The Danish Pesticide Leaching Assessment Programme

Monitoring results May 1999–June 2004

Jeanne Kjær, Preben Olsen, Heidi C. Barlebo, Trine Henriksen, Rene K. Juhler, Finn Plauborg, Ruth Grant, Per Nygaard and Lasse Gudmundsson

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Preface

In 1998, the Danish Parliament initiated the Danish Pesticide Leaching Assessment Programme (PLAP), an intensive monitoring programme aimed at evaluating the leaching risk of pesticides under field conditions. The Danish Government funded the first phase of the programme from 1998 to 2001, while the Ministry of the Environment and the Ministry of Food, Agriculture and Fisheries are funding a prolongation from 2002 to 2009.

The work was conducted by the Geological Survey of Denmark and Greenland (GEUS), the Danish Institute of Agricultural Sciences (DIAS) and the National Environmental Research Institute (NERI) under the direction of a management group comprising Jeanne Kjær (GEUS), Walter Brüsch (GEUS), Ole Hørbye Jacobsen (DIAS), Preben Olsen (DIAS), Ruth Grant (NERI), Christian Ammitsøe (Danish Environmental Protection Agency) and Steen Marcher (Danish Environmental Protection Agency).

This report presents the results for the period May 1999–June 2004. Results covering part of the period (May 1999–June 2003) have been reported previously (Kjær *et al.*, 2002, Kjær *et al.*, 2003 and Kjær *et al.*, 2004). The present report should therefore be seen as a continuation of previous reports with the main focus being on the leaching risk of pesticides applied during 2002.

The report was prepared jointly by Jeanne Kjær, Heidi C. Barlebo, Trine Henriksen, Rene K. Juhler, Per Nygaard and Lasse Gudmundsson (all GEUS), Preben Olsen and Finn Plauborg (DIAS) and Ruth Grant (NERI). While all authors contributed to the whole report, the aspects for which authors were mainly responsible are as follows:

- Pesticide and bromide leaching: Jeanne Kjær and Preben Olsen
- Soil water dynamics and water balances: Heidi C. Barlebo, Finn Plauborg and Ruth Grant
- Pesticide analysis quality assurance: Trine Henriksen

Jeanne Kjær October 2005

Summary

In 1998, the Danish Parliament initiated the Pesticide Leaching Assessment Programme (PLAP), an intensive monitoring programme aimed at evaluating the leaching risk of pesticides under field conditions. The objective of the PLAP is to improve the scientific foundation for decision making in the Danish registration procedures for pesticides. The specific aim is to analyse whether pesticides applied in accordance with current regulations leach to the groundwater in unacceptable concentrations. The programme presently evaluates the leaching risk of 29 pesticides applied at five agricultural sites ranging in size from 1.1 to 2.4 ha. The results so far show that:

- Of the 29 pesticides applied, seven did not leach during the current monitoring period.
- The monitoring data indicate pronounced leaching of eight of the applied pesticides or their degradation products. Thus ethofumesate, bentazone, glyphosate and its degradation product AMPA, metamitron and its degradation product desamino-metamitron, as well as the degradation products of metribuzin, terbutylazine, pirimicarb, and rimsulfuron leached from the root zone (1 m b.g.s.) in average concentrations exceeding the maximum allowable concentration of 0.1 μ g/l. Except for a degradation product of metribuzin, pronounced leaching was mainly confined to a depth of 1 m, where pesticides were frequently detected in samples from suction cups and drainage systems. Only the metribuzin degradation product was detected beneath this depth at an average concentration exceeding 0.1 μ g/l.
- The monitoring data also indicate leaching of a further 14 pesticides, but not in high concentrations. Thus although the concentration exceeded 0.1 μ g/l in several samples, the average leaching concentration did not.

The PLAP initially evaluated the leaching risk at six agricultural sites representing a range of Danish soil and climate conditions. Monitoring at the Slaeggerup site was terminated on 1 July 2003, and results from that site are not included in the present report. For the monitoring results from this site see Kjær *et al.* (2004). The pesticides were all applied at the maximum permitted rate. In order to describe water transport a bromide tracer was also applied to the fields. Bromide and pesticide concentrations are measured monthly in both the unsaturated and the saturated zones, and weekly in the drainage water. This report presents the monitoring results from the five agricultural sites at which monitoring is still performed and covers the period May 1999–June 2004. The main focus is on evaluating the leaching risk of those pesticides applied during 2002. The report should be viewed as an interim report because not all of the pesticides applied have been monitored for at least two consecutive years.

Dansk sammendrag

I 1998 vedtog Folketinget at iværksætte projektet "Varslingssystem for udvaskning af pesticider til grundvandet" (VAP). VAP er et omfattende moniteringsprogram, der undersøger udvaskning af pesticider under reelle markforhold. Programmet har til formål at undersøge, om godkendte pesticider eller deres nedbrydningsprodukter – ved regelret brug – udvaskes til grundvandet i koncentrationer over grænseværdien, for herigennem at udvide det videnskabelige grundlag for danske myndigheders (Miljøstyrelsens) procedurer for registrering af sprøjtemidler. 29 stoffers udvaskningsrisiko undersøges således på fem marker af en størrelse på mellem 1,1 og 2,6 ha. De hidtidige resultater viser at:

- Af de 29 pesticider, der er blevet udbragt, blev de syv ikke fundet udvasket i løbet af perioden 1999–2004.
- Otte af de udbragte stoffer, eller nedbrydningsprodukter heraf, gav anledning til en markant udvaskning. Ethofumesat, bentazon, metamitron, dettes nedbrydningsprodukt desamino-metamitron, glyphosat, dettes nedbrydningsprodukt AMPA, samt nedbrydningsprodukter fra henholdsvis pirimicarb, metribuzin, terbutylazine og rimsulfuron blev udvasket fra rodzonen (1 m.u.t.) i gennemsnitskoncentrationer over grænseværdien på 0,1 µg/l. På nær gældende metribuzins nedbrydningsprodukt var udvaskningen primært begrænset til 1 m.u.t., hvor stofferne hyppigt blev fundet i prøver udtaget i sugeceller og dræn. Markant udvaskning under denne dybde blev kun observeret for metribuzins nedbrydningsprodukt, som i større dybder blev fundet i gennemsnitskoncentrationer over 0.1 µg/l.
- Andre 14 stoffer gav anledning til udvaskning. Selv om flere af disse stoffer ofte blev fundet i koncentrationer over $0,1 \mu g/l$, var der ikke tale om, at udvaskningen som årsmiddel oversteg grænseværdien på $0,1 \mu g/l$.

VAP-programmet omfattede oprindeligt seks marker placeret så de repræsenterer forskellige typer geologi og tillige tager hensyn til de klimatiske variationer i Danmark, specielt hvad angår nedbørforhold. Monitering på den ene forsøgsmark (Slæggerup) stoppede 1 juli 2003. Resultater fra denne mark er ikke inkluderet i denne rapport, men kan findes i Kjær *et al.* (2004). De anvendte pesticider bliver udbragt i maksimalt tilladte doser. Bromid anvendes som sporstof for at beskrive vandtransporten. Bromid- og pesticidkoncentrationer bliver analyseret månedligt i prøver udtaget i den umættede og mættede zone og ugentligt i prøver af drænvand. I denne rapport præsenteres moniteringsresultaterne for de fem områder for perioden maj 1999-juni 2004, primært med fokus på pesticider udbragt i 2002. En del af stofferne har kun været inkluderet i moniteringsprogrammet i én udvaskningssæson, og for disse er det derfor for tidligt at konkludere noget endeligt.

1 Introduction

There is growing public concern in Denmark about pesticide contamination of our surface waters and groundwater. Pesticides and their degradation products have increasingly been detected in the groundwater during the past decade and are now present in much of the Danish groundwater. Pesticides and their degradation products have so far been detected in 45% of all screens monitored under the Danish National Groundwater Monitoring Programme (GRUMO) (Jørgensen, 2005).

Due to the increasing detection of pesticides in groundwater over the past 10 years the desire has arisen to enhance the scientific foundation for the existing approval procedure for pesticides and to improve the present risk assessment tools. A main issue in this respect is that the EU assessment and hence also the Danish assessment of the risk of pesticide leaching to the groundwater is largely based on data from modelling, laboratory or lysimeter studies. However, these types of data may not suffice to adequately characterize the leaching that may occur under actual field conditions. Although models are widely used within the registration process their validation requires further work, not least because of the limited availability of field data (Boesten, 2000). Moreover, laboratory and lysimeter studies do not include the spatial variability of the soil parameters (hydraulic, chemical and microbiological soil properties) affecting pesticide leaching. This is of particular importance for silty and loamy soils, where preferential transport may have a major impact on pesticide leaching. In fact, various field studies suggest that considerable preferential transport of several pesticides occurs to a depth of 1 m under conditions comparable to those pertaining in Denmark (Kördel, 1997).

The inclusion of field studies, i.e. test plots exceeding 1 ha, in risk assessment of pesticide leaching to the groundwater is considered an important improvement in risk assessment procedures. For example, the US Environmental Protection Agency (US-EPA) has included field-scale studies in its risk assessments since 1987. Pesticides that may potentially leach to the groundwater are required to be included in field studies as part of the registration procedure. The US-EPA has therefore conducted field studies of more than 50 pesticides (US Environmental Protection Agency, 1998). A similar concept has also been adopted within the European Union (EU), where Directive 91/414/EEC, Annexe VI (Council Directive 97/57/EC of 22 September 1997) enables field study results to be included in the risk assessments.

1.1 Objective

In 1998, the Danish Government initiated the Pesticide Leaching Assessment Programme (PLAP), an intensive monitoring programme aimed at evaluating the leaching risk of pesticides under field conditions. The PLAP is intended to serve as an early warning system providing decision makers with advance warning if approved pesticides leach in unaccept

able concentrations. The programme focuses on pesticides used in arable farming and monitors leaching at five agricultural test sites representative of Danish conditions.

The objective of the PLAP is to improve the scientific foundation for decision making in the Danish registration and approval procedures for pesticides, enabling field studies to be included in risk assessment of selected pesticides. The specific aim is to analyse whether pesticides applied in accordance with current regulations leach at levels exceeding the maximum allowable concentration of $0.1 \mu g/l$.

1.2 Structure of the PLAP

The pesticides included in the PLAP were selected by the Danish Environmental Protection Agency on the basis of expert judgement. At present, 29 pesticides and several of their degradation products are included in the PLAP. All the compounds analysed are listed in Appendix 1.



Figure 1. Location of the PLAP sites Tylstrup, Jyndevad, Silstrup, Estrup and Faardrup. Monitoring at Slaeggerup was terminated on 1 July 2003.

Soil type and climatic conditions are considered to be some of the most important parameters controlling pesticide leaching. The PLAP initially encompassed six test sites representative of the dominant soil types and the climatic conditions in Denmark (Figure 1). Monitoring at the Slaeggerup site was terminated on 1 July 2003, and results from that site are not included in the present report. For the monitoring results from this site see Kjær *et al.* (2003). The groundwater table at all the sites is shallow, thereby enabling pesticide leaching to the groundwater to be rapidly detected (Table 1). Cultivation of the PLAP sites is in line with conventional agricultural practice in the vicinity. The pesticides are applied in the maximum permitted dosage and in the manner specified in the regulations. Hence any occurrence of pesticides or degradation products in the groundwater downstream of the sites can be related to the current approval conditions pertaining for the individual pesticides. The PLAP was initiated in autumn 1998. The five test sites encompassed by the present report were selected and established during 1999. Monitoring was initiated at Tylstrup, Jyndevad and Faardrup in 1999, and at Silstrup and Estrup in 2000 (Table 1).

	Tylstrup	Jyndevad	Silstrup	Estrup	Faardrup
Location	Brønder- slev	Tinglev	Thisted	Vejen	Slagelse
Precipitation ¹⁾ (mm/y)	668	858	866	862	558
Pot. evapotransp. ¹⁾ (mm/y)	552	555	564	543	585
W x L (m)	70 x 166	135 x 184	91 x 185	105 x 120	150 x 160
Area (ha)	1.1	2.4	1.7	1.3	2.3
Tile drain	No	No	Yes	Yes	Yes
Monitoring initiated	May 1999	Sep 1999	Apr 2000	Apr 2000	Sep 1999
Geological characteristics					
– Deposited by	Saltwater	Meltwater	Glacier	Glacier/meltwater	Glacier
– Sediment type – DGU symbol	Fine sand YS	Coarse sand TS	Clayey till ML	Clayey till ML	Clayey till ML
– Depth to the calcareous					
matrix (m b.g.s.) - Depth to the reduced matrix (m b.g.s.)	6 >12	5–9 10–12	1.3 5	$1-4^{(2)}$ >5 ⁽²⁾	1.5 4.2
$-$ Max. fracture depth $^{3)}$ (m)	_	_	4	>6.5	8
- Fracture intensity 3-4 m depth (fractures/m)	_	_	<1	11	4
– Ks in C horizon (m/s)	$2.0 \cdot 10^{-5}$	$1.3 \cdot 10^{-4}$	3.4.10-6	8.0.10-8	7.2.10-6
Topsoil characteristics					
- DK classification	JB2	JB1	JB7	JB5/6	JB5/6
– Classification	Loamy sand	Sand	Sandy clay loam/ sandy loam	Sandy loam	Sandy loam
– Clay content (%)	6	5	18–26	10-20	14–15
– Silt content (%)	13	4	27	20-27	25
– Sand content (%)	78	88	8	50-65	57
– pH	4-4.5	5.6-6.2	6.7–7	6.5-7.8	6.4–6.6
– TOC (%)	2.0	1.8	2.2	1.7-7.3	1.4

Table 1.	Characteristics	of the five	PLAP sites	(modified from	Lindhardt et al., 2	001).
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¹⁾ Yearly normal based on a time series for the period 1961–90. The data refer to precipitation measured 1.5 m above ground.

²⁾ Large variation within the field.

³⁾ Maximum fracture depth refers to the maximum fracture depth found in excavations and wells.

Site characterization and monitoring design are described in detail in Lindhardt *et al.* (2001). This report presents the results of the monitoring period May 1999–June 2004. Results covering part of the monitoring period (May 1999–June 2003) have been published previously (Kjær *et al.*, 2002; Kjær *et al.*, 2003 and Kjær *et al.*, 2004). The present report should therefore be seen as a continuation of the latter reports, with the main focus being on the leaching risk of pesticides applied during 2002. For a detailed description of the first part of the monitoring period (May 1999–June 2002), see Kjær *et al.* (2003) and Kjær *et al.* (2004).

Under the PLAP the leaching risk of pesticides is evaluated on the basis of at least two years of monitoring data. For some pesticides the present report must be considered preliminary because they have been monitored for an insufficient period of time.

Hydrological modelling of the unsaturated zone at each PLAP site supports the monitoring data. The MACRO model (version 5.0) is used to describe the soil water dynamics at each site during the full monitoring period July 1999–June 2004. In addition, bromide transport is simulated at the two sandy sites Tylstrup and Jyndevad. In previous PLAP modelling studies (Kjær *et al.*, 2004), an older version of MACRO (version 4.2) was used. Due to the change in model version, the five site models have been recalibrated for the full monitoring period. The model set-up is closely similar to that reported in Kjær *et al.* (2003), but has been adjusted to the requirements of the new version.

Scientifically valid methods of analysis are essential for the integrity of the PLAP. The field monitoring work has therefore been supported by intensive quality assurance entailing continuous evaluation of the analyses employed. The quality assurance methodology and results are presented in Section 7.

2 Pesticide leaching at Tylstrup

2.1 Materials and methods

2.1.1 Site description and monitoring design

Tylstrup is located in northern Jutland (Figure 1). The test field covers a cultivated area of 1.1 ha (70 x 166 m) and is practically flat, with a windbreak bordering the eastern and western sides. Based on two soil profiles dug in the buffer zone around the test field the soil was classified as a Humic Psammentic Dystrudept (Soil Survey Staff, 1999). The topsoil is characterized as loamy sand with 6% clay and 2.0% total organic carbon (Table 1). The aquifer material consists of about 20 metres of marine sand sediment deposited in the Yoldia Sea. The southern part is rather homogeneous, consisting entirely of fine-grained sand, whereas the northern part is more heterogeneous due to the intrusion of several silt and clay lenses (Lindhardt *et al.*, 2001). During the monitoring period the groundwater table was 3–4.5 m b.g.s. The overall direction of groundwater flow was towards the west (Figure 2). A brief description of the sampling procedure is provided in Appendix 2. The monitoring design and test site are described in detail in Lindhardt *et al.* (2001), and the analysis methods in Kjær *et al.* (2002).

