of pesticide occurrence in streamflow related to pesticide properties and quantities applied. Chemosphere 37/2, 189-207.

Kreuger, J. (2000) Övervakning av bekämpelsesmedel i vatten från et avrinningsområde i Skåne (in Swedish). Ekohydrologi 54, Swedish University of Agricultural Sciences, Uppsala, Sweden.

Kronvang B., Søndergaard M., Mogensen B.B., Nyeland, Andersen K.J., Schwærter R.C. & Nielsen P.V. (1999) Overvågning af miljøfremmede stoffer i ferskvand. NOVA 2003 (in Danish). Danmarks Miljøundersøgelser. 27 s. – Technical Instruction from NERI No. 17.

Kronvang, B., Strøm, H.L., Iversen, H.L., Hoffmann, C.C., Laubel, A., Jørgensen, J.O. & Friberg, N. (2002) Transporteres pesticider via dræn til vandløb, Vand & Jord 9(3), 99-104.

Køppen, B. & Spliid, N. H. (1998) Determination of acidic herbicides using liquid chromatography with pneumatically assisted electrospray ionization mass spectrometric and tandem mass spectrometric detection. J. Chromatogr. A 803 (1998) 157-168.

Laubel, A. Jacobsen, O.H., Kronvang, B. and Grant, R. (1998) Subsurface drainage loss of particles and phosphorus from field plot experiments and a tile-drained catchment. J. Environ. Qual. 28, 576-584.

Liess, M., Schultz, R., Liess, M.H-D., Rother, B. and Kreuzig, R. (1999) Determination of insecticide contamination in agricultural headwater streams. Wat. Res. 33(1), 239-247.

Mogensen, B.B. and Spliid, N.H. (1995) Pesticides in Danish watercourses: Occurrence and effects. Chemosphere 31, 3977-3990.

Mogensen, B.B. & Kronvang, B. (2000) Påvisninger af pesticider i overfladevand.
17 Danske Planteværnskonference, Danmarks Jordbrugsforskning, DJF. rapport,
Markbrug 23, 51-61.

Ovesen, N. B., Iversen, H. L., Larsen, S. E., Müller-Wohlfeil, D.-I. & Svendsen, L. M. (2000) Afstrømningsforhold i danske vandløb (in Danish). Danmarks Miljøundersøgelser. 238 s. – NERI Technical Report No. 340.

Pedersen, S.E. (1996) Pesticidundersøgelser i fynske vandløb 1994-1995 (in Danish). Indlæg ved Det KGL. Danske Landhusholdningsselskab's seminar "Vandforurening med pesticider", afviklet i Eigtveds Pakhus, den 20. marts 1996. Trykt i "Tidsskrift for landøkonomi, 2/96, juni 1996".

Prescott, P. & Walden, A. T. (1983) Maximum Likelihood estimation of the three-parameter generalized extreme-value distribution from censored samples. Journal of Statistical Computing and Simulation 16, 241-250.

Spalding, R.F. and Snow, D.D. (1989) Stream levels of agrichemicals during a spring discharge event. Chemosphere 19(8/9), 1129-1140.

Traub-Eberhard, U., Kördel, W. and Klein, W. (1994) Pesticide movement into subsurface drains on a loamy silt soil. Chemosphere 28, 273-284.

Vejrup, K. V. & Ljungqvist, A. (1998) Udvidet pesticidmetode i forbindelse med grundvandsovervågning (in Danish). NERI Technical Report No. 261.

Villholdt K.G., Jarvis N.J., Jacobsen O.H. and de Jonge H. (2000). Field investigations and modelling of particle-facilitated pesticide transport in macroporous soil. Soil J. Environ. Qual. 29, 1298-1309.

Appendix 4.1

Quarterly report from July 1998 to mid-October 2000 on the use of active substances (grammes) within the entire Lillebæk catchment, where environmental occurrence of these active substances or metabolites is included in this study.