2.1.2 Agricultural management

Management practice during the 2002 and 2003 growing seasons is briefly summarized below and detailed in Appendix 3 (Table A3.1). For information about management practice during the first two monitoring periods see Kjær *et al.* (2003).

The 2002 crop was winter rape (cv. Artus). Due to the rainy conditions in August 2001, sowing had to be postponed until 3 September, more than 2 weeks later than normal. Clomazone was sprayed to combat weeds 2 days after sowing, i.e. before the crop emerged. On 16 October, when the crop had 4 unfolded leaves, weeds were sprayed with clopyralid (this substance was not included in the monitoring, however). Due to the unusually warm weather in October, the rape was well developed at the onset of winter. At the end of 2001, temperatures dropped below zero, and on 1 January the field was covered with approx. 15 cm of snow. At the beginning of January, temperatures rose above zero, and on 8 January there was 1–2 cm of standing meltwater at both ends of the field. One week later, all of the water had infiltrated. The rape was fertilized once on 22 March using commercial fertilizer. The crop was irrigated three times between 24 April and 31 May. The yield of rapeseed was just 26 hkg/ha at 91% dry mater, the low yield being attributable to the late sowing time.

On 19 September 2002 the field was sown with winter wheat (cv. Solist). On 9 October, when the crop had 2 unfolded leaves, weeds were sprayed with a mixture of prosulfocarb, ioxynil and bromoxynil. Prosulfocarb was not included in the monitoring programme, how

ever. Potassium bromide tracer was applied on 27 May, the second application since the start of the monitoring program. On 8 May, when the first joint of the wheat was detectable, the herbicide fluroxypyr was applied. Seven days later, when the second joint was detectable, an additional herbicide, flamprop-M-isopropyl, was applied. The fungicide propiconazole was applied on 28 May and 17 June (not included in the monitoring, however) and the pesticide dimethoate was applied on 8 July. Irrigation was performed once on 24 June using 23 mm/ha. The yield of grain was disappointingly low – 54.5 hkg/ha (85% dry matter). In field trials conducted this year on sandy soils by the Danish Farmers Association the average yield was 74.5 hkg/ha. The low yield at Tylstrup may be attributable to the local conditions. Considering the time of sowing, a plant density of 270 plants/m² was too low. Furthermore, due to heavy sand drift in the spring the plants suffered mechanical damage.



Figure 2. Overview of the Tylstrup test site. The innermost white area indicates the cultivated land, while the grey area indicates the surrounding buffer zone. The positions of the various installations are indicated, as is the direction of groundwater flow (by an arrow).

2.1.3 Model set-up and calibration

The MACRO model is applied to the Tylstrup site covering the soil profile to a depth of 5 m b.g.s., always including the groundwater table. The model is used to simulate water and bromide transport in the unsaturated zone during the full monitoring period May 1999–June 2004 and to establish an annual water balance.

Due to application of a newer version of MACRO than used in the previous report (version 5.0 vs 4.2) (Kjær *et al.*, 2004) the model for the Tylstrup site has been recalibrated for the whole period to the observed groundwater table measured in the piezometers located in the buffer zone, to time series of soil water content measured at three different depths (25, 60 and 110 cm b.g.s.) from the two profiles S1 and S2 (see Figure 2) and to the bromide concentration measured in the suction cups located 1 and 2 m b.g.s. Data acquisition and model set-up are described in Appendix 4. The main calibration parameters were the empirical parameter, BGRAD, which regulates the boundary flow, the "boundary" pressure head (XMPOR), its corresponding water content (CTEN), the hydraulic conductivity (KSM), the dispersivity (DV), the mixing depth (ZMIX) and the effective diffusion path length (ASCALE), which controls the exchange of water and solute between the two flow domains (see Appendix 4 for details).

2.2 Results and discussion

2.2.1 Soil water dynamics and water balances

The model simulations are generally consistent with the observed data, thus indicating a good model description of the overall soil water dynamics in the unsaturated zone. The results for previous years obtained with MACRO 5.0 are very similar to those obtained with MACRO 4.2 (Kjær *et al.*, 2004). The model provides a good simulation of the measured fluctuations in the groundwater table (Figure 3B). The dynamics is captured, but as with previous simulations the amplitude of the fluctuations is less well described. The overall trends in soil water content are modelled successfully, with the model capturing soil water dynamics at all depths (Figure 3C-E).

The resulting annual water balance is shown for each monitoring period (July–June) in Table 2. It is very similar to the balance calculated with MACRO 4.2 (Kjær *et al.*, 2004). Precipitation in the latest monitoring year, July 2003–June 2004, was the lowest since monitoring began at the site and is characterized by a very dry late summer/autumn (August– October) (Appendix 5). This resulted in almost no percolation 1 m b.g.s. during the summer months, and less percolation than in previous monitoring years. For information about the water balance in previous monitoring periods see Kjær *et al.* (2004).



Figure 3. Soil water dynamics at Tylstrup: Measured precipitation, irrigation and simulated percolation 1 m b.g.s. (A), simulated and measured groundwater level (B), and simulated and measured soil water saturation (SW sat.) at three different soil depths (C, D and E). The measured data in B derive from piezometers located in the buffer zone. The measured data in C, D and E derive from TDR probes installed at S1 and S2 (Figure 2).

	Normal precipitation ²⁾	Precipitation	Irrigation	Actual evapotranspiration	Groundwater recharge ³⁾
1.5.99–30.6.99 ¹⁾	120	269	0	154	115
1.7.99-30.6.00	773	1073	33	511	595
1.7.00-30.6.01	773	914	75	467	522
1.7.01-30.6.02	773	906	80	534	452
1.7.02-30.6.03	773	918	23	503	438
1.7.03-30.6.04	773	758	0	507	251

Table 2. Annual water balance for Tylstrup (mm/y). Precipitation is corrected to the soil surface according to the method of Allerup and Madsen (1979).

¹⁾ Accumulated for a two-month period

²⁾ Normal values based on time series for 1961–1990

³⁾ Groundwater recharge is calculated as precipitation + irrigation - actual evapotranspiration

2.2.2 Bromide leaching

Bromide has now been applied twice at Tylstrup. The bromide concentrations measured up to April 2003 (Figure 4 and Figure 5) relate to the bromide applied in May 1999, as described further in Kjær *et al.* (2003). Transport of the bromide applied in March 2003 will be evaluated in due course as the results become available.



Figure 4. Measured bromide concentration in the unsaturated zone at Tylstrup. The measured data derive from suction cups installed 1 m b.g.s. and 2 m b.g.s. at locations S1 and S2 indicated in Figure 2. The green vertical lines indicate the dates of bromide application.

2.2.3 Pesticide leaching

Monitoring at Tylstrup began in May 1999 and presently encompasses 15 pesticides and several degradation products, as indicated in Table 3. Pesticide application during the two most recent growing seasons is shown together with precipitation and simulated precipitation in Figure 6.

It should be noted that precipitation in Table 3 is corrected to the soil surface according to Allerup and Madsen (1979), whereas percolation (1 m b.g.s.) refers to accumulated percolation as simulated with the MACRO model. It should also be noted that as mancozeb (applied here as Dithane DG) and tribenuron methyl (applied here as Express) degrade rapidly, the leaching risk is more associated with their respective degradation products, ETU and triazinamin-methyl. For the same reasons it is the degradation products and not the parent compounds that are monitored in the PLAP (Table 3). Pesticides applied later than April 2004 are not evaluated in this report and hence are not included in Table 3 and Figure 6.

The leaching risk of pesticides applied in 1999, 2000 and 2001 has been evaluated previously (Kjær *et al.*, 2002, 2003 and 2004). The leaching of metribuzin is further detailed in Kjær *et al.* (2005b).

The leaching risk of the *clomazone* applied to the 2002 winter rape crop was found to be negligible at the Tylstrup site. Thus neither clomazone nor its degradation product propropanamide-clomazone were detected in any of the water samples analysed. The leaching risk of clomazone should be viewed in relation to an autumn application during the fairly dry September 2002, when precipitation input was almost counterbalanced by actual evapotranspiration such that only 24 mm percolated during the first month after pesticide application (Table 3, Figure 6 and Appendix 5).

The leaching risk of pesticides applied to the 2003 winter wheat crop will not be evaluated until the 2005 monitoring results become available, i.e. when two years of monitoring data have been collated. It should be noted, though, that none of the applied pesticides or their degradation products listed in Table 3 were detected in any of the water samples analysed



Figure 5. Bromide concentration in the groundwater at Tylstrup. The data derive from monitoring wells M1–M7. Screen depth is indicated in m b.g.s. The green vertical lines indicate the dates of bromide application.

Table 3. Pesticides analysed at Tylstrup with the products used shown in parentheses. Degradation products are in italics. Precipitation (prec.) and percolation (perc.) are accumulated from date of first application until the end of monitoring. 1st month perc. refers to accumulated percolation within the first month after the application. C_{mean} refers to average leachate concentration at 1 m b.g.s. the first year after application. The number of pesticide-positive samples is indicated in parentheses.

Crop and analysed pesticides	Application date	End of monitoring	Prec.	Perc.	1 st month perc.	C _{mean}
			(mm)	(mm)	(mm)	(µg/l)
Potatoes 1999						
Linuron (Afalon)	May 99	Jul 01	2550	1226	56	< 0.01 (0)
- ETU^{l} (Dithane DG)	Jun 99	Oct 01	2381	1172	55	< 0.01(9)
Metribuzin (Sencor WG)	Jun 99	Jul 03	4223	2098	56	< 0.01 (3)
- metribuzin-diketo		Jul 04 [†]				0.05-0.36(527)
- metribuzin-desamino		Jul 03				< 0.02 (0)
- metribuzin-desamino-diketo		Jul 04 [†]				0.14-0.97 (312)
Spring barley 2000						
Triasulfuron (Logran 20 WG)	May 00	Apr 03	2740	1327	9	< 0.02 (0)
- triazinamin						< 0.02 (0)
Propiconazole (Tilt Top)	Jun 00	Jul 03	2947	1398	16	< 0.01 (0)
Fenpropimorph (Tilt Top)	Jun 00	Jul 03	2947	1398	16	< 0.01 (0)
- fenpropimorphic acid						< 0.02 (0)
Pirimicarb (Pirimor G)	Jun 00	Apr 03	2622	1309	22	< 0.01 (0)
- pirimicarb-desmethyl						< 0.02 (0)
- pirimicarb-desmethyl-formamido						< 0.02 (0)
Winter rye 2001						
Pendimethalin (Stomp SC)	Nov 00	Apr 03	2271	1247	112	< 0.01 (0)
Triazinamin-methyl ²⁾ (Express)	Nov 00	Apr 03	2271	1247	112	< 0.02 (0)
Propiconazole (Tilt Top)	May 01	Jul 03	2947	1398	16	< 0.01 (0)
Fenpropimorph (Tilt Top)	May 01	Jul 03	2947	1398	16	< 0.01 (0)
- fenpropimorphic acid	-					< 0.01 (0)
Winter rape 2002						
Clomazone (Command CS)	Sep 01	Jul 04	1194	2534	24	< 0.01 (0)
- propanamide-clomazone						< 0.02 (0)
Winter wheat 2003						
Bromoxynil (Oxitril CM)	Oct 02	Jul 04 [†]	631	1373	60	< 0.01 (0)
Ioxynil (Oxitril CM)	Oct 02	Jul 04 [†]	631	1373	60	< 0.01(0)
Fluroxypyr (Starane 180)	May 03	Jul 04 [†]	361	955	51	< 0.01(0)
Flamprop-M-isopropyl (Barnon	May 03	Jul 04 [†]	346	931	39	< 0.01(0)
Plus)						
- Flamprop-M (free acid)						
Dimethoate (Perfekthion 500 S)	Jul 03	Jul 04 [†]	291	718	6	< 0.01(0)

Systematic chemical nomenclature for the analysed pesticides is given in Appendix 1 ¹⁾ Degradation product of mancozeb. The parent compound degrades too rapidly to be detected by monitoring

²⁾ Degradation product of tribenuron methyl. The parent compound degrades too rapidly to be detected by monitoring

† Monitoring will continue during the following year. The values for prec. and perc. are accumulated up to July 2003



Figure 6. Pesticide application, precipitation and irrigation (primary axis) together with simulated percolation 1 m b.g.s. (secondary axis) at Tylstrup in 2002/2003 (upper) and 2003/2004 (lower).

3 Pesticide leaching at Jyndevad

3.1 Materials and methods

3.1.1 Site description and monitoring design

Jyndevad is located in southern Jutland (Figure 1). The test site covers a cultivated area of 2.4 ha (135 x 184 m) and is practically flat. A windbreak borders the eastern side of the test site. The area has a shallow groundwater table ranging from 1 to 2 m b.g.s. The overall direction of groundwater flow is towards northwest (Figure 7). The soil can be classified as Arenic Eutrudept and Humic Psammentic Dystrudept (Soil Survey Staff, 1999) with coarse sand as the dominant texture class and topsoil containing 5% clay and 1.8% total organic carbon (Table 1). The geological description points to a rather homogeneous aquifer of meltwater sand, with local occurrence of thin clay and silt beds. A brief description of the sampling procedure is provided in Appendix 2. The monitoring design and test site are described in detail in Lindhardt *et al.* (2001) and the analysis methods in Kjær *et al.* (2002).

3.1.2 Agricultural management

Management practice during the 2002 and 2003 growing seasons is briefly summarized below and detailed in Appendix 3 (Table A3.2). For information about management practice during the first two monitoring periods see Kjær *et al.* (2003).

The 2002 crop was potato (cv. Oleva) for starch production sown on 22 April. Before the potatoes emerged the field was treated with metribuzin to combat weeds on 13 May. Weeds were sprayed with rimsulfuron on 23 May, at which time the potatoes had just emerged. The field was irrigated with 20 mm/ha on 13 June and 25 mm on 12 August. Fungicide spraying was carried out 10 times between 18 June and 20 August, each time using fluazinam at a rate of 0.2 l Shirlan/ha. The potatoes were harvested on 24 September with a tuber yield of 515.8 hkg/ha, equivalent to 118.8 hkg/ha (100% dry matter) and slightly less than the average for that year. It should be noted that neither metribuzin nor fluazinam are included in the monitoring programme.

Prior to the sowing of spring barley (cv. Otira) on 9 April 2003, potassium bromide tracer was applied on 12 March. The bromide application was the second since the monitoring programme began. On 6 May, when 2 leaves had unfolded, the barley was sprayed with the herbicide metsulfuron-methyl. MCPA was applied on 3 June. Metsulfuron-methyl was not monitored, however. On 6 June, when the second joint was detectable, the fungicide propiconazole was used. The crop was irrigated once on 8 June using 26 mm/ha. On 25 June the fungicide propiconazole and the pesticide dimethoate were applied in combination. The barley was harvested on 4 August with a grain yield of 73.3 hkg/ha (85% dry matter), which was about the average for the year.



Figure 7. Overview of the Jyndevad test site. The innermost white area indicates the cultivated land, while the grey area indicates the surrounding buffer zone. The positions of the various installations are indicated, as is the direction of groundwater flow (by an arrow).

3.1.3 Model set-up and calibration

The MACRO model was applied to the Jyndevad site covering the soil profile to a depth of 5 m b.g.s., always including the groundwater table. The model was used to simulate water flow and bromide transport in the unsaturated zone during the full monitoring period July 1999–June 2004 and to establish an annual water balance.

Due to the application of a newer version of MACRO than used in the previous report (version 5.0 vs 4.2) (Kjær *et al.*, 2004) the model for the Jyndevad site has been recalibrated for the whole period to the observed groundwater table measured in the piezometers located in the buffer zone, to time series of soil water content measured at three different depths (25, 60 and 110 cm b.g.s.) from the two profiles S1 and S2 (see Figure 7) and to the bromide concentration measured in the suction cups located 1 and 2 m b.g.s. Data acquisition and model set-up are described in Appendix 4. The main calibration parameters were the empirical parameter BGRAD, which regulates the boundary flow, the "boundary" pressure head (XMPOR), its corresponding water content (CTEN), the hydraulic conductivity (KSM), the dispersivity (DV), the mixing depth (ZMIX) and the effective diffusion path length (ASCALE), which controls the exchange of water and solute between the two flow domains (see Appendix 4 for details).

3.2 Results and discussion

3.2.1 Soil water dynamics and water balances

The model simulations are generally consistent with the observed data, thus indicating a good model description of the overall soil water dynamics in the unsaturated zone (Figure 8). The dynamics of the simulated groundwater table is well described with MACRO 5.0 (Figure 8B), and better so than with MACRO 4.2 (Kjær *et al.*, 2004). As noted earlier (Kjær *et al.*, 2003), the model has some difficulty in capturing the degree of soil water saturation 1.1 m b.g.s. – a difference that is still apparent with the new model (Figure 8E).

The resulting water balance for Jyndevad for the five monitoring periods is shown in Table 4. It is very similar to the balance calculated with MACRO 4.2 (Kjær *et al.*, 2004). Compared to the normal year, precipitation during the previous monitoring year is characterized by a drier summer and a wet January (Appendix 5). Due to the dry summer, percolation was almost negligible until mid September. For information about the water balance in previous monitoring periods see Kjær *et al.* (2004).

Table 4. Ar	Innual water	balance fo	r Jyndevad	(mm/yr).	Precipitation	is corr	rected	to the	soil	surface	according
to the method	od of Alleru	p and Mad	sen (1979).								

	Normal			Actual	Groundwater
	precipitation ¹⁾	Precipitation	Irrigation	evapotranspiration	recharge ²⁾
1.7.99-30.6.00	995	1073	29	489	613
1.7.00-30.6.01	995	810	0	453	357
1.7.01-30.6.02	995	1204	81	527	758
1.7.02-30.6.03	995	991	51	460	582
1.7.03-30.6.04	995	936	27	431	532

1) Normal values based on time series for 1961–1990

2) Groundwater recharge is calculated as precipitation + irrigation - actual evapotranspiration



Figure 8. Soil water dynamics at Jyndevad: Measured precipitation, irrigation and simulated percolation 1 m b.g.s. (A), simulated and measured groundwater level (B), and simulated and measured soil water saturation (SW sat.) at three different soil depths (C, D and E). The measured data in B derive from piezometers located in the buffer zone. The measured data in C, D and E derive from TDR probes installed at S1 and S2 (see Figure 7).

3.2.2 Bromide leaching

Bromide has now been applied twice at Jyndevad. The bromide concentrations measured up to April 2003 (Figure 9 and Figure 10) relate to the bromide applied in autumn 1999, as described further in Kjær *et al.* (2003). Leaching of the bromide applied in March 2003 will be evaluated in due course as the results become available.



Figure 9. Simulated (solid line) and measured bromide concentration at Jyndevad. The data derive from suction cups installed 1 m b.g.s. and 2 m b.g.s. at locations S1 and S2 (see Figure 7). The green vertical lines indicate the dates of bromide application.



Figure 10. Bromide concentration in the groundwater at Jyndevad. The data derive from monitoring wells M1–M7. Screen depth is indicated in m b.g.s. The green vertical lines indicate the dates of bromide application.

3.2.3 Pesticide leaching

Monitoring at Jyndevad began in September 1999 and presently encompasses 9 pesticides and several degradation products, as indicated in Table 5. Pesticide application during the two most recent growing seasons is shown together with precipitation and simulated precipitation in Figure 11. It should be noted that precipitation in Table 5 is corrected to the soil surface according to Allerup and Madsen (1979), whereas percolation (1 m b.g.s.) refers to accumulated percolation as simulated with the MACRO model. It should also be noted that as tribenuron methyl (applied here as Express) and pyridate (applied here as Lido) degrade rapidly, the leaching risk is more associated with their respective degradation products, triazinamin-methyl and PHCP. For the same reasons it is the degradation products and not the parent compounds that are monitored in the PLAP (Table 5). Pesticides applied later than April 2004 are not evaluated in this report and hence are not included in Table 5 and Figure 11.

Table 5. Pesticides analysed at Jyndevad with the product used shown in parentheses. Degradation products are in italics. Precipitation (prec.) and percolation (perc.) are accumulated from date of first application until end of monitoring. 1^{st} month perc. refers to accumulated percolation within the first month after application. C_{mean} refers to average leachate concentration 1 m b.g.s the first year after application. The number of pesticide-positive samples is indicated in parentheses.

Crop and analysed pesticides	Application	End of	Prec.	Perc.	1 st month	C _{mean}
	date	monitoring	(mm)	(mm)	perc.	(µg/l)
					(mm)	
Winter rye 2000						
Glyphosate (Roundup 2000)	Sep 99	Apr 02	2759	1661	139	< 0.01 (0)
- AMPA						< 0.01 (3)
<i>Triazinamin-methyl</i> ¹⁾ (Express)	Nov 99	Apr 02	2534	1505	86	< 0.02 (0)
Propiconazole (Tilt Top)	Apr 00	Jul 02	2301	1107	4	< 0.01 (0)
Fenpropimorph (Tilt Top)	Apr 00	Apr 02	2015	1083	4	< 0.01(2)
- fenpropimorphic acid		- r				< 0.01 (0)
Maize 2001						
Terbutylazine (Lido)	May 01	Jul 04 [†]	3376	1823	4	< 0.01 (0)
- desethylterbutylazine						<0.01-0.02 (28)
PHCP ²⁾ (Lido)	May 01	Jul 03	2413	1339	4	< 0.02 (0)
Potatoes 2002						
Rimsulfuron (Titus)	May 02	Jul 04	2168	1147	9	< 0.01 (0)
- PPU	-	Jul 04 [†]				$0.06^{3} - 0.13$ (44)
- PPU-desamido		Jul 04^{\dagger}				0.01-0.03 (37)
Spring barley 2003						
MCPA (Metaxon)	June 03	Jul 04 [†]	1035	484	0	< 0.01 (0)
- 4-chlor,2-methylphenol						< 0.01 (0)
Dimethoate (Perfekthion 500 S)	June 03	Jul 04 [†]	973	484	1	< 0.01 (0)

Systematic chemical nomenclature for the analysed pesticides is given in Appendix 1

¹⁾ Degradation product of tribenuron methyl. The parent compound degrades too rapidly to be detected by monitoring

²⁾ Degradation product of pyridate. The parent compound degrades too rapidly to be detected by monitoring

³⁾ Leaching increased the second year after application (see Table 6)

† Monitoring will continue during the following year. The values for prec. and perc. are accumulated up to July 2003



Figure 11. Pesticide application, precipitation and irrigation (primary axis) together with simulated percolation 1 m b.g.s. (secondary axis) at Jyndevad in 2002/2003 (upper) and 2003/2004 (lower).

The leaching risk of pesticides applied in 1999, 2000 and 2001 has already been evaluated in Kjær *et al.* (2003, 2004).

The leaching risk of the pesticides applied in 2002 can be summarized as follows:

Rimsulfuron (applied May 2002) has not been found in any of the water sampled, although its two degradation products PPU and PPU-desamido were detected at 1 m depth in the suction cups at S1 and S2 (Figure 12). PPU was detected for the first time on 3 June 2002, and PPU-desamido was detected the following month. Both compounds were characterized by continuous leaching over a long period of time. Elevated concentrations of PPU in particular were still seen towards the end of the current monitoring period, thus indicating that leaching of the compound from the uppermost metre of the soil has not yet ceased. Nevertheless, the average yearly concentration of PPU and PPU-desamido reached 0.10–0.13 and 0.04 μ g/l, respectively (Table 6). The primary data and calculation methods are given in Appendix 6. Neither PPU nor PPU-desamido have been detected in the groundwater monitoring screens situated downstream of the test site.



Figure 12. Precipitation, irrigation and simulated percolation 1 m b.g.s. (A) together with measured concentration of *PPU* and *PPU-desamido* (B) at Jyndevad. The measured data derive from suction cups installed 1 m b.g.s. at location S1 and S2 (see Figure 7). The red vertical line indicates the date of pesticide application. Concentrations below the detection limit of 0.01 μ g/l are indicated by open circles and triangles.

When evaluating these results it should be noted that precipitation input following the application of rimsulfuron (23 May 2002) was much higher than normal (Appendix 5). June and July 2002 were characterized by high precipitation (121 mm and 147 mm, respectively) that exceeded the monthly normal by 58% and 68%, respectively. 20 mm of precipitation felt the day before application, and two heavy storm events (precipitation >30 mm/day) occurred during the two months following pesticide application (Figure 12). This precipitation pattern – in terms of daily/monthly precipitation occurring in either June or July – is not unusual for the Jyndevad region, similar patterns having occurred at other times during the period 1990–2004 (Appendix 6).

Table 6. Percolation together with estimated average concentration (μ g/l) of PPU and PPU-desamido 1 m b.g.s. at Jyndevad. Leached mass refers to the total mass (% of applied rimsulfuron) leached during the monitoring period 1.7.02–30.6.04. The primary data and calculation methods are detailed in Appendix 6.

	Percolation	PI	PU	PPU-de	esamido
	(mm/y)	Suction cup – S1	Suction cup – S2	Suction cup – S1	Suction cup – S2
1.7.02-30.6.03	648	0.13	0.06	0.03	< 0.02
1.7.03-30.6.04	467	0.12	0.10	0.04	0.04
Leached mass ¹⁾		22%	14%	7%	4%

1) Expressed as rimsulfuron equivalent.

Finally, it should be noted that the concentration of PPU is likely to be underestimated by 23–33% due to stability problems (Section 7.2.2). Results from the field-spiked samples thus indicated that PPU is unstable and tends to degrade further to PPU-desamido during storage and transport. Thus the observed PPU-desamido probably derives from degradation in the sample during subsequent storage and transport rather than from degradation occurring in the soil. As a consequence the concentration of PPU is likely to be underestimated, while that of PPU-desamido is likely to be overestimated

The leaching risk of pesticides applied to the 2003 spring barley crop will not be evaluated until the 2005 monitoring results become available, i.e. when two years of monitoring data have been collated. It should be noted, though, that none of the applied pesticides or their degradation products listed in (Table 5) were detected in any of the water samples analysed.

4 Pesticide leaching at Silstrup

4.1 Materials and methods

4.1.1 Site description and monitoring design

The test field at Silstrup is located south of Thisted in northwestern Jutland (Figure 1). The cultivated area is 1.69 ha (91 x 185 m) and slopes gently $1-2^{\circ}$ to the north (Figure 25). Based on two profiles excavated in the buffer zone bordering the field the soil was classified as Alfic Argiudoll and Typic Hapludoll (Soil Survey Staff, 1999). The topsoil content of clay in the two profiles was 18.3 and 26.6%, and the organic carbon content was 3.4 and 2.8%, respectively. The geological description showed a rather homogeneous clay till rich in chalk and chert, containing 20–35% clay, 20–40% silt and 20–40% sand. In some intervals the till was more sandy, containing only 12–14% clay. Moreover, thin lenses of silt and sand were found in some of the wells. The gravel content was approx. 5%, but could be as high as 20%. A brief description of the sampling procedure is provided in Appendix 2. The monitoring design and test site are described in detail in Lindhardt *et al.* (2001) and the analysis methods in Kjær *et al.* (2002).

4.1.2 Agricultural management

Management practice during the three most recent growing seasons is briefly summarized below and detailed in Appendix 3 (Table A3.3). For information about management practice during the first two monitoring periods see Kjær *et al.* (2003).

On 25 October 2001 the field was sprayed with glyphosate in the form of Roundup Bio (4.0 l/ha). The field was ploughed to a depth of 22 cm on 18 December. Maize (cv. Loft) was sown on 25 April 2002 after the field had been fertilized with cattle slurry (40.3 tonnes/ha) on 22 April. When two leaves had unfolded the maize was sprayed with pyridate + terbutylazine to combat weeds. This was repeated on 3 June. On 19 June the maize was sprayed with clopyralid to combat weeds. The crop was harvested on 23 September yielding 134.3 hkg/ha (100% dry matter), somewhat less than other cultivars in the area that year.

Peas (cv. Attica) were sown on 14 April 2003. Only herbicides were applied to the crop. On 17 May, when four leaves had unfolded, bentazone and pendimethalin were applied. At the time, when nearly all the pea pods had attained their full size, rooks (*Corvus frugilegus*) invaded the field causing significant crop damage. As a consequence the yield was only 39.8 hkg/ha (86% dry matter), about 5–8 hkg/ha less than expected.

On 15 September, some 5 weeks after harvesting the peas, the field was sprayed with glyphosate (Roundup Bio 4.0 l/ha). Winter wheat (cv. Deben) was sown on 26 September. On



29 October, when the wheat had 2 leaves, the herbicide prosulfocarb was applied. Herbicide

Figure 13. Overview of the Silstrup site. The innermost white area indicates the cultivated land, while the grey area indicates the surrounding buffer zone. The positions of the various installations are indicated, as is the direction of groundwater flow (by an arrow).
treatment with MCPA was done on 12 May when the flag leaf was just visible. Fungus was treated with azoxystrobin on 14 June at the end of heading, and pests were treated with pirimicarb on 20 July, at the medium milk stage. Due to the high precipitation the winter wheat was not harvested until 23 August. The grain yield was 97.6 hkg/ha (85% dry matter), well above the average for this variety and year (Pedersen, 2004). 40.8 hkg/ha (100% dry matter) of straw was also removed from the field.

4.1.3 Model set-up and calibration

The MACRO model is applied to the Silstrup site covering the soil profile to a depth of 5 m b.g.s., always including the groundwater table. The model is used to simulate the water flow in the unsaturated zone during the full monitoring period April 2000–June 2004 and to establish an annual water balance.

Due to the application of a newer version of MACRO than used in the previous report (version 5.0 vs 4.2) (Kjær *et al.*, 2004) the model for the Silstrup site was recalibrated for the whole period to the observed groundwater table measured in the piezometers located in the buffer zone, to time series of soil water content measured at three depths (25, 60 and 110 cm b.g.s.) from the two profiles S1 and S2 (see Figure 13) and to the measured drainage flow. Data acquisition and model set-up are described in Appendix 4. The main calibration parameters were the empirical parameter BGRAD, which regulates the boundary flow, the "boundary" pressure head (XMPOR), its corresponding water content (CTEN), the hydraulic conductivity (KSM) and the effective diffusion path length (ASCALE), which controls the exchange of water and solute between the two flow domains (see Appendix 4 for details).

4.2 Results and discussion

4.2.1 Soil water dynamics and water balances

The model simulations are largely consistent with the observed data, thus indicating a reasonable model description of the overall soil water dynamics in the unsaturated zone (Figure 14). Compared to simulations made with MACRO 4.2 (Kjær et al., 2004), the groundwater table fluctuates much more (Figure 14B). A closer study of measured groundwater table in the different piezometers show that it varies significantly, especially between the upstream (P2 and P3, see Figure 13) and downstream (P1 and P4) piezometers, as shown in Figure 14B. Calibration to the groundwater table measured in P1 and P4 led to erroneous simulation of drainage, which was approximately 200 mm too high for each monitoring year. Calibration to the much more fluctuating groundwater table measured in piezometer P3 yielded a significantly better description of measured drainage. As in previous years (Kjær et al., 2004), though, the initial rise in the autumn when percolation and drainage flow are initiated is poorly captured. With the last monitoring period, in particular, the initial rise is simulated very late. The delayed rise results in a delayed response in modelled drainage flow in the autumn (Figure 14C). As in the previous monitoring periods, the overall trends in soil water content were described reasonably well (Figure 14D) and the model tended to describe the subsoil as being dryer during the summer period than measured by the deeper TDR probes (Figure 14E and F).