Active substance	1998		1999				2000			
	3rd	4th	1st	2nd	3rd	4th	1st	2nd	3rd	1-15 Oct.
Atrazine										
BAM (2,6 dichlorobenzamide)										
Benazolin										
Bentazone				2158				3137		
Bromoxynil	3336	672		8725		1780	105	2250		5114
Carbofuran										
Chloridazon										
Chlorsulfuron										
Cyanazine										
Desethylatrazine										
Desethylterbuthylazine										
Desisopropylatrazine										
Dicamba										
Dichlorprop										
Dimethoate										
Dinoseb										
Diuron				960			6720	3840		
DNOC										
Ethofumesate				2704				2919		
Fenpropimorph	1584			23695	1215			14487		
Flamprop				1015						
Fluazifop	776			1626				975	1517	
Hexazinone										
Hydroxyatrazine										
Hydroxysimazine										
Hydroxyterbuthylazine										
Hydroxycarbofuran										
Ioxynil	2224	448		10282		1780	105	2415		3664
Isoproturon		2200				24300				
Lenacil										
Linuron										
MCPA				6871				21748		
Mecoprop								7700		
Methabenzthiazuron										
Metamitron				16688				15087		
Metribuzin										
Metsulfuron-methyl				360			4	121		
Nitrophenol										
Pendimethalin		7260		1012	540	56420		880		15208
Pirimicarb	946			5017	1958			3382	928	
Prochloraz				162						
Propiconazole	528			6536	506			3543		
Propyzamide										
Simazine					800		24583			
Terbuthylazine				3525				3500		
Thifensulfuron								4		
Triadimenol										
Triasulfuron										
2,4-D										
2,4-dichlorphenol										

Appendix 4.2

Quarterly report from July 1998 to mid-October 2000 on the use of active substances (grammes) within the upper sub-catchment (Topenden) of Lillebæk, where environmental occurrence of these active substances or metabolites is included in this study.

Active substance	1998		1999				2000			
	3rd	4th	1st	2nd	3rd	4th	1st	2nd	3rd	1-15 Oct.
Atrazine										
BAM (2,6-dichlorobenzamide)										
Benazolin										
Bentazone				18				1659		
Bromoxynil	2208	313		5942		367	55	1514		2105
Carbofuran										
Chloridazon										
Chlorsulfuron										
Cyanazine										
Desethylatrazine										
Desethylterbuthylazine										
Desisopropylatrazine										
Dicamba										
Dichlorprop										
Dimethoate										
Dinoseb										
Diuron				960				3840		
DNOC										
Ethofumesate				1058				2231		
Fenpropimorph	377			14853	1215			12187		
Flamprop				1015						
Fluazifop	722							975	1342	
Hexazinone										
Hydroxyatrazine										
Hydroxysimazine										
Hydroxyterbuthylazine										
Hydroxycarbofuran										
Ioxynil	1472	209		6794		367	55	1438		1403
Isoproturon		1550				18500				
Lenacil										
Linuron										
MCPA				2205				15373		
Mecoprop								2000		
Methabenzthiazuron										
Metamitron				7056				12572		
Metribuzin										
Metsulfuron-methyl				203			2	57		
Nitrophenol										
Pendimethalin		4343		28	540	36470		120		9936
Pirimicarb	302			1500	1703			770	928	
Prochloraz				162						
Propiconazole	126			3364	506			2948		
Propyzamide										
Simazine										
Terbuthylazine				2400				3500		
Thifensulfuron										
Triadimenol										
Triasulfuron										
2,4-D										
2,4-dichlorphenol										

Appendix 4.3

Quarterly report from July 1998 to mid October 2000 on the use of active substances (grammes) within the catchment of Odderbæk, where environmental occurrence of these active substances or metabolites is included in this study.

Active substance	1998		1999				2000			
	3rd	4th	1st	2nd	3rd	4th	1st	2nd	3rd	1-15 Oct
Atrazine										
BAM (2,6-dichlorobenzamide)										
Benazolin										
Bentazone				42.942				61.799		
Bromoxynil				25.802		1.576		29.115		4.238
Carbofuran										
Chloridazon										
Chlorsulfuron										
Cyanazine										
Desethylatrazine										
Desethylterbuthylazine										
Desisopropylatrazine										
Dicamba								0.901		
Dichlorprop										
Dimethoate								8.442		
Dinoseb										
Diuron										
DNOC										
Ethofumesate				22.835				10.206		
Fenpropimorph	3.938			34.466	3.713			48.244		
Flamprop										
Fluazifop										
Hexazinone										
Hydroxyatrazine										
Hydroxysimazine										
Hydroxyterbuthylazine										
Hydroxycarbofuran										
Ioxynil				27.616		1.576		29.115		4.092
Isoproturon	15.050	-16.878?		8.250		92.795			32.310	99.910
Lenacil										
Linuron								19.620		
MCPA				15.267				10.073		
Mecoprop										
Methabenzthiazuron										
Metamitron				28.028				56.158		
Metribuzin								5.341		
Metsulfuron-methyl				0.054				0.366		
Nitrophenol										
Pendimethalin	19.040	68.876		47.412		105.568		44.990	38.772	97.114
Pirimicarb	1.613			2.050						
Prochloraz	3.375									
Propiconazole	1.775			10.886	1.238			13.183		
Propyzamide										
Simazine										
Terbuthylazine				41.186				59.838		
Thifensulfuron										
Triadimenol										
Triasulfuron				0.032				0.077		
2,4-D										
2,4-dichlorphenol										

Appendix 6.1

	470032			
	Number of samples	Number of findings	medi	max
Atrazine	126	106	0.005	0.463
BAM (2.6-dichlorobenzamide)	126	97	0.045	0.209
Benazolin	126	6	0.0015	0.005
Bentazone	126	74	0.002	0.18
Bromoxynil	126	33	0.005	0.042
Carbofuran	126	2	0.004	0.004
Chloridazon	126	21	0.002	0.005
Chlorsulfuron	126	1	1.421781	1.421781
Cyanazine	126	33	0.049	20.0
Desethylatrazine	126	98	0.01	0.048
desethylterbuthylazine	126	119	0.017	0.522
desisopropylatrazine	126	70	0.007	0.050
Dicamba	101	13	0.004	0.008
Dichlorprop	126	23	0.002	0.006
Dimethoate	126	16	0.014	0.036
Dinoseb	126	14	0.001	0.003
Diuron	126	83	0.027	1.632
DNOC	126	80	0.003	0.271
Ethofumesate	126	27	0.003	0.039
Fenpropimorph	106	19	0.012	0.029
Flamprop	126	0		
Fluazifop	126	25	0.01	0.097
Hexazinone	118	110	0.01	0.253
hydroxyatrazine	126	66	0.01	0.080
Hydroxycarbofuran	126	0		
hydroxysimazine	126	7	0.032	1.577
hydroxyterbuthylazine	126	101	0.026	0.429
Ioxynil	126	19	0.005	0.098
Isoproturon	126	98	0.061	6.9
Lenacil	126	7	0.033	0.23
Linuron	126	9	0.004	0.013
MCPA	126	85	0.023	1.61
Mecoprop	126	52	0.003	0.021
Methabenzthiazuron	126	0		
Metamitron	126	26	0.0205	0.079
Metribuzin	126	2	0.0125	0.014
Metsulfuron-methyl	126	0		
Nitrophenol	126	81	0.0165	0.744
Pendimethalin	126	43	0.014	0.168
Pirimicarb	126	20	0.006	0.039
Prochloraz	126	4	0.001	0.001
Propiconazole	126	64	0.013	0.251
Propyzamide	126	12	0.011	0.117
Simazine	126	59	0.006	1.727
Terbuthylazine	126	122	0.076	4.318
Thifensulfuron	126	0		
Triadimenol	126	9	0.003	0.007
Triasulfuron	126	0		
2.4-D	126	13	0.001	0.002
2.4-dichlorphenol	126	0		