Hydraulic conductivity and water content have been measured downstream of the field (close to P1 and P4), but no such data are available upstream where P3 is located. As mentioned above, the calibration shows that the hydraulic conditions around P3 considerably affect the measurements. To be able to model the measured values the calibrated hydraulic conductivity curves are fitted less well to the measured data from P1 and P4 than from the other sites (Appendix 4, figure A4.4).

The resulting water balance for the five monitoring periods is shown in Table 7 (July to June). Apart from the better fit to measured drainage, there were no major differences between this balance and the one calculated with MACRO 4.2 (Kjær *et al.*, 2004). Precipitation in the latest monitoring year, July 2003–June 2004, was the lowest since monitoring began at the site and is characterized by an exceptionally dry period from July to October (Appendix 5). As a result, drainage flow started late and simulated percolation was lower. Due to the above-mentioned problem in capturing the initial rise in groundwater table in the autumn, simulated drainage flow for the latest monitoring was much smaller than the measured flow. For information about the water balance in previous monitoring periods see Kjær *et al.* (2004).

Table 7. Annual water balance for Silstrup (mm/year). Precipitation is corrected to the soil surface according to the method of Allerup and Madsen (1979).

	Normal precipitation ²⁾	Precipitation	Actual evapotrans- piration	Measured drainage	Simulated drainage	Groundwater recharge ³⁾
1.7.99–30.6.00 ¹⁾	976	1175	436	_	412	327 ⁴⁾
1.7.00-30.6.01	976	909	386	217	212	307
1.7.01-30.6.02	976	1034	419	227	265	389
1.7.02-30.6.03	976	879	458	81	94	339
1.7.03-30.6.04	976	758	433	148	65	176

1) The monitoring was started in April 2000

2) Normal values based on time series for 1961–1990 corrected to soil surface

3) Groundwater recharge is calculated as precipitation - actual evapotranspiration - measured drainage 4) Where drainage flow measurements are lacking, simulated drainage flow was used to calculate groundwater recharge

4.2.2 Bromide leaching

The bromide concentration shown in Figure 15 and Figure 16 relate to the bromide applied in May 2000, as described further in Kjær *et al.* (2003) and (2004).



Figure 14. Soil water dynamics at Silstrup: Measured precipitation and simulated percolation 1 m b.g.s. (A), simulated and measured groundwater level (B), simulated and measured drainage flow (C), and simulated and measured soil water saturation (SW sat.) at three different soil depths (D, E and F). The measured data in B derive from piezometers located in the buffer zone. The measured data in D, E and F derive from TDR probes installed at S1 and S2 (see Figure 13).



Figure 15. Bromide concentration at Silstrup. A and B refer to suction cups located at S1 and S2. The bromide concentration is also shown for drainage runoff (C), the horizontal monitoring wells H1 and H2 (D) and the vertical monitoring well M5 (E). The green vertical line indicates the date of bromide application.



Figure 16. Bromide concentration at Silstrup. The data derive from the vertical monitoring wells (M5–M12). Screen depth is indicated in m b.g.s. The green vertical line indicates the date of bromide application.

4.2.3 Pesticide leaching

Monitoring at Silstrup began in May 2000 and presently encompasses 17 pesticides and several degradation products, as indicated in Table 8. Pesticide application during the two most recent growing seasons is shown together with precipitation and simulated precipitation in

Figure 17. It should be noted that precipitation in Table 8 is corrected to soil surface according to Allerup and Madsen (1979), whereas percolation (1 m b.g.s.) refers to accumulated percolation as simulated with the MACRO model. It should also be noted that as tribenuron methyl (applied here as Express) and pyridate (applied here as Lido) degrade rapidly, the leaching risk is more associated with their respective degradation products, triazinamin-methyl and PHCP. For the same reasons it is the degradation products and not the parent compounds that are monitored in the PLAP (Table 8).



Figure 17. Pesticide application, precipitation and irrigation (primary axis) and simulated percolation 1 m b.g.s. (secondary axis) at Silstrup in 2002/2003 (upper) and 2003/2004(lower). Pesticides applied later than April 2004 are not included. As pyridate degrades rapidly it is the degradation product PHCP, that is monitored.

Table 8. Pesticides analysed at Silstrup with the product used shown in parentheses. Degradation products are in italics. Precipitation (prec.) and percolation (perc.) are accumulated from date of first application until end of monitoring. 1st month perc. refers to accumulated percolation within the first month after application. C_{mean} refers to average leachate concentration in the drainage water within the first drainage season after application (See Appendix 2 for calculation methods). The number of pesticide-positive samples is indicated in parentheses.

Crop and analysed pesticides	Application date	End of monitoring	Prec. (mm)	Perc. (mm)	1 st month perc. (mm)	C_{mean} (µg/l)
		6		. ,	1 ()	
Fodder beet 2000						
Metamitron (Goltix WG)	May 00	Apr 03	2634	1328	57	0.05 (69)
- metamitron-desamino	-	-				0.06 (61)
Ethofumesate (Betanal Optima)	May 00	Apr 03	2634	1328	57	0.03 (24)
Desmedipham (Betanal Optima)	May 00	Apr 03	2634	1328	57	< 0.01 (1)
- EHPC						< 0.02 (0)
Phenmedipham (Betanal Optima)	May 00	Apr 03	2634	1328	57	< 0.01 (0)
- MHPC						< 0.02 (0)
- 3-aminophenol						< 0.02 (0)
Fluazifop-P-butyl (Fusilade X-tra)	Jun 00	Jul 02	1953	1019	5	< 0.01 (0)
- fluazifop (free acid)						< 0.02 (1)
Pirimicarb (Pirimor)	Jul 00	Apr 03	2528	1268	4	0.01 (17)
- pirimicarb-desmethyl						< 0.02 (1)
- pirimicarb-desmethyl-formamido						< 0.02 (0)
Spring barley 2001						
Triazinamin-methyl ¹⁾ (Express)	May 01	Jul 03	1941	951	13	< 0.02 (0)
Flamprop-M-isopropyl (Barnon Plus)	Jun 01	Jul 03	1928	944	7	<0.01 (13)
- flamprop (free acid)						< 0.01 (7)
Propiconazole (Tilt Top)	Jun 01	Jul 03	1928	944	7	<0.01 (6)
Fenpropimorph (Tilt Top)	Jun 01	Jul 03	1928	944	7	< 0.01 (0)
- fenpropimorphic acid						<0.01(1)
Dimethoate (Perfekthion 500 S)	Jul 01	Jul 03	1882	937	7	0.02 (2)
Maize 2002						
Glyphosate (Roundup Bio)	Oct 01	Jul 04 [†]	2246	1096	42	< 0.13 (69)
- AMPA						$0.06(110^{*})$
PHCP ²⁾ (Lido)	May 02	Jul 04	1764	738	16	0.06 (18)
Terbutylazine (Lido)	May 02	Jul 04 [†]	1764	738	16	0.07 (92)
- desethylterbutylazine						0.15 (165)
- 2-hydroxy terbutylazine						see text (22)
- 2-hydroxy-desethyl-terbutylazine						see text (29)
- desisopropylatrazine						see text (35)
Peas 2003		÷				
Bentazone (Basagran 480)	May 03	Jul 04'	914	381	67	0.26 (50)
- AIBA		- 1 - 1				< 0.01 (0)
Pendimethalin (Stomp SC)	May 03	Jul 04	914	381	67	< 0.01 (0)
Glyphosate (Roundup Bio)	Sep 03	Jul 04'	651	293	0	<0.01 (69)
- AMPA						0.02 (110)
Winter wheat 2004	0 1 0 2	T 1 0 4 [†]		0.01	6	0.01.(0)
Prosulfocarb (Boxer EC)	Oct 03	Jul 04	570	291	0	0.01(6)

¹⁾ Degradation product of tribenuron methyl. The parent compound degrades too rapidly to be detected by monitoring

²⁾ Degradation product of pyridate. The parent compound degrades too rapidly to be detected by monitoring

† Monitoring will continue during the following year. The values for prec. and perc. are accumulated up to July 2004

* Pesticide has been applied twice, and the findings are not necessarily related to one specific application

Terbutylazine has four relevant degradation products, of which only desethylterbutylazine was included in the monitoring programme from the time of terbutylazine application. From February 2003 onwards the three remaining metabolites were also included, see Table 8. Pesticides applied later than April 2004 are not evaluated in the present report and hence are not included in Table 8. The leaching risk of pesticides applied during and 2000 and 2001 has been evaluated in Kjær *et al.* (2003) and Kjær *et al.* (2004), respectively. The leaching risk of pesticides applied during 2002 are summarized below.

In 2002 the field was sprayed with Lido, which contains pyridate and terbutylazine. Pyridate is rapidly degraded and the leaching risk is therefore more associated with its degradation product PHCP. Besides terbutylazine, at least four relevant degradation products are at risk of leaching. Unfortunately, however, only one of them, i.e. desethylterbutylazine, was included from the start of the monitoring. Literature findings suggest that desethylterbutylazine together with terbutylazine pose the primary risk, whereas the remaining degradation products will mainly be mobilized later on in the degradation pathway (Guzella *et al.*, 2003).

PHCP: As for terbutylazine/desethylterbutylazine (see below), single precipitation events (occurring shortly after application) caused rapid leaching of PHCP, which reached both the drainage system and several groundwater monitoring screens (Appendix 7). On 3 July the PHCP concentration was 0.042 and 0.035µg/l, respectively, in two of the horizontal screens of H1 located 3.5 m b.g.s. (Figure 13). In samples from the uppermost screens of the vertical monitoring wells M9 and M13 located alongside the test field (1.5 to 2.5 m b.g.s.), the PHCP concentration was 0.048 and 0.041 µg/l, respectively. In M5 located downstream of the test field, PHCP was present in the three upper screens (1.5 to 4.5 m b.g.s.) in concentrations decreasing with depth from 0.309 μ g/l in the uppermost to 0.091 μ g/l in the lowermost. In M9 and M13, PHCP was detected just once. In the shallowest two screens of M5, PHCP was present in the following month. In the deeper screen it could be found 4 months after the initial detection in steadily decreasing concentrations (see Appendix 7). PHCP was first detected in drainage water on 25 June (2.64µg/l) in a time-proportional sample and subsequently on 16 July in time- and flow-proportional samples (1.107 and 0.207 µg/l, respectively). The following week it was detected in a concentration of 0.987 µg/l in a timeproportional sample. No PHCP was detected in any of the subsequent drainage samples.

Terbutylazine and its degradation product *desethylterbutylazine* leached from the root zone to both the drainage system (Figure 18) and several groundwater monitoring screens (Appendix 7). Some 3 weeks after the second application of Lido, terbutylazine and desethylterbutylazine were thus found in a time-proportional sample of drainage water in concentrations of 1.55 and 1.08 μ g/l, respectively (Figure 18). At the time of the first detection, drainage runoff was negligible, however. Total precipitation between the time of application and detection was 85 mm, of which 65 mm fell on 3 separate days, the largest storm event amounting to 30 mm. Both compounds leached continuously throughout the whole drainage runoff period in 2002/2003, the weighted average concentration of terbutylazine and desethylterbutylazine being 0.07 μ g/l and 0.15 μ g/l, respectively. Although the concentration level was much lower, continuous leaching of desethylterbutylazine in particular was also observed during the drainage runoff in 2003/2004 (Table 9 and Figure 18).

Table 9. Desethylterbutylazine and terbutylazine in drainage water at Silstrup during the two monitoring years. C_{mean} refers to the weighted average concentration (µg/l), Detection to percent of detection (% of analysed samples) and C_{max} to the maximum concentration found (µg/l).

	D	esethylterbutyla	azine	Terbutylazine			
	$C_{mean}(\mu g/l)$	C_{max} (µg/l) Detection (%)		$C_{mean}(\mu g/l)$	C_{max} (µg/l)	Detection (%)	
1.7.02-30.6.03	0.15	0.47	100%	0.07	0.43	100%	
1.7.03-30.6.04	0.09	0.22	97%	0.01	0.044	68%	

Terbutylazine and desethylterbutylazine have both been frequently detected in groundwater samples from both vertical and horizontal monitoring wells (Appendix 7). The concentrations of terbutylazine and desethylterbutylazine in monitoring well M5 are shown in Figure 20. On 18 June, the day before the second application, it rained 30 mm, yielding a modelled percolation of 7 mm. On the day of pesticide application itself it did not rain, but 14 mm fell the following day yielding 3 mm of percolation. From then on until sampling on 25 June the average daily percolation was calculated to be less than 0.5 mm. In view of the time of the first detection – June – the likely explanation is preferential flow.

While terbutylazine ceased to be detected at the end of 2003, desethylterbutylazine were detected in several monitoring screens throughout the monitoring period. Concentrations exceeding 0.1 g/l were only observed during the first three months after application, however (Figure 20 and Appendix 7).

The concentrations of the remaining three metabolites are shown in Figure 19B C and D. These were much lower than those of terbutylazine and desethylterbutylazine. However, since they were not included from the beginning, it is difficult to determine whether the low concentrations are due to leaching prior to the start of the monitoring, or a time lag in their formation as compared to that of desethylterbutylazine. Consequently their mean average concentrations have not been calculated. Re-evaluation of chromatograms revealed that desisopropylatrazine was not present at concentrations exceeding 0.03 μ g/l, however.

One of the three degradation products, i.e. 2-hydroxy-terbutylazine, has not been detected beneath the drains. The degradation product 2-hydroxy-desethyl-terbutylazine has been found just once in the M5.1, i.e. the uppermost filter, in a concentration of 0.016 μ g/l. The last of the three degradation products, desisopropylatrazine, has been detected in M5 (1.5–2.5. m b.g.s.) in concentrations around 0.01 μ g/l on three occasions – 4 February, 1 April and 1 July. In one instance, 3 June, desisopropylatrazine was detected in M5 (3.5–4.5 m b.g.s.) at a concentration of 0.047 μ g/l.



Figure 18. Precipitation and simulated percolation 1 m b.g.s (A) together with concentration of desethylterbutylazine (B) and terbutylazine (C) in the drainage runoff at Silstrup. The green vertical lines indicate the dates of application. Open diamonds indicate values below the detection limit of 0.01 μ g/l.



Figure 19. Precipitation and simulated percolation 1 m b.g.s. (A) together with concentration of desisopropylatrazine (B) and 2-hydroxy-desethyl-terbutylazine (C) and 2-hydroxy-terbutylazine (D) in the drainage runoff at Silstrup. The substances have been included in the monitoring programme since February 2003. The green vertical lines indicate the dates of terbutyl application. Open diamonds indicate values below the detection limit of 0.01 μ g/l.



Figure 20. Concentration of desethylterbutylazine and terbutylazine in well M5. The green vertical lines indicate the dates of application.

When evaluating the results it should be noted that precipitation input following the application of pyridate and terbutylazine (applied on 19 May and 3 June 2002) amounted to 50 mm in May 2002 (20% lower than normal) and 97 mm in June 2002 (40% higher than normal) (Appendix 5). This is not unusual for the Silstrup region, however, a similar pattern having been seen at other times during the period 1990–2004 (data not shown). Although – as previously described – a large precipitation event (>30 mm) occurred shortly after pesticide application, percolation during the subsequent month amounted to 16 mm, which is also not unusual for Silstrup (Table 8).

The leaching risk of pesticides applied in 2003 will not be evaluated until the 2005 monitoring results become available, i.e. when two years of monitoring data have been collated. It should be noted, though, that all of the applied pesticides leached except pendimethalin, as illustrated in Figure 22,

Figure 21 and Appendix 7 (Table A7.1 and A7.3).



Figure 21. Precipitation and simulated percolation 1 m b.g.s. (A) together with the concentration of bentazone (B) and prosulfocarb (C) in the drainage runoff at Silstrup. The green vertical lines indicate the dates of terbutyl application. Open diamonds indicate values below the detection limit of 0.01 μ g/l.



Figure 22. Precipitation and simulated percolation 1 m b.g.s. (A) together with concentration of glyphosate (B) and AMPA (C) in the drainage runoff at Silstrup. The green vertical line indicates the date of application.