	470033			
	Number of samples	Number of findings	medi	max
Atrazine	97	76	0.004	0.012
BAM (2.6-dichlorobenzamide)	97	69	0.038	0.084
Benazolin	97	0		
Bentazone	97	80	0.003	0.090
Bromoxynil	97	17	0.002	0.019
Carbofuran	97	0		
Chloridazon	97	5	0.003	0.004
Chlorsulfuron	97	0		
Cyanazine	97	9	0.011	0.218
Desethylatrazine	97	39	0.009	0.02
desethylterbuthylazine	97	78	0.005	0.051
desisopropylatrazine	97	25	0.006	0.014
Dicamba	89	6	0.0035	0.01
Dichlorprop	97	10	0.003	0.017
Dimethoate	97	3	0.001	0.001
Dinoseb	97	4	0.001	0.001
Diuron	97	58	0.016	0.725
DNOC	97	58	0.002	0.294
Ethofumesate	97	1	0.001	0.001
Fenpropimorph	86	4	0.002	0.062
Flamprop	97	0		
Fluazifop	97	6	0.004	0.014
Hexazinone	92	71	0.005	0.085
hydroxyatrazine	97	12	0.011	0.025
Hydroxycarbofuran	97	0		
hydroxysimazine	97	4	0.016	0.039
hydroxyterbuthylazine	97	40	0.012	0.061
Ioxynil	97	7	0.002	0.014
Isoproturon	97	82	0.046	1.830
Lenacil	97	4	0.077	0.119
Linuron	97	2	0.001	0.001
MCPA	97	57	0.017	0.638
Mecoprop	97	28	0.005	0.083
Methabenzthiazuron	97	0		
Metamitron	97	11	0.014	0.069
Metribuzin	97	2	0.004	0.004
Metsulfuron-methyl	97	0		
Nitrophenol	97	56	0.014	0.884
Pendimethalin	97	23	0.013	0.095
Pirimicarb	97	12	0.006	0.049
Prochloraz	97	3	0.015	0.016
Propiconazole	97	16	0.020	0.053
Propyzamide	97	7	0.026	0.068
Simazine	97	16	0.004	0.091
Terbuthylazine	97	84	0.016	0.330
Thifensulfuron	97	0		
Triadimenol	97	0		
Triasulfuron	97	0		
2.4-D	97	5	0.002	0.004
2.4-dichlorphenol	97	1	0.02	0.02

	470041			
	Number of samples	Number of findings	medi	max
Atrazine	28	0		
BAM (2.6-dichlorobenzamide)	28	1	0.004	0.004
Benazolin	28	0		
Bentazone	28	16	0.001	0.002
Bromoxynil	28	1	0.001	0.001
Carbofuran	28	0		
Chloridazon	28	0		
Chlorsulfuron	28	0		
Cyanazine	28	0		
Desethylatrazine	28	1	0.001	0.001
desethylterbuthylazine	28	3	0.001	0.001
desisopropylatrazine	28	5	0.001	0.005
Dicamba	23	0		
Dichlorprop	28	0		
Dimethoate	28	0		
Dinoseb	28	0		
Diuron	28	0		
DNOC	28	14	0.001	0.022
Ethofumesate	28	0		
Fenpropimorph	22	0		
Flamprop	28	0		
Fluazifop	28	0		
Hexazinone	28	0		
hydroxyatrazine	28	0		
Hydroxycarbofuran	28	2	1.336	1.586
hydroxysimazine	28	1	0.008	0.008
hydroxyterbuthylazine	28	4	0.0015	0.05
Ioxynil	28	2	0.002	0.003
Isoproturon	28	15	0.005	0.122
Lenacil	28	0		
Linuron	28	0		
MCPA	28	0		
Mecoprop	28	1	0.003	0.003
Methabenzthiazuron	28	0		
Metamitron	28	1	0.001	0.001
Metribuzin	28	0		
Metsulfuron-methyl	28	0		
Nitrophenol	28	11	0.01	0.125
Pendimethalin	28	0		
Pirimicarb	28	0		
Prochloraz	28	0		
Propiconazole	28	2	0.0025	0.004
Propyzamide	28	0		
Simazine	28	0		
Terbuthylazine	28	2	0.001	0.001
Thifensulfuron	28	0		
Triadimenol	28	0		
Triasulfuron	28	0		
2.4-D	28	0		
2.4-dichlorphenol	28	0		

	470045			
	Number of samples	Number of findings	medi	max
Atrazine	25	16	0.004	0.037
BAM (2.6-dichlorobenzamide)	25	0		
Benazolin	25	0		
Bentazone	25	16	0.002	0.076
Bromoxynil	25	1	0.001	0.001
Carbofuran	25	0		
Chloridazon	25	1	0.001	0.001
Chlorsulfuron	25	0		
Cyanazine	25	0		
Desethylatrazine	25	19	0.036	0.076
desethylterbuthylazine	25	14	0.002	0.016
desisopropylatrazine	25	8	0.005	0.014
Dicamba	20	0		
Dichlorprop	25	0		
Dimethoate	25	0		
Dinoseb	25	0		
Diuron	25	0		
DNOC	25	10	0.002	0.008
Ethofumesate	25	0		
Fenpropimorph	17	0		
Flamprop	25	0		
Fluazifop	25	0		
Hexazinone	24	0		
hydroxyatrazine	25	20	0.014	0.244
Hydroxycarbofuran	25	0		
hydroxysimazine	25	0		
hydroxyterbuthylazine	25	18	0.012	0.043
Ioxynil	25	0		
Isoproturon	25	12	0.040	0.154
Lenacil	25	0		
Linuron	25	0		
MCPA	25	0		
Mecoprop	25	1	0.003	0.003
Methabenzthiazuron	25	0		
Metamitron	25	0		
Metribuzin	25	0		
Metsulfuron-methyl	25	0		
Nitrophenol	25	6	0.006	0.025
Pendimethalin	25	3	0.007	0.026
Pirimicarb	25	0		
Prochloraz	25	0		
Propiconazole	25	1	0.002	0.002
Propyzamide	25	0		
Simazine	25	0		
Terbuthylazine	25	5	0.002	0.010
Thifensulfuron	25	0		
Triadimenol	25	0		
Triasulfuron	25	0		
2.4-D	25	0		
2.4-dichlorphenol	25	0		

Appendix 7.1

	130011			
	Number of samples	Number of findings	median	max
Atrazine	72	6	0.001	0.002
BAM (2.6-dichlorobenzamide)	72	12	0.003	0.020
Benazolin	72	9	0.001	0.003
Bentazone	72	51	0.003	2.910
Bromoxynil	72	9	0.014	0.162
Carbofuran	72	0		
Chloridazon	72	2	0.016	0.031
Chlorsulfuron	72	0		
Cyanazine	72	10	0.014	0.068
Desethylatrazine	72	4	0.001	0.001
desethylterbuthylazine	72	13	0.003	0.028
desisopropylatrazine	72	21	0.002	0.010
Dicamba	61	0		
Dichlorprop	72	1	0.001	0.001
Dimethoate	72	1	0.002	0.002
Dinoseb	72	1	0.014	0.014
Diuron	72	18	0.007	0.140
DNOC	72	25	0.004	0.072
Ethofumesate	60	1	0.006	0.006
Fenpropimorph	60	2	0.022	0.042
Flamprop	72	0		
Fluazifop	72	0		
Hexazinone	72	2	0.035	0.068
hydroxyatrazine	72	5	0.001	0.001
Hydroxycarbofuran	72	0		
hydroxysimazine	72	1	0.008	0.008
hydroxyterbuthylazine	72	11	0.002	0.008
Ioxynil	72	2	0.004	0.004
Isoproturon	72	42	0.059	0.129
Lenacil	72	6	0.037	0.065
Linuron	72	1	0.001	0.001
MCPA	72	9	0.006	0.021
Mecoprop	72	14	0.005	0.015
Methabenzthiazuron	72	3	0.001	0.001
Metamitron	72	1	0.001	0.001
Metribuzin	72	5	0.002	0.006
Metsulfuron-methyl	72	0		
Nitrophenol	72	26	0.007	0.104
Pendimethalin	72	21	0.024	0.195
Pirimicarb	72	2	0.008	0.014
Prochloraz	72	3	0.001	0.019
Propiconazole	72	5	0.007	0.044
Propyzamide	72	1	0.001	0.001
Simazine	72	1	0.001	0.001
Terbuthylazine	72	25	0.004	0.136
Thifensulfuron	72	0		
Triadimenol	69	1	0.003	0.003
Triasulfuron	72	0		
2.4-D	72	1	0.003	0.003
2.4-dichlorphenol	72	0		