5 Pesticide leaching at Estrup

5.1 Material and methods

5.1.1 Site description and monitoring design

Estrup is located in central Jutland (Figure 1) west of the Main Stationary Line on a hillisland, i.e. a glacial moraine preserved from the Weischselian Glaciation. Estrup has thus been exposed to weathering, erosion, leaching and other geomorphologic processes for a much longer period than that of the other sites. The test field covers a cultivated area of 1.26 ha (105 x 120 m) and is virtually flat (Figure 36). The site is highly heterogeneous with considerable variation in both topsoil and aquifer characteristics (Table 1). Such heterogeneity is quite common for this geological formation, however. Based on three profiles excavated in the buffer zone bordering the field the soil was classified as Abruptic Argiudoll, Aquic Argiudoll and Fragiaquic Glossudalf (Soil Survey Staff, 1999). The topsoil is characterized as sandy loam with a clay content of 10-20% and an organic carbon content of 1.7-7.3%. The site is also characterized by a C horizon of low permeability. The saturated hydraulic conductivity in the C horizon is 10⁻⁸ m/s, which is about two orders of magnitude lower than that at the other loamy sites (Table 1). The geological structure is complex comprising a clay till core with deposits of different age and composition (Lindhardt et al. (2001). A brief description of the sampling procedure is provided in Appendix 2. The monitoring design and test site are described in detail in Lindhardt et al. (2001) and the analysis methods in Kjær et al. (2002). Please note that the geological conditions only allowed one of the planned horizontal wells to be installed as drilling in sand proved impossible.

5.1.2 Agricultural management

Management practice during the 2002 and 2003 growing seasons is briefly summarized below and detailed in Appendix 3 (Table A3.4). For information about management practice during the first two monitoring periods see Kjær *et al.* (2003).

Winter wheat (cv. Ritmo) was sown on 19 October 2001, much later than usual due to the very wet weather in August and September. Due to the unusually high temperatures in October, however, the wheat emerged just 12 days later. Weeds were sprayed in autumn with ioxynil and bromoxynil on 20 November and again in spring using amidosulfuron on 25 April and MCPA on 13 May. Propiconazole was sprayed to combat fungi on 27 May and 17 June, while pirimicarb was sprayed to combat pests on 24 June. The winter wheat was harvested on 9 August yielding 69.4 hkg/ha (85% dry matter). A higher yield could have been obtained had the crop been sown in due time. Ponding was observed at a small area of the southeastern part of the field near S2. In autumn 2002 this problem was solved by re

pairing a drainpipe inadvertently damaged, presumably during installation of the monitoring equipment in the buffer zone (Lindhardt *et al.*, 2001).

On 2 September 2002 the field was sprayed with glyphosate. On 14 April 2003 cattle slurry (60.8 tonnes/ha) was applied, and the field ploughed the following day. On 16 April the field was sown with fodder beet (cv. Magnum). On the day of emergence, 8 May, the field was sprayed for the first of three times using the herbicides metamitron, phenmedipham, desmedipham and ethofumesate. Phenmedipham and desmedipham are not included in the monitoring programme, however. The second and third applications were on 22 May and 16 June. Wind drift of Amistar (azoxystrobin) and Stereo (cyprodinil and propiconazole) from the field to the west was observed on 13 June. This did not cause any visible damage to the crop, however. The pesticide pirimicarb was sprayed on 28 July to combat aphids. The crop was harvested on 20 October yielding 189.5 hkg/ha roots and 34.2 hkg/ha tops (both 100% dry matter).

5.1.3 Model set-up and calibration

The MACRO model is applied to the Estrup site covering the soil profile to a depth of 5 m b.g.s., always including the groundwater table. The model is used to simulate the water flow in the unsaturated zone during the monitoring period from July 2000–June 2004 and to establish an annual water balance.

Due to the application of a newer version of MACRO than used in the previous report (version 5.0 vs 4.2) (Kjær et al., 2004) the model for the Estrup site has been recalibrated for the whole period to the observed groundwater table measured in the piezometers located in the buffer zone, to measured drainage flow and to time series of soil water content measured at one depth (25 cm b.g.s.) from a single soil profile S1 (Figure 23). The TDR probes installed at the other depths yielded unreliable data with saturations far exceeding 100% and dynamics with increasing soil water content during the drier summer periods. No explanation can presently be given for the unreliable data, and they have been excluded from the analysis. The data from the soil profile S2 have also been excluded due to a problem of water ponding above the TDR probes installed at S2, as mentioned in Kjær et al. (2003). Because of the erratic TDR data, calibration data are limited at this site. Data acquisition and model set-up are described in Appendix 4. The main calibration parameters were the empirical parameter BGRAD, which regulates the boundary flow, the "boundary" pressure head (XMPOR), its corresponding water content (CTEN), the hydraulic conductivity (KSM) and the effective diffusion path length (ASCALE), which controls the exchange of water and solute between the two flow domains (see Appendix 4 for details).



Figure 23. Overview of the Estrup site. The innermost white area indicates the cultivated land, while the grey area indicates the surrounding buffer zone. The positions of the various installations are indicated, as is the direction of groundwater flow (by an arrow).

5.2 Results and discussion

5.2.1 Soil water dynamics and water balances

The model simulations are generally consistent with the observed data (which are limited compared to other PLAP sites, as noted above), indicating a reasonable model description of the overall soil water dynamics in the unsaturated zone (Figure 24). The model provides an acceptable simulation of the overall level of the groundwater table. Compared to the simulations made with MACRO 4.2 (Kjær et al., 2004), the groundwater table fluctuates more, and the falling groundwater table during the dry summer periods is better described (Figure 24B). This is also more consistent with the automatic measurements (Figure 24B) in piezometer P1 situated upstream (Figure 23). A drop in measured groundwater table was seen after short periods of low precipitation (Figure 24A). The simulated groundwater table still does not seem as sensitive to these short periods of low precipitation and tends not to drop as low as the measured values. As with MACRO 4.2 results, this could be due to inaccurate modelling of the macropore-matrix interaction causing drainage of macropores without the correct exchange to the matrix taking place. This aspect will be studied later. As already mentioned, TDR data are limited in the subsoils, thus making the study of dynamics in these layers difficult. Nothing special is noted for the groundwater table in the latest monitoring period (July 2003-June 2004). As in previous years (Kjær et al., 2004), the simulated groundwater table often fluctuates slightly above the drain depth during periods of drainage flow.

The simulated drainage (Figure 24C) matches the measured drainage flow quite well, but the peaks at the onset of the drainage flow in 2002 and 2003 are too high compared to the measurements. As was the case with the simulations made with MACRO 4.2 (Kjær *et al.*, 2004), the high peak flows cannot be simulated adequately. The differences are most likely due to the above-mentioned inaccuracies in the simulated groundwater table. The drainage runoff season during the latest monitoring period (July 2003–June 2004) is very similar to that during the 2000-2001 monitoring period. Drainage runoff over the whole monitoring period is high compared with that in the other three till sites investigated in the PLAP, this being due to the significantly lower permeability of the C horizon than that of the overlying A and B horizons (Kjær *et al.*, 2003).

During the latest monitoring period (July 2003–June 2004) precipitation was low during the late summer/autumn (August–October) and high in the winter (December–January) (Appendix 5). This normal precipitation pattern is reflected in the drainage season, which starts in November and continues throughout April (Figure 24C). The drainage season is a little shorter than in previous years, and runoff is slightly lower. Percolation at Estrup is shown for 0.6 m b.g.s. rather than for 1 m b.g.s. because the soil at 1 m b.g.s. is saturated for longer periods (Figure 24). In the latest monitoring period percolation occurred continuously from November to the end of May, very much like in the years 2000–2001 (Figure 24A).



Figure 24. Soil water dynamics at Estrup: Measured precipitation and simulated percolation 0.6 m b.g.s. (A), simulated and measured groundwater level (B), simulated and measured drainage flow (C), and simulated and measured soil saturation (SW sat.) at two different soil depths (D and E). The measured data in B derive from piezometers located in the buffer zone. The measured data in D and E derive from TDR probes installed at S1 (see Figure 23).

The resultant annual water balance for Estrup is shown for the five modelled periods (July–June) in Table 10 Compared to the balance calculated with MACRO 4.2 (Kjær *et al.*, 2004) the yearly actual evapotranspiration is somewhat higher and the groundwater recharge lower. The water balance for the latest monitoring period is very similar to that for the previous year. For information about the water balance in previous monitoring periods see Kjær *et al.* (2004).

to the method of Anerup and Wadsen (1979).									
	Normal precipitation ²⁾	Precipitation	Actual evapotrans- piration	Measured drainage	Simulated drainage	Groundwater recharge ³⁾			
1.7.99–30.6.00 ¹⁾	968	1174	464	_	515	194 ⁴⁾			
1.7.00-30.6.01	968	887	433	356	307	97			
1.7.01-30.6.02	968	1291	479	505	530	307			
1.7.02-30.6.03	968	939	450	329	331	160			
1.7.03-30.6.04	968	928	468	298	292	162			

Table 10. Annual water balance for Estrup (mm/year). Precipitation is corrected to the soil surface according to the method of Allerup and Madsen (1979).

¹⁾ Monitoring started in April 2000

²⁾ Normal values based on time series for 1961–1990 corrected to the soil surface

³⁾ Groundwater recharge is calculated as precipitation - actual evapotranspiration - measured drainage

⁴⁾ Where drainage flow measurements are lacking, simulated drainage flow was used to calculate groundwater recharge

5.2.2 Bromide leaching

The bromide concentration shown in Figure 25 and Figure 26 relate to the bromide applied in May 2000, as described further in Kjær *et al.* (2003) and (2004).



Figure 25. Bromide concentration at Estrup. A and B refer to suction cups located at S1 and S2, respectively. The bromide concentration is also shown for drainage runoff (C) and the horizontal monitoring well H1 (D). The green vertical line indicates the date of bromide application.



→ 1.5-2.5 m b.g.s → 2.5-3.5 m b.g.s → 3.5-4.5 m b.g.s → 4.5-5.5 m b.g.s

Figure 26. Bromide concentration at Estrup. The data derive from the vertical monitoring wells (M2–M7). Screen depth is indicated in m b.g.s. The green vertical line indicates the date of bromide application.

5.2.3 Pesticide leaching

Monitoring at Estrup began in May 2000 and presently encompasses 15 pesticides and several degradation products, as indicated in Table 11. Pesticide application during the two most recent growing seasons is shown together with precipitation and simulated precipitation in Figure 27. It should be noted that precipitation in Table 11 is corrected to the soil surface according to Allerup and Madsen (1979), whereas percolation (0.6 m b.g.s.) refers to accumulated percolation as simulated with the MACRO model (Section 5.2.1). Moreover, pesticides applied later that April 2004 are not evaluated in this report and hence are not included in Table 11.



Figure 27. Pesticide application and precipitation (primary axis) together with simulated percolation 0.6 m b.g.s. (secondary axis) at Estrup in 2002/2003 (upper) and 2003/2004 (lower). Pesticides applied later than April 2004 are not included.

Table 11. Pesticides analysed at Estrup with the product used shown in parentheses. Degradation products are in italics. Precipitation (prec.) and percolation (perc.) are accumulated from the date of first application until the end of monitoring. 1st month perc. refers to accumulated percolation within the first month after application. C_{mean} refers to average leachate concentration in the drainage water within the first drainage season after application (See Appendix 2 for calculation methods). The number of pesticide-positive samples is indicated in parentheses.

Crop and analysed pesticides	Application	End of	Prec.	Perc.	1 st month	C _{mean}
	date	monitoring	(mm)	(mm)	perc. (mm)	(µg/l)
Spring barley 2000						
Metsulfuron-methyl (Ally)	May 00	Apr 03	2990	1456	29	< 0.01(1)
- triazinamin	2	1				< 0.02(1)
Flamprop-M-isopropyl (Barnon Plus)	May 00	Apr 03	2914	1434	0	0.02(20)
- flamprop (free acid)	2	1				0.01(13)
Propiconazole (Tilt Top)	Jun 00	Jul 04 [†]	4077	1911	0	$0.01(27^*)$
Fenpropimorph (Tilt Top)	Jun 00	Jul 02	2211	1048	0	< 0.01(1)
- fenpropimorphic acid						< 0.02(0)
Dimethoate (Perfekthion 500 S)	Jun 00	Jul 02	2211	1048	0	< 0.01(0)
Pea 2001						
Glyphosate (Roundup Bio)	Oct 00	Jul 04 [†]	3827	1929	128	$0.54(151^*)$
- AMPA						$0.17(176^{*})$
Bentazone (Basagran 480)	May 01	Jul 04	3230	1503	1	0.03(54)
- AIBA	-					< 0.02(1)
Pendimethalin (Stomp)	May 01	Jul 03	2208	1096	1	< 0.01(4)
Pirimicarb (Pirimor)	Jun 01	Jul 04 [†]	3163	1503	6	$0.01(40^*)$
- pirimicarb-desmethyl						< 0.02(0)
- pirimicarb-desmethyl-formamido						$<0.02(24^{*})$
Winter wheat 2002						
Ioxynil (Oxitril CM)	Nov 01	Jul 03	1580	860	52	$0.04(20)^1$
Bromoxynil (Oxitril CM)	Nov 01	Jul 03	1580	860	52	$0.01(3)^{1}$
Amidosulfuron (Gratil 75 WG)	Apr 02	Jul 04	2148	928	21	< 0.01 (0)
MCPA (Metaxon)	May 02	Jul 04	2091	928	21	< 0.0(12)
- 4-chlor,2-methylphenol						< 0.01(1)
Propiconazole (Tilt 250 EC)	May 02	Jul 04 [†]	2060	927	59	$0.02(27^*)$
Pirimicarb (Pirimor)	Jun 02	Jul 04 [†]	1894	870	62	$0.01(40^*)$
- pirimicarb-desmethyl						< 0.02(0)
- pirimicarb-desmethyl-formamido						$< 0.02(24^{*})$
Fodder beet 2003						
Glyphosate (Roundup Bio)	Sep 02	Jul 04 [†]	1632	806	9	$0.43(151^*)$
- AMPA	1					0.19(176*)
Ethofumesat (Betanal Optima)	May 03	Jul 04 [†]	1113	455	44	0.11(34)
Metamitron (Goltix WG)	May 03	Jul 04 [†]	1113	455	44	1.1(32)
-metamitron-desamino	-					0.21(27)
Pirimicarb (Pirimor)	Jul 03	Jul 04 [†]	984	400	0	$< 0.01(40^{*})$
- pirimicarb-desmethyl						< 0.01(0)
- pirimicarb-desmethyl-formamido						0.12(24*)

Systematic chemical nomenclature for the analysed pesticides is given in Appendix 1

* Pesticide have been applied twice, and the findings are not necessarily related to one specific application

[†] Monitoring will continue during the following year. The values for prec. and perc. are accumulated up to July 2003 ¹⁾Drainage runoff commenced about two and a half months prior to the application of ioxynil and bromoxynil, and the weighted concentrations refer to the period from the date of application until 1 July 2002

The leaching risk of pesticides applied during 2000 and 2001 has been evaluated in Kjær *et al.* (2003) and Kjær *et al.* (2004), respectively.

The pesticides applied during 2002 did leach from the root zone, but not at unacceptable levels. The findings are briefly summarized below. For a detailed description of the leaching pattern, see Kjær *et al.* (2003).

Amidosulfuron did not leach. It should be noted that the leaching risk of amidosulfuron is mainly associated with its two degradation products. Unfortunately, methods for analysing these substances are not yet available. Minor leaching was observed with *pirimicarb*, *propiconazole* and *MCPA*. All three substances were detected in several drainage water samples. Apart from a few samples taken shortly after application (containing 0.34 and 0.86 μ g/l propiconazole, 0.15 and 3.9 μ g/l MCPA), all concentrations were below 0.1 μ g/l (Figure 28). When evaluating these results it should be noted that these pesticides were applied during spring/summer 2002, when precipitation input and corresponding percolation were much higher than normal (Table 11 and Section 5.2.1). Leaching of the degradation product pirimicarb-desmethyl-formamido was observed during the 2003/2004 drainage period. This leaching appears to be related to the latest application of pirimicarb in 2003, and these results will not be evaluated until the 2005 monitoring results become available, i.e. when two years of monitoring data following the latest application of the pesticide have been collated.