	130013			
	Number of samples	Number of findings	median	max
Atrazine	45	3	0.003	0.004
BAM (2.6-dichlorobenzamide)	45	3	0.001	0.001
Benazolin	45	6	0.001	0.002
Bentazone	45	26	0.003	0.017
Bromoxynil	45	6	0.012	0.037
Carbofuran	45	1	0.001	0.001
Chloridazon	45	3	0.041	0.043
Chlorsulfuron	45	0		
Cyanazine	45	0		
Desethylatrazine	45	0		
desethylterbuthylazine	45	0		
desisopropylatrazine	45	8	0.001	0.002
Dicamba	38	0		
Dichlorprop	45	0		
Dimethoate	45	0		
Dinoseb	45	1	0.006	0.006
Diuron	45	0		
DNOC	45	4	0.003	0.004
Ethofumesate	45	1	0.112	0.112
Fenpropimorph	31	0		
Flamprop	45	0		
Fluazifop	45	0		
Hexazinone	45	0		
hydroxyatrazine	45	0		
Hydroxycarbofuran	45	0		
hydroxysimazine	45	0		
hydroxyterbuthylazine	45	0		
Ioxynil	45	0		
Isoproturon	45	19	0.071	0.129
Lenacil	45	0		
Linuron	45	0		
MCPA	45	3	0.008	0.011
Mecoprop	45	0		
Methabenzthiazuron	45	0		
Metamitron	45	0		
Metribuzin	45	1	0.012	0.012
Metsulfuron-methyl	45	0		
Nitrophenol	45	14	0.004	0.037
Pendimethalin	45	2	0.014	0.026
Pirimicarb	45	0		
Prochloraz	45	0		
Propiconazole	45	2	0.002	0.002
Propyzamide	45	0		
Simazine	45	0		
Terbuthylazine	45	0		
Thifensulfuron	45	0		
Triadimenol	42	0		
Triasulfuron	45	0		
2.4-D	45	3	0.020	0.026
2.4-dichlorphenol	45	0		

Appendix 8.1

Quarterly report from January 1998 to October 2000 on the transport of active substances (grammes) and time of calculation (hours) within the entire Lillebæk catchment.