Glyphosate and its degradation product AMPA leached from the root zone in average concentrations considerably exceeding 0.1 μ g/l, especially in the case of glyphosate. Thus the average concentration in the drainage water during the 2002/2003 leaching period was 0.43 μ g/l, while that of AMPA was 0.19 μ g/l (Table 11 and Figure 30). Four days after the pesticide had been applied on 2 September 2002, 13 mm of precipitation caused leaching of both glyphosate and AMPA in concentrations reaching 1.1 µg/l and 0.058 µg/l, respectively. The following period was remarkably dry (A). Marked precipitation was only seen in mid October (one and a half months after application), when as much as 131 mm fell within a twoweek period. The drainage runoff responded rapidly to these heavy storm events, inducing marked, rapid leaching of both glyphosate and AMPA (Figure 30B, C). Both substances leached continuously during the whole 2002/2003 drainage runoff period (Appendix 8, Figure 30B, C). These results should be viewed in relation to a monitoring period characterised by a rather irregular precipitation pattern yielding very little precipitation and drainage runoff during autumn/winter 2002/2003. September was particularly dry with only 22 mm precipitation, 77% less than normal. The present results are consistence with previous data that also indicate marked root zone leaching of glyphosate and AMPA at Estrup (Kjær et al., 2003). When glyphosate was applied at Estrup in autumn 2000, it was followed by marked precipitation and percolation reaching as much as 128 mm within the first month (Table 11), very unlike the situation following the recent application in 2002. Despite the very different hydrological conditions following the two applications, the leaching pattern was somewhat similar. Both were characterized by continuous leaching over a relatively long time period and by weighted average concentrations exceeding 0.1 μ g/l (Figure 30).



Figure 28. Precipitation and simulated percolation (A) together with concentration of propiconazole (B) and pirimicarb (C) and MCPA (D) in the drainage runoff at Estrup in 2002/2003. The green vertical lines indicate the dates of application. Open diamonds and triangles indicate values below the detection limit of 0.01 μ g/l.

With glyphosate, leaching was mainly confined to the first four to six months after application. Leaching decreased with time, and the amount leached during the second year after application was negligible. The leaching pattern of AMPA differed from that of glyphosate in that minor leaching occurred over a much longer time period. The total amount of AMPA leached was 55% lower than that of glyphosate (Kjær *et al.*, 2005a). Leaching decreased with time, but unlike with glyphosate continued throughout the second year after both applications. The decreased leaching of glyphosate is likely to be attributable to the glyphosate being either sorbed or degraded into AMPA. The latter is illustrated by the fact that AMPA was detected in both the very first water samples and in an increasing fraction of samples with time The fact that leaching of AMPA occurred as long as two years after the latest application may indicate that AMPA can be retained within the soil and be gradually released over a very long period of time. Thus the possibility cannot be excluded that the application of glyphosate in 2000 may have contributed to the observed AMPA leaching in 2002–2004. For a detailed description of the leaching pattern, see Kjær *et al.* (2005a).

The leaching risk of pesticides applied in 2003 will not be evaluated until the 2005 monitoring results become available, i.e. when two years of monitoring data have been collated. It should be noted, though, that all of the 2003 applied pesticides leached from the root zone reaching the drainage system, as illustrated in Figure 29 and Table 11.

Pesticide leaching at Estrup has hitherto mainly been confined to the depth of the drainage system. Apart from eight samples containing 0.01–0.04 μ g/l glyphosate, pesticides have only sporadically been detected in groundwater monitoring screens below the depth of the drainage system (Appendix 9). The bulk of pesticide leaching at Estrup occurred with drainage runoff. The water balance suggests that 61–78% of the percolation ran off through the drainage system (Section 5.2.1). Due to decreased hydraulic conductivity and lower degree of preferential flow, transport of water and solutes at Estrup was much slower beneath the drainage system than above it. Slow transport may allow for dispersion, dilution, sorption and degradation, thereby further reducing the deep transport.

Compared to the other loamy soils investigated, the retention characteristics at Estrup suggest that the C horizon (situated beneath the drainage depth) is less permeable with a lower degree of preferential flow occurring through macropores. At Silstrup and Faardrup, measured conductivity in the C horizon increased markedly when approaching full saturation, thus indicating a high degree of preferential flow through macropores when the soil is fully saturated (Figure A4.4 and A4.6 in Appendix 4). A similar increase in measured conductivity when approaching saturation was not seen in the C horizon of Estrup (Figure A4.5 in appendix 4), indicating a much lower degree of preferential flow.



Figure 29. Precipitation and simulated percolation (A) together with concentration of pirimicarb (B), pirimicarb-desmethyl-formamido (C), ethofumesate (D), metamitron (E) and metamitron-desamino (F) in the drainage runoff at Estrup in 2003/2004. The green vertical lines indicate the dates of application. Open diamonds and triangles indicate values below the detection limit of 0.01 μ g/l. DR.: Drainage runoff



Figure 30. Precipitation and simulated percolation (A) together with the concentration of glyphosate (B) and AMPA (C) in the drainage runoff at Estrup. Data represent a four-year period including two applications of glyphosate as indicated by the green vertical lines. Open diamonds and triangles indicate values below the detection limit of $0.01 \mu g/l$.

6 Pesticide leaching at Faardrup

6.1 Materials and methods

6.1.1 Site description and monitoring design

Faardrup is located in southern Zealand (Figure 1). The test field covers a cultivated area of 2.3 ha (150 x 160 m). The terrain slopes gently to the west by $1-3^{\circ}$ (Figure 45). Based on three profiles in the buffer zone bordering the field, the soil was classified as Haplic Vermudoll, Oxyaquic Hapludoll and Oxyaquic Argiudoll (Soil Survey Staff, 1999). The topsoil is characterized as sandy loam with 14-15% clay and 1.4% organic carbon (Table 1). Within the upper 1.5 m numerous desiccation cracks coated with clay are present. The test field contains glacial deposits dominated by sandy till to a depth of about 1.5 m overlying a clayey till. The geological description shows that small channels or basins filled with meltwater clay and sand occur both interbedded in the till and as a large structure crossing the test field (Lindhardt *et al.*, 2001). The calcareous matrix and the reduced matrix begin at 1.5 m and 4.2 m b.g.s., respectively (Table 1). The dominant direction of groundwater flow is towards the west in the upper part of the aquifer (Figure 45). During the monitoring period the groundwater table was located 1-2 and 2-3 m b.g.s. in the lower and upper parts of the area, respectively. During fieldwork within the 5 m deep test pit it was observed that most of the water entering the pit came from an intensely horizontally fractured zone in the till at a depth of 1.8-2.5 m. The intensely fractured zone could very well be hydraulically connected to the sand fill in the deep channel, which might drain part of the percolation. The bromide tracer study showed that virtually none of the applied bromide reached the vertical monitoring well (M6) located in the sand-filled basin (Section 6.2.2), however, thus indicating that hydraulic contact with the surface in the "basin" does not differ from that in other parts of the test field, and that the basin is a small pond filled with sediments from local sources. A brief description of the sampling procedure is provided in Appendix 2. The monitoring design and test site are described in detail in Lindhardt et al. (2001) and the analysis methods in Kjær et al. (2002).



Figure 31. Overview of the Faardrup site. The innermost white area indicates the cultivated land, while the grey area indicates the surrounding buffer zone. The positions of the various installations are indicated, as is the direction of groundwater flow (by an arrow).

6.1.2 Agricultural management

Management practice during the three most recent growing seasons is briefly summarized below and detailed in Appendix 3 (Table A3.5). For information about management practice during the first two monitoring periods see Kjær *et al.* (2003).

The field was ploughed on 30 October 2001. Due to the good weather conditions, spring barley (cv. Barke) was sown earlier than usual on 28 March 2002. When the barley had 2 leaves, weeds were sprayed with tribenuron methyl on 7 May. Herbicide spraying was also carried out on 22 May using MCPA and on 25 May using flamprop-M-isopropyl. The barley was sprayed with the fungicide propiconazole and the pesticide dimethoate on 4 June. The crop was harvested on 9 August yielding 65.6 hkg/ha of grain (85% dry matter), which was a high yield for that particular cultivar that year. Ten days later the field was ploughed. Management practice at the site is detailed in Appendix 3 (Table A3.5).

After fertilization with 30 kg N/ha the field was sown with winter rape (cv. Canberra) on 22 August 2002. The next day the herbicide clomazone was applied. On 25 September, when the rape had 5 leaves unfolded, the herbicide clopyralid was applied. Clopyralid was not included in the monitoring, however. An additional 145 kg N was applied on 24 March. The crop was treated with the pesticide alpha-cypermethin on 24 April, but this is not included in the monitoring program. The rape was windrowed on 17 July and threshed on 28 July. Rapeseed yield was just 28.7 hkg/ha (91% dry matter), a low yield when compared to trials by the Danish Farmers Association. There may be several reasons for the low yield. Thus the crop suffered from frost die back during the winter time, and the plots to be used for the yield measurements were not laid out at the sowing time, which may have caused spillage of seeds both when windrowing and in the long interval between windrowing and harvest due to rainy conditions.

On 19 September 2003 the field was sown with winter wheat (cv. Galicia). 10 days later the crop had emerged. The herbicide prosulfocarb was sprayed on 17 October. A combination of MCPA and azoxystrobin was applied on 3 June 2004 to combat weeds and fungi, respectively. The amounts of grain and straw harvested on 7 September were 89.3 hkg/ha (85% dry mater) and 69.3 hkg/ha (100% dry mater), respectively. Grain yield was almost 20 hkg/ha better than in the field trails on Zealand performed by the Farmers Union.

6.1.3 Model set-up and calibration

The MACRO model is applied to the Faardrup site covering the soil profile to a depth of 5 m b.g.s., always including the groundwater table. The model is used to simulate the water flow in the unsaturated zone during the full monitoring period September 1999–June 2004 and to establish an annual water balance.

Due to application of a newer version of MACRO than used in the previous report (version 5.0 vs 4.2) (Kjær *et al.*, 2004) the model for the Faardrup site has been recalibrated for the whole period to the observed groundwater table measured in the piezometers located in the buffer zone, to time series of soil water content measured at three depths (25, 60 and 110 cm b.g.s.) from the two profiles S1 and S2 (Figure 31) and to the measured drainage flow. Data acquisition and model set-up are described in Appendix 4. The main calibration parameters were the empirical parameter BGRAD, which regulates the boundary flow, the

"boundary" pressure head (XMPOR), its corresponding water content (CTEN), the hydraulic conductivity (KSM) and the effective diffusion path length (ASCALE), which controls the exchange of water and solute between the two flow domains (see Appendix 4 for details).

As stated in the previous report (Kjær *et al.*, 2003), precipitation measured at Flakkebjerg 3 km east of Faardrup was used for the monitoring periods July 1999–June 2002 due to an electronic noise problem. The problem has now been solved, and precipitation measured at Faardrup was used for the monitoring periods July 2002–June 2004.

6.2 Results and discussion

6.2.1 Soil water dynamics and water balances

The model simulations are generally consistent with the observed data, thus indicating a good model description of the overall soil water dynamics in the unsaturated zone (Figure 32). The results are almost identical to the simulations made with MACRO 4.2 (Kjær *et al.*, 2004). The dynamics and level of the measured groundwater table are well described by the present model. As with the previous model (Kjær *et al.*, 2004), however, the drop in measured groundwater table during the dry summer periods is not fully reflected in the simulations. Furthermore, the measured quick rise in groundwater table after the summer period is too slow in the simulation. The level and dynamics of the soil water content in all three horizons are well described by the model (Figure 32D, E and F). The groundwater table and soil water content patterns during the dry period in the latest monitoring period (July 2003–June 2004) are similar to those in the period 2000–2001.

The drainage flow simulated with MACRO 5.0 closely matches the measured drainage flow (Figure 32C). As with the simulations made using MACRO 4.2 (Kjær *et al.*, 2004), the simulated peak at the onset of the drainage flow in the monitoring period is less well described. This is probably attributable to the above-mentioned problems with the groundwater table. The drainage runoff season in the latest monitoring period (July 2003–June 2004) was very short (four months), as was also the case in the previous monitoring period, but started two months later.

	Normal		Actual	Measured	Simulated	Groundwater
	precipitation 1)	Precipitation ²⁾	evapotranspiration	drainage	drainage	recharge ³⁾
1.7.99-30.6.00	626	715	515	192	150	7
1.7.00-30.6.01	626	639	447	50	52	142
1.7.01-30.6.02	626	810	518	197	128	98
1.7.02-30.6.03	626	633	460	49	56	124
1.7.03-30.6.04	626	587	426	36	13	125

Table 12. Annual water balance for Faardrup (mm/year). Precipitation is corrected to the soil surface according to the method of Allerup and Madsen (1979).

¹⁾ Normal values based on time series for 1961–1990

²⁾ For 1.7.99–30.6.02, measured at the DIAS Flakkebjerg meteorological station located 3 km from the test site (see text) ³⁾ Groundwater recharge is calculated as precipitation - actual evapotranspiration - measured drainage The resultant annual water balance for Faardrup is shown for each monitoring period (July–June) in Table 12. Compared to the balance calculated with MACRO 4.2 (Kjær *et al.*, 2004), actual evapotranspiration has generally increased, and groundwater recharge has decreased. Annual precipitation in the latest monitoring period (July 2003–June 2004) is the lowest since monitoring began at the site and is characterized by a very dry late summer/autumn (August-October) and a dry December and February (Appendix 5). January and April were very wet, but could not compensate for the many dry months. This is reflected in the lowest measured drainage runoff since monitoring began at the site. Due to the dry autumn the drainage season for the latest monitoring period began at the end of January, two or more months later than in previous years. Percolation at 1 m b.g.s. also started later than in previous years. For information about the water balance in previous monitoring periods see Kjær *et al.* (2004).

6.2.2 Bromide leaching

The bromide concentration shown in Figure 33 and Figure 34 relate to the bromide applied in May 2000, as described further in Kjær *et al.* 2003, and 2004.



Figure 32. Soil water dynamics at Faardrup: Measured precipitation and simulated percolation 1 m b.g.s. (A), simulated and measured groundwater level (B), simulated and measured drainage flow (C) and simulated and measured soil water saturation (SW sat.) at three different soil depths (D, E, and F). The measured data in B derive from piezometers located in the buffer zone. The measured data in D, E and F derive from TDR probes installed at S1 and S2 (see Figure 31).


Figure 33. Bromide concentration at Faardrup. A and B refer to suction cups located at S1 and S2. The bromide concentration is also shown for drainage runoff (C) and the horizontal monitoring wells (D). The green vertical line indicates the date of bromide application.



Figure 34. Bromide concentration at Faardrup. The data derive from the vertical monitoring wells (M2–M7). Screen depth is indicated in m b.g.s. The green vertical line indicates the date of bromide application.

6.2.3 Pesticide leaching

Monitoring at Faardrup began in September 1999 and presently encompasses 18 pesticides and several degradation products, as indicated in Table 13. Pesticide application during the two most recent growing seasons is shown together with precipitation and simulated precipitation in Figure 35. It should be noted that precipitation is corrected to the soil surface according to Allerup and Madsen (1979), whereas percolation (1 m b.g.s.) refers to accumulated values as simulated with the MACRO model. It should also be noted that as tribenuron methyl (applied here as Express) degrades rapidly, the leaching risk is more associated with its degradation product, triazinamin-methyl. For the same reason it is the degradation product and not the parent compound that is monitored in the PLAP (Table 12).



Figure 35. Pesticide application, precipitation (primary axis) together with simulated percolation (secondary axis) at Faardrup in 2002/2003 (upper) and 2003/2004 (lower). Pesticides applied later than April 2004 are not included.

Table 13. Pesticides analysed at Faardrup with the product used shown in parentheses. Degradation products are in italics. Precipitation (prec.) and percolation (perc.) are accumulated from the date of first application (app. date) until the end of monitoring. 1^{st} month perc. refers to accumulated percolation within the first month after application. C_{mean} refers to average leachate concentration in the drainage water the first drainage season after application (See Appendix 2 for calculation methods). The number of pesticide-positive samples is indicated in parentheses.

Crop and analysed pesticides	Application	End of	Prec.	Perc.	1 st month	C _{mean}
	date	monitoring	(mm)	(mm)	perc. (mm)	(µg/l)
Winter wheat 1999						
Glyphosate (Roundup 1999)	Aug 99	Apr 03	2529	985	10	< 0.01(8*)
- AMPA						< 0.01(17*)
Bromoxynil (Briotril)	Oct 99	Apr 02	1728	766	28	< 0.01(0)
Ioxynil (Briotril)	Oct 99	Apr 02	1728	766	28	< 0.01(2)
Fluroxypyr (Starane 180)	Apr 00	Apr 02	1397	508	8	< 0.01(1)
Propiconazole (Tilt Top)	May 00	Jul 03	2154	703	0	$< 0.01(1^*)$
Fenpropimorph (Tilt Top)	May 00	Jul 02	1521	497	4	< 0.01(1)
- fenpropimorphic acid						< 0.01(0)
Pirimicarb (Pirimor G)	Jun 00	Jul 03	2069	723	4	< 0.01(9*)
- pirimicarb-desmethyl						< 0.01(9*)
- pirimicarb-desmethyl-formamido						$<0.02(5^{*})$
Sugar beet 2001						
Glyphosate (Roundup 2000)	Oct 00	Jul 03	1750	712	0	< 0.01(8 [*])
- AMPA						$0.01(17^*)$
Metamitron (Goltix WG)	May 01	Jul 03	1515	483	0	0.01(35)
- metamitron-desamino						0.01(63)
Ethofumesate (Betanal Optima)	May 01	Jul 03	1515	483	0	0.06(45)
Desmedipham (Betanal Optima)	May 01	Jul 03	1515	483	0	< 0.01(0)
- EHPC						< 0.02(0)
Phenmedipham (Betanal Optima)	May 01	Jul 03	1515	483	0	< 0.01(2)
- MHPC						< 0.02(3)
Fluazifop-P-butyl (Fusilade X-tra)	Jun 01	Jul 03	1463	491	0	< 0.01(0)
- fluazifop (free acid)						0.02(17)
Pirimicarb (Pirimor G)	Jul 01	Jul 03	1463	491	0	< 0.01(9)
- pirimicarb-desmethyl						< 0.01(9)
- pirimicarb-desmethyl-formamido						< 0.02(5*)
Spring barley 2002						
Flamprop-M-isopropyl (Barnon Plus)	May 02	Jul 04	1319	358	0	< 0.01(1)
- Flamprop-M (free acid)						< 0.01(1)
MCPA (Metaxon)	May 02	Jul 04	1339	358	0	< 0.01(0)
- 4-chlor,2-methylphenol						< 0.02(0)
- Triazinamin-methyl ¹⁾ (Express)	May 02	Jul 04	1343	364	5	< 0.02(0)
Dimethoate (Perfekthion 500 S)	Jun 02	Jul 04	1307	359	0	< 0.01(0)
Propiconazole (Tilt 250 EC)	Jun 02	Jul 04	1307	359	0	< 0.01(1*)
Winter rape 2003						
Clomazone (Command CS)	Aug 02	Jul 04 ⁺	1109	372	5	< 0.02(0)
-propanamide-clomazone (FMC65317)						< 0.02(0)
Winter wheat 2004						
Prosulfocarb (Boxer EC)	Oct 03	Jul 04^{\dagger}	471	178	0	< 0.01 (0)

Systematic chemical nomenclature for the analysed pesticides is given in Appendix 1

¹⁾ Degradation product of tribenuron methyl. The parent compound degrades too rapidly to be detected by monitoring

* Pesticide has been applied twice, and the findings are not necessarily related to one specific application

† Monitoring will continue during the following year. The values for prec. and perc. are accumulated up to July 2004

The leaching risk of pesticides applied during 2000 and 2001 has been evaluated in Kjær *et al.* (2003) and Kjær *et al.* (2004), respectively.

The leaching risk of pesticides applied in 2002 was found to be negligible at Faardrup. Apart from one sample (drainage water sampled on 16 July 2002) containing 0.037 μ g/l flamprop-M-isopropyl and 0.089 μ g/l flamprop-M (free acid) and another (M5 sampled on 3 July 2002) containing 0.035 μ g/l propiconazole, however, none of the applied pesticides or the degradation products listed in Table 13 have yet been detected. The pesticide were applied during summer 2002, when precipitation input was close to normal and was counterbalanced by actual evapotranspiration such that only 0–7 mm percolated during the first month after pesticide application (Appendix 5 and Figure 35).

The leaching risk of pesticides applied in 2003 will not be evaluated until the 2005 monitoring results become available, i.e. when two years of monitoring data have been collated. It should be noted, though, that none of the applied pesticides were detected in any of the water samples analysed.

7 Pesticide analysis quality assurance

Reliable results and scientifically valid methods of analysis are essential for the integrity of the present monitoring programme. Consequently, the field monitoring work has been supported by intensive quality assurance entailing continuous evaluation of the analyses employed. Two types of sample are used in the quality control – samples with known pesticide composition and concentration are used for *internal monitoring* of the laboratory method, while *external spiked samples* are used to incorporate additional procedures such as sample handling, transport and storage. Pesticide analysis quality assurance (QA) data for the period July 2002–June 2003 are presented below, while those for the preceding monitoring periods are given in Kjær *et al.* (2002, 2003, and 2004).

7.1 Materials and methods

The pesticide analyses were carried out at two commercial laboratories selected on the basis of a competitive tender. In order to assure the quality of the analyses, the call for tenders included requirements as to the laboratories' quality assurance (QA) system comprising both an internal and an external control procedure. In addition to specific quality control under the PLAP, each of the laboratories takes part in the proficiency test scheme employed by the Danish Environmental Protection Agency when approving laboratories for the Nationwide Monitoring and Assessment Programme for the Aquatic and Terrestrial Environments (NOVANA).

7.1.1 Internal QA

With each batch of samples the laboratories analysed one or two control samples prepared at each laboratory as a part of their standard method of analysis. The pesticide concentration in the internal QA samples was generally in the range 0.04–0.08 μ g/l. Using these data it was possible to calculate and separate the analytical standard deviation into within-day (S_w), between-day (S_b) and total standard deviation (S_t). Total standard deviation was calculated using the following formula (Wilson 1970, Danish EPA 1997):

$$s_t = \sqrt{s_w^2 + s_b^2}$$

7.1.2 External QA

Every fourth month, two external control samples were analysed at the laboratories along with the various water samples from the six test sites. Two stock solutions of different concentrations were prepared from two standard mixtures in ampoules prepared by Promochem, Germany (Table 14). Fresh ampoules were used for each set of low- and high-standard solutions. 150 μ l or 350 μ l of the pesticide mixture was pipetted into a preparation glass containing 10 ml of ultrapure water. The glass was closed and shaken thoroughly and shipped to the staff collecting the samples. The staff finished the preparation of control samples in the field by quantitatively transferring the standard solution to a 3-1 measuring flask. The standard solution was diluted and adjusted to the mark with groundwater from an

upstream well. After thorough mixing, the control sample was transferred to a sample bottle and transported to the laboratories together with the regular samples. The standard solutions were prepared two days before a sampling day. The pesticide concentration in the solution is indicated in Table 14. Blank samples consisting of HPLC water were also included in the external QA procedure every month. All samples included in the control were labelled with coded reference numbers so that the laboratories were unaware of which samples were controls and blanks.

Compound	Spike solution (mg/l)	High-level control (ng/l)	Low-level control (ng/l)
AMPA	1	117	50
Bentazone	1	117	50
Bromoxynil	1	117	50
Clomazone	1	117	50
Desethyl terbutylazine	1	117	50
Dimethoate	1	117	50
Ethofumesate	1	117	50
Flamprop (free acid)	1	117	50
Fluazifop (free acid)	1	117	50
Fluroxypyr	1	117	50
Glyphosate	1	117	50
Ioxynil	1	117	50
Metamitron	1	117	50
Pendimethalin	1	117	50
РНСР	1	117	50
Pirimicarb	1	117	50
PPU	1	117	50
Propiconazole	1	117	50
Terbutylazine	1	117	50

Table 14. Pesticide concentrations in the spike solution and in the high-level and low-level external control samples. $^{1)}$

¹⁾ Due to a dilution error, the spike level in the high-level and low-level external control samples in October 2003 was 1,170 ng/l and 500 ng/l, respectively.

7.2 Results and discussion

7.2.1 Internal QA

Ideally, the analytical procedure should provide precise and accurate results. However, the pesticide analyses that form the basis of the PLAP programme are subject to a certain standard deviation. Such standard deviation may be the combined result of several contributing factors. Overall, the accuracy of an analytical result reflects two types of error: random errors related to precision and systematic errors relating to bias. In a programme like PLAP it is relevant to consider possible changes in analytical "reliability over time". As these errors may change over time it is relevant to distinguish between standard deviations resulting from *within-day* variation as opposed to those associated with *between-day* variation in the analytical result. To this end, control samples are included in the analytical process as described above. Thus, by means of statistical analysis of the internal QA data it is possible to separate and estimate the different causes of the analytical variation in two categories: dayto-day variation and within-day variation (Miller *et al.*, 2000; Funk *et al.*, 1995). This kind of analysis can provide an indication of the reliability of the analytical results used in the PLAP. The statistical tool used is an analysis of variance (ANOVA) and encompasses all duplicate pesticide analyses, single analyses being excluded. The analysis can be divided into three stages:

- 1. NORMALITY: An initial test for normality is made as this is an underlying assumption for the one-way ANOVA.
- 2. BETWEEN-DAY CONTRIBUTION: Explained simply, this test will reveal any day-to-day contribution to the variance in the measurements. If there is none, the total standard deviation can be considered to be attributable to the within-day error of the analysis. For this purpose an ANOVA-based test is used to determine if the between-day standard deviation (S_b) differs significantly from 0 (this test is made as an F-test with the H_0 between-day mean square = within-day mean square).
- 3. CALCULATING STANDARD DEVIATIONS. If the F-test described above reveals a contribution from the between-day standard deviation (S_b) it is relevant to calculate three values: The within-day standard deviation S_w , the between-day standard deviation S_b , and the total standard deviation S_t .

As the error associated with the analytical result is likely to be highly dependent on the compound analysed, the QA applied is pesticide-specific. The results of the internal QA statistical analysis for each pesticide are presented Table 15. For reference, estimated S_b values are listed for all pesticides, including those for which the between-day variance is not significantly greater than the within-day variance. ANOVA details and variance estimates are also included, even in the case of pesticides where the requirement for normality is not fulfilled. Such data should obviously be interpreted with caution.

As a "rule of thumb" the between-day standard deviation should be no more than double the within-day standard deviation. From Table 15 it can be seen that S_b/S_w ratios greater than two were observed for several compounds. As mentioned, the analysis is only conclusive for pesticide data that meet the normality requirement. Among the pesticides or degradation products meeting the requirement, the Sb/Sw ratio is highest for PPU, PPU-desamido, and prosulfocarb. Overall, the results indicate that day-to-day variation makes a significant contribution. However, the day-to-day variation is markedly reduced compared to last year (Kjær *et al.*, 2004), in particular for laboratory 1.

The total standard deviations (S_t) of the various pesticide analyses lie within the range 0.002–0.024 µg/l (only data with n≥3 are included in the analysis). The overall mean S_t was 0.007 µg/l. S_t was in the range 0.002–0.022 µg/l for the pesticides and 0.002–0.024 µg/l for the degradation products. The pesticide and degradation product with the poorest reproducibility were bentazone and 2-hydroxy-desethyl-terbutylazine. Analysing S_t with a *t*-test revealed no significant differences between pesticides and degradation products (*t*-test, equal variances, α =0.05). Neither did S_t differ significantly between the two laboratories (*t*-test, equal variances, α =0.05), probably due to the improved reproducibility at laboratory 1.

Table 15 Internal QA of pesticide analyses from laboratory 1 and laboratory 2. Results of the test for normality, one-way analysis of variance (ANOVA), and the estimated values of standard deviations (w: within-day, b: between-day, t: total – see text for details), and number of duplicate samples (n) is given for each pesticide. Degradation products are indicated with 'D' following the compound name. For tests the P value α =0.05 was used. Only data for n≥3 are included.

Pesticide/Degradation product		Normal	Significant S _b	Sw	Sb	St	Ratio	n
		distribution	between-day	(μg/l)	(µg/l)	(µg/l)	Sb/Sw	
		α=0.05	contribution					
			ANOVA α =0.05					
Laboratory 1								
2-hydroxy-desethyl-terbutylazine	D		yes	0.011	0.021	0.024	1.884	18
2-hydroxy-terbutylazine	D	yes	yes	0.008	0.016	0.017	2.070	22
4-chlor-2-methylphenol	D	yes	yes	0.004	0.005	0.006	1.009	34
AMPA	D	yes	yes	0.003	0.004	0.005	1.411	28
Propanamide-clomazone	D	yes	yes	0.001	0.004	0.005	3.029	29
PPU	D	yes	yes	0.002	0.007	0.007	3.832	12
PPU-desamido	D	yes	yes	0.001	0.009	0.009	7.063	12
MCPA		yes	yes	0.005	0.012	0.013	2.482	36
Bentazone			yes	0.015	0.015	0.022	1.005	24
Clomazone		yes	yes	0.001	0.003	0.003	2.221	29
Desethylterbutylazine	D		yes	0.001	0.005	0.005	3.324	34
Desisopropylatrazine	D		yes	0.002	0.005	0.006	2.661	26
Dimethoate		yes	yes	0.002	0.004	0.005	1.807	33
Flamprop (free acid)	D	yes	yes	0.003	0.004	0.005	1.145	28
Flamprop-M-isopropyl			yes	0.003	0.003	0.004	1.086	28
Glyphosate		yes	yes	0.003	0.004	0.005	1.589	28
Pendimethalin		yes	yes	0.003	0.006	0.007	1.787	25
Propiconazole			yes	0.002	0.008	0.008	3.382	29
Prosulfocarb		yes	yes	0.003	0.010	0.011	2.944	24
Terbutylazine			yes	0.001	0.005	0.006	3.606	25
Triazinamin-methyl	D		yes	0.001	0.008	0.008	5.254	23
Laboratory 2								
2-amino-N-isopropylbenzamid	D	yes		0.009	0.003	0.009	0.349	9
4-chlor-2-methylphenol	D	yes	yes	0.002	0.002	0.003	1.009	13
Amidosulfuron		yes		0.002	0.001	0.002	0.442	11
Propanamide-clomazone	D			0.008	0.005	0.009	0.555	14
MCPA		yes		0.002	0.002	0.003	0.749	13
Bentazone		yes	yes	0.001	0.002	0.003	1.907	13
Bromoxynil			yes	0.001	0.003	0.003	3.290	16
Clomazone		yes	yes	0.001	0.002	0.003	1.380	12
Dimethoate		yes	yes	0.001	0.001	0.002	0.957	14
Ethofumesate				0.004	0.003	0.005	0.803	13
Flamprop (free acid)	D	yes		0.002	0.001	0.002	0.457	12
Flamprop-M-isopropyl		yes	yes	0.001	0.002	0.002	1.556	14
Fluroxypyr			yes	0.004	0.009	0.010	2.489	12
Ioxynil			yes	0.001	0.002	0.003	1.390	16
Metamitron			yes	0.001	0.004	0.004	2.989	13
Metamitron-desamino	D		yes	0.003	0.008	0.009	2.623	14
Metribuzin-desamino-diketo	D			0.006	0.005	0.007	0.870	13
Metribuzin-diketo	D		yes	0.009	0.012	0.015	1.275	14
Pirimicarb			yes	0.004	0.008	0.009	2.026	8
Pirimicarb-desmethyl	D		yes	0.003	0.004	0.005	1.494	11
Pirimicarb-desmethyl-formamido	D		yes	0.002	0.012	0.012	7.307	12
Propiconazole			yes	0.001	0.004	0.004	3.903	13

7.2.2 External QA

Table 16 provides an overview of the recovery of all externally spiked samples based on one to three observations. Recovery of the spiked samples is generally good (>70%). Exceptions are the pesticides fluroxypyr, metamitron, PHCP, and phendimethalin, for which recovery was low at some of the field sites, and even zero in a few samples.