Active substance	1999				2000		
	1st	2nd	3rd	4th	1st	2nd	3rd
Time of calculation	24	58	28	26	76	825	92
Atrazine		0.0026	0.0160	0.0006	0.1146	0.1573	0.0134
BAM (2.6 dichlorobenzamide)		0.0209	0.0031	0.0001	0.7113	1.7664	0.1779
Benazolin							
Bentazone		0.0036	0.0861	0.0345	0.0647	0.3454	0.0106
Bromoxynil		0.0010			0.0235	0.0533	
Carbofuran							
Chloridazon			0.0002	0.0001		0.0094	0.0001
Chlorsulfuron							
Cyanazine			0.2545	0.0001	0.0102	0.0845	
Desethylatrazine		0.0041	0.0120	0.0001	0.2823	0.1958	0.0037
Desethylterbuthylazine		0.0096	0.0828	0.0180	0.2806	0.2894	0.0676
Desisopropylatrazine		0.0020	0.0151	0.0004	0.1271	0.0138	0.0033
Dicamba						0.0427	0.0002
Dichlorprop		0.0005			0.0102	0.0542	
Dimethoate							
Dinoseb		0.0005					
Diuron		0.0041	0.7875	0.0009	0.0375	2.2245	0.0487
DNOC		0.0005		0.1291	0.0569	0.0927	0.0745
Ethofumesate					0.0102		
Fenpropimorph		0.0010					0.0031
Flamprop							
Fluazifop		0.0005		0.0059		0.0124	
Hexazinone		0.0483	0.0130	0.1396	0.1900	0.2898	0.0046
Hydroxyatrazine			0.0138	0.0003	0.2445		0.0006
Hydroxycarbofuran							
Hydroxysimazine				0.0058	0.1878		0.0006
Hydroxyterbuthylazine		0.0010	0.0827		0.1756	0.2631	0.0457
Ioxynil		0.0005				0.0333	
Isoproturon		0.0005	0.0001	1.3176	3.3969	3.7596	0.2043
Lenacil						0.4116	
Linuron				0.0001	0.0027		
MCPA		0.0026	0.1726	0.2197		4.4203	0.0226
Mecoprop		0.0015	0.0001	0.0509	0.0272	0.0982	
Methabenzthiazuron							
Metamitron		0.0015		0.0346		0.0576	
Metribuzin				0.0006	0.0410		
Metsulfuron-methyl							
Nitrophenol		0.0026	0.0744	0.4863	0.2955	0.7296	0.1417
Pendimethalin				0.0183	0.3093	0.0141	0.0067
Pirimicarb			0.0506		0.0717	0.0059	0.0447
Prochloraz							0.0017
Propiconazole		0.1108	0.0411			0.0272	0.0003
Propyzamide					1.1190	0.0026	
Simazine			0.0255	0.0328	0.0034	0.0244	0.0002
Terbuthylazine		0.0729	0.1527	0.0136	0.4811	1.5827	0.4059
Thifensulfuron							
Triadimenol							
Triasulfuron							
2.4-D						0.0101	
2.4-dichlorphenol						0.0277	

Appendix 8.2

Quarterly report from January 1998 to October 2000 on the transport of active substances (grammes) and time of calculation (hours) within the upper sub-catchment of Lillebæk.

Active substance	1999				2000		
	1st	2nd	3rd	4th	1st	2nd	3rd
Time of calculation	24	122	82	131	34	877	82
Atrazine		0.2180	0.0326	0.0086	0.0299	0.0981	0.0022
BAM (2.6-dichlorobenzamide)		0.0825	0.0501	0.0565	0.2455	0.7609	0.0447
Benazolin		0.0003		0.0013			
Bentazone	0.0272	0.1022	0.0054	0.0094	0.0108	0.0422	0.0000
Bromoxynil		0.0308		0.0022		0.0198	
Carbofuran							
Chloridazon		0.0022	0.0014	0.0092			
Chlorsulfuron				1.0870			
Cyanazine		0.0236	0.4217	0.0001		0.0921	
Desethylatrazine		0.0414	0.0176	0.1428	0.0713	0.1231	0.0026
Desethylterbuthylazine		0.4238	0.1840	0.4380	0.1042	0.3773	0.0510
Desisopropylatrazine		0.0180	0.0196	0.0163	0.0369	0.0577	0.0030
Dicamba				0.0009	0.0026	0.0154	
Dichlorprop		0.0044	0.0013	0.0019			0.0000
Dimethoate		0.0083				0.0224	
Dinoseb		0.0025					
Diuron		1.0000	0.0367	0.0076	0.0052	2.4716	0.0358
DNOC		0.0143	0.0093	0.0064	0.0230	0.1976	0.0355
Ethofumesate		0.0176	0.0027	0.0179		0.0608	
Fenpropimorph		0.0277		0.0028			
Flamprop							
Fluazifop		0.0300		0.0003		0.0239	
Hexazinone		0.0551	0.1998	0.2345	0.0741	0.3029	0.0036
Hydroxyatrazine		0.0050	0.0356	0.1530	0.0487	0.0187	0.0058
Hydroxycarbofuran							
Hydroxysimazine		0.0896		0.0012	0.0017		
Hydroxyterbuthylazine		0.2206	0.1269	0.6728	0.0653	0.4006	0.0972
Ioxynil		0.0444		0.0025		0.0046	
Isoproturon		0.0048	0.0070	12.3925	0.3319	2.2893	0.0328
Lenacil		0.0005				0.1526	0.0033
Linuron		0.0071		0.0000			
MCPA		0.4300	0.7111	0.0029		1.3352	0.0737
Mecoprop		0.0074	0.0053	0.0079	0.0017	0.0936	0.0004
Methabenzthiazuron							
Metamitron		0.0820		0.0170		0.0722	
Metribuzin				0.0003			0.0001
Metsulfuron-methyl							
Nitrophenol		0.0598	0.0540	0.0301	0.1015	1.3724	0.0657
Pendimethalin		0.0110	0.0392	2.0180	0.0210	0.0721	0.0043
Pirimicarb		0.0029	0.0084	0.0004			0.0010
Prochloraz		0.0003		0.0004			
Propiconazole		0.1452	0.0376	0.0018		0.0804	0.0072
Propyzamide				0.0010	0.0925	0.1527	
Simazine		0.1102	0.4320	0.1058	0.0017	0.0456	0.0014
Terbuthylazine		3.5239	0.4115	0.8535	0.1228	5.0753	0.2174
Thifensulfuron							
Triadimenol		0.0003		0.0005			0.0009
Triasulfuron							
2.4-D		0.0014				0.0034	
2.4-dichlorphenol							

Appendix 9.1

Quarterly report from January 1998 to October 2000 on the transport of active substances (grammes) and time of calculation (hours) within the catchment of Odderbæk.

Active substance	1999				2000		
	1st	2nd	3rd	4th	1st	2nd	3rd
Time of calculation	46	122	28	98	76	78	30
Atrazine			0.0386			0.0084	0.0048
BAM (2.6-dichlorobenzamide)				0.1629		0.0271	0.0546
Benazolin				0.1256			
Bentazone	0.0485	66.964	4.6133	0.2744	0.1842	3.1456	0.0956
Bromoxynil					0.1030	0.0114	
Carbofuran							
Chloridazon			0.0386				
Chlorsulfuron							
Cyanazine						0.0545	
Desethylatrazine					0.0205		
Desethylterbuthylazine		0.0521	0.1159	0.0344		0.0547	0.0662
Desisopropylatrazine			0.0386	0.0742	0.0246	0.0430	0.0032
Dicamba							
Dichlorprop			0.0386				
Dimethoate			0.0773				
Dinoseb							0.0403
Diuron			0.8157	0.4451	0.0063	0.5172	0.0326
DNOC			0.1932	0.0750	0.0274	0.1525	0.2441
Ethofumesate			0.2318				
Fenpropimorph				0.0062			0.0189
Flamprop							
Fluazifop							
Hexazinone		0.7088					0.0043
Hydroxyatrazine			0.0386	0.0224			
Hydroxycarbofuran							
Hydroxysimazine			0.3091				
Hydroxyterbuthylazine		0.0006	0.2318	0.0855		0.0152	
Ioxynil			0.1546			0.0076	
Isoproturon	1.4794	2.1345	0.1159	6.7914	2.9444	0.8165	0.3994
Lenacil						0.1235	
Linuron			0.0386				
MCPA			0.1932			0.1471	0.0287
Mecoprop			0.0386	0.0105			
Methabenzthiazuron				0.0344			
Metamitron			0.0386				
Metribuzin			0.0386	0.1377			
Metsulfuron-methyl							
Nitrophenol			0.5814	0.2479	0.0488	0.0299	0.1324
Pendimethalin		1.9081	0.1159	2.4536	0.0538	0.6393	0.0520
Pirimicarb				0.0004			0.0304
Prochloraz				0.0100			0.0086
Propiconazole		1.0243	0.1159	0.0131			
Propyzamide				0.0062			
Simazine			0.0386				
Terbuthylazine		0.1256	0.5796	0.0511		0.1864	0.3205
Thifensulfuron							
Triadimenol			0.1159				
Triasulfuron							
2.4-D						0.0072	
2.4-dichlorphenol							