As the results are based on only one to three observations, this should not be interpreted rigorously. However, the data may indicate possible recovery problems for pesticides at one or several sites. With fluroxypyr and phendimethalin, recovery was very low in a few samples or a single sample, whereas recovery was acceptable in the other samples. Recovery of metamitron is generally low, and in one case the substance was undetectable. Recovery of the pyridate degradation product PHCP dropped considerably within the present period, following a clear downward trend, and PHCP could not be detected in the single low-level spiked sample during the period. Control analysis of the spike solution with respect to PHCP and a review of the relevant sample data by the laboratory did not provide an explanation for the decrease in recovery. There is consequently a risk of false negative results with respect to PHCP in the analyses performed between 1 July 2003 and 30 June 2004 as PCHP could not be detected at the 0.05 $\mu g/l$ level.

A possible explanation for low recovery could be degradation of the spiked compound during transport, storage or analysis. In agreement with this hypothesis, the degradation product PPU-desamido was observed in a few samples even though this substance is not included in the spike solution (indicated by asterisks in Table 16). As PPU-desamido was not detected in the blank sample matrix used for spiking, its presence in the spiked samples is likely to derive from the added PPU, the primary degradation product of rimsulfuron degradation. The secondary degradation product was only observed in the high-level spiked samples, whereas it was not detected in the low-level spiked samples. However, the concentration of PPU-desamido in the high-level spiked samples was rather close to the detection limit, which may explain its absence in the low-level spiked samples. Since the recovery of PPU was similar in the high- and low-level spiked samples, degradation of PPU probably occurred in the low-level samples as well even if PPU-desamido was not detected. The measured concentration of PPU-desamido corresponds to 23–33% of the added amount of PPU. Consequently, the concentration of PPU detected at Jyndevad (Figure 12) may be underestimated to some extent.

Due to dilution error, the spike concentration in the external control samples from October 2003 was an order of magnitude too high (500 ng/l and 1,170 ng/l, respectively). Recoveries from these samples are included in Table 17, however, as there was no systematic difference between these recoveries and the recoveries from samples having the correct concentration. The results are excluded from the QA control charts in Appendix 9, however, as the measured concentrations in ng/l are far off scale compared to the other samples.

During the 2003/2004 monitoring period a total of eight pesticides and nine degradation products were detected in samples from the experimental fields, and the external and internal QA data relating to these particular pesticides/degradation products are of special interest. These data (when available) are therefore described in detail in Appendix 9.

No pesticides were detected in blank samples, thus indicating that no contamination of the samples occurred in the laboratory. Samples found to contain pesticides and their degradation products are thus regarded as true positive findings. With the exceptions of PHCP and

metamitron, as described above, all the pesticides in the spiked samples were detected in all samples.

	Tylstrup		Jyndevad		Silstrup		Estrup		Faardrup		Average
	Low	High	Low	High	Low	High	Low	High	Low	High	
AMPA					84	69	93	94			83
Bentazone			76	74	90	86	85	75			82
Bromoxynil	77	89					70	79			79
Clomazone	90	108							77	72	88
Desethylterbutylazine			96	93	99	93					95
Dimethoate	72	83	92	94					86	81	85
Ethofumesate							104	97			101
Flamprop (free acid)	82	83							68	84	80
Fluazifop-P (free acid)	88	85	86	77							84
Fluroxypyr	55	50					66	74			58
Glyphosate					92	78	94	68			82
Ioxynil	92	98					100	97			96
Metamitron							42	33			39
Pendimethalin			64	59	70	43					56
РНСР					34	48					42
Pirimicarb							73	75			74
PPU	78	81	78	79							79
PPU-desamido *				*							
Propiconazole							100	93	77	79	88
Terbutylazine			62	66	72	70					68

Table 16. External spiked samples. Average recovery (%) of the nominal concentration at low/high concentration level indicated for each site.

* Indicates that the compound was detected even if it was not included in the spiking solution – see text for details

7.3 Summary and concluding remarks

The overall quality of the pesticide analysis was considered satisfactory. The QA system showed that:

- Reproducibility of the pesticide analyses was good, total standard deviation being in the range 0.002-0.024 μg/l.
- No differences in reproducibility were observed between pesticides and degradation products, or between the two laboratories.
- Recovery was generally good (70–125%) in external spiked samples. Low recovery of the pesticides fluroxypyr, metamitron, and phendimethalin was observed at single sites.
- Recovery of PHCP decreased steadily during the present monitoring period, possibly due to analytical or spiking problems, and there is consequently a risk of false negatives with respect to PHCP. This requires further examination.
- Degradation of the rimsulfuron metabolite PPU was observed in the spiked samples, with detection of the secondary degradation product PPU-desamido in amounts corresponding to 23–33% of the added PPU. Findings of PPU at Jyndevad (section 3.2.3) may thus be underestimated.
- Contamination of samples was not observed during collection, storage and analysis.

8 Summary of monitoring results

This section summarizes monitoring data from the entire monitoring period, i.e. both data from the two most recent monitoring years (detailed in this report) and data from the previous monitoring years (detailed in previous reports Kjær *et al.*, 2002, 2003 and 2004). The monitoring data reveal that the applied pesticides exhibit three different leaching patterns – no leaching, slight leaching and pronounced leaching (see Table 19). Pronounced leaching is here defined as root zone leaching (1 m b.g.s.) exceeding an average concentration of 0.1 μ g/l. On sandy and loamy soils, leaching is determined as the weighted average concentration in soil water and drainage water, respectively (See Appendix 2 and 4 for calculation methods). It should be noted, though, that the present evaluation of the leaching risk of some of these pesticides is still preliminary as their potential leaching period extends beyond the current monitoring period. This applies to those pesticides marked with a single asterisk in Table 19. Seven of the applied pesticides or their degradation products exhibited pronounced leaching.

- Two degradation products of metribuzin metribuzin-diketo and metribuzin-desaminodiketo – leached from the root zone (1 m b.g.s.) at average concentrations exceeding 0.1 µg/l at the sandy soil at Tylstrup. Both degradation products appear to be relatively stable and leached for a long period of time. Average concentrations reaching 0.1 µg/l were thus seen as much as three years after application. Evidence was also found that their degradation products might be present in the groundwater several years after application. At both sandy sites (Tylstrup and Jyndevad), previous application of metribuzin has caused marked groundwater contamination with its degradation products (see Kjær *et al.*, 2005b for details).
- Glyphosate was found to leach through the root zone at high average concentrations on • loamy soils. At the loamy sites Estrup and Silstrup, glyphosate leached from the root zone into the drainage water at average concentrations exceeding 0.1 µg/l. At Estrup its degradation product AMPA leached at an average concentration exceeding 0.1 µg/l. The leaching of glyphosate was mainly governed by pronounced macropore flow occurring within the first months after application. AMPA was frequently detected as long as two years after application. That leaching of AMPA occurs a relatively long time after application indicates that it can be retained within the soil and gradually released over a very long period of time. So far, marked leaching of AMPA and glyphosate has mainly been confined to the depth of the drainage system and they have rarely been detected in monitoring screens located below the depth of the drainage system. Glyphosate and AMPA were also detected in drainage water at the other loamy site, Faardrup (as well as at the now discontinued Slaeggerup site), but in low concentrations (Kjær et al., 2004). Evidence of glyphosate leaching was only seen in the loamy soil, and the leaching risk was negligible at the coarse, sandy soil site at Jyndevad. Infiltrating water passed through a matrix rich in aluminium and iron, thereby providing good conditions for sorption and degradation (see Kjær et al., 2004 and Kjær et al., 2005a for details).

Table 17. Pesticide leaching at the five PLAP sites. An asterisk indicates pesticides that have been included in the monitoring programme for less than two years. The colours indicate the degree of leaching and the letters H, F and I indicate the type of pesticide: herbicide, fungicide and insecticide respectively. Pesticides applied in spring 2004 are not included in the table.

Tylstrup	Jyndevad	Silstrup	Estrup	Faardrup
(Sandy soil)	(Sandy soil)	(Loamy soil)	(Loamy soil)	(Loamy soil)
		*		
			*	
	1)			
			*	
			*	
*	*			
*				
*				
	*			
		*		
		*		*
			2)	
	Tylstrup (Sandy soil)	Tylstrup (Sandy soil) Jyndevad (Sandy soil) Image: Sandy soil Image: Sandy soil Image: Sandy soil Image: Sandy soil </td <td>Tylstrup (Sandy soil) Jyndevad (Sandy soil) Silstrup (Loamy soil) * * *</td> <td>Tylstrup (Sandy soil)Jyndevad (Sandy soil)Silstrup (Loamy soil)Estrup (Loamy soil)***********************************</td>	Tylstrup (Sandy soil) Jyndevad (Sandy soil) Silstrup (Loamy soil) * * *	Tylstrup (Sandy soil)Jyndevad (Sandy soil)Silstrup (Loamy soil)Estrup (Loamy soil)***********************************

Derived from previous application (see Kjær *et al.*, 2002)
 Degradation products are not monitored (see text)

^b Degradation products are not monitored (see text)

Pesticide (or its degradation products) leached from the root zone (1 m b.g.s.) in average concentrations exceeding 0.1 μ g/l.

Pesticide (or its degradation product) was detected in either several (more than three) consecutive samples or in a single sample in concentrations exceeding $0.1 \mu g/l$; average concentration below $0.1 \mu g/l$

Pesticide either not detected or only detected in very few samples in concentrations below 0.1 μ g/l

I yistrup Jyndevad Silstrup Estrup	Faardrup
Bentazone $50(6.4)$ $54(0.73)$	
-AIBA 1(0.026)	
Ethofumesate $24(0.227) 34(3.362)$	45(12)
Glyphosate $0 69(4.7) 151(2.1)$	8(0.093)
-AMPA 3(0.022) 110(0.35) 176(0.83)	17(0.11)
Metamitron 69(0.551) 32(26.369)	35(1.7)
<i>- metamitron-desamino</i> 61(0.67) 27(5.549)	63(2.5)
Metribuzin 3(0.024)	
<i>- metribuzin-desamino-diketo</i> 312(2.1) 20(1.831)	
<i>- metribuzin-diketo</i> 527(0.69) 29(1.372)	
Pirimicarb 0 17(0.054) 40(0.077)	9(0.056)
- pirimicarb-desmethyl 0 $1(0.052)$ 0	9(0.053)
<i>- pirimicarb-desmethyl-formamido</i> 0 0 24(0.379)	5(0.076)
Rimsulfuron 0	
<i>- PPU</i> 44(0.21)	
- <i>PPU-desamido</i> 37(0.092)	
Terbutylazine 0 92(1.55)	
- desethylterbutylazine 28(0.056) 165(1.08)	
- desisopropylatrazine 35(0.047)*	
- 2-hydroxy-desethyl-terbutylazine 29(0.11)*	
- 2-hydroxy-terbutylazine 22(0.039)*	
Bromoxynil 0 3(0.6)	0
Dimethoate $0 0 2(1.417) 0$	0
$- ETU^l$ 9(0.038)	
Fenpropimorph 0 2(0.038) 0 1(0.01)	1(0.015)
- fenpropimorph-acid 0 0 $1(0.019)$ 0	0
Flamprop-M-isopropyl 0 13(0.109) 20(0.069)	1(0.037)
- flamprop (free acid) 7(0.096) 13(0.031)	1(0.089)
Fluazifop-P (free acid) ² $1(0.072)$	17(3.8)
Fluroxypyr	1(0.19)
Ioxynil 0 20(0.25)	2(0.011)
MCPA 0 12(3.894)	0
- 4-chlor-2-methylphenol 1(0.046)	0
Pendimethalin 0 0 $4(0.042)$	
Phenmedipham 0	2(0.025)
- MHPC 0	3(0.19)
$PHCP^3$ 0 18(2.69)	- ()
Propiconazole $0 0 6(0.033) 27(0.862)$	1(0.035)
Prosulfocarb 6(0.18)	0

Table 18. Number of samples in which the various pesticides were detected at each site with the maximum concentration $(\mu g/l)$ in parentheses. Degradation products are indicated in italics The table only encompasses those pesticides/degradation products detected in either several (more than three) consecutive samples or in a single sample in concentrations exceeding 0.1 µg/l. Pesticides applied in spring 2004 are not included.

¹⁾ Degradation product of mancozeb; ²⁾ Degradation product of fluazifop-P-butyl; ³⁾ Degradation product of pyridate;

*) Included in the monitoring at Silstrup from February 2003, eight months after application of terbutylazine.

- The degradation product of terbutylazine desethylterbutylazine also leached through the root zone at high average concentrations in loamy soils. At the loamy site Silstrup, desethylterbutylazine leached from the root zone into the drainage water at average concentrations exceeding 0.1 µg/l and was frequently detected in the monitoring screen situated beneath the drainage system. Apart from a few samples the concentrations here were all below 0.1 µg/l. Minor leaching of desethylterbutylazine was also seen at the sandy site Jyndevad, where desethylterbutylazine was frequently detected in low concentration (<0.1 µg/l) in the soil water sampled 1 m b.g.s. Desethylterbutylazine has not been detected in the groundwater monitoring screens located downstream of the Jyndevad test site (see Kjær *et al.*, 2004 for details).
- The degradation product of rimsulfuron PPU leached from the root zone (1 m b.g.s.) in average concentrations reaching 0.10–0.13 µg/l at the sandy soil site at Jyndevad. PPU has not been detected in the groundwater monitoring screens located downstream of the test site. It should be noted that the concentration of PPU is likely to be underestimated by 23–33% due to stability problems. Results from the field-spiked samples thus indicated that PPU is unstable and may have further degraded to PPU-desamido during subsequent storage and transport. The concentration was still elevated towards the end of the current monitoring period, thus indicating that leaching of the compound from the uppermost metre of the soil has not yet ceased.
- Ethofumesate, metamitron and its degradation product metamitron-desamino also leached through the root zone at high average concentrations in one loamy soil. At the loamy site Estrup, these compounds leached from the root zone into the drainage water at average concentrations exceeding 0.1 µg/l. Leaching has hitherto been confined to the depth of the drainage system, and the compounds have not been detected in deeper monitoring screens. The leaching risk cannot be fully evaluated until the 2005 monitoring data become available, i.e. when two years of monitoring data have been collated (Table 17). These compounds also leached from the root zone at Silstrup and Faardrup, reaching both drainage system and groundwater monitoring screens. Average concentrations in drainage water were not as high as at Estrup, although concentrations exceeding 0.1 µg/l were observed in both drainage system and groundwater monitoring screens. 2004 for details).
- Pirimicarb-desmethyl-formamido (degradation product of pirimicarb) also leached through the root zone at high average concentrations in one loamy soil. At the loamy site Estrup, this compound leached from the root zone into the drainage water at average concentrations exceeding 0.1 µg/l. Leaching has hitherto been confined to the depth of the drainage system, and pirimicarb-desmethyl-formamido has not been detected in deeper monitoring screens. The leaching risk cannot be fully evaluated until the 2005 monitoring data become available, i.e. when two years of monitoring data have been collated (Table 17). Similar high leaching of pirimicarb-demethyl-formamido has not been observed with any of the previous applications of pirimicarb at the five PLAP sites (Table 18 and Kjær *et al.*, 2004).

• Bentazone leached through the root zone at high average concentrations in loamy soils. Thus at the loamy site Silstrup, bentazone leached into the drainage water at average concentrations exceeding 0.1 μ g/l. Moreover, bentazone was frequently detected in the monitoring screen situated beneath the drainage system. Apart from a few samples the concentrations here were all below 0.1 μ g/l. The leaching risk cannot be fully evaluated until the 2005 monitoring data become available, i.e. when two years of monitoring data have been collated (Table 17).

The monitoring data also indicate leaching of a further 14 pesticides, but not in such high concentrations. Although the concentration exceeded 0.1 μ g/l in several samples, the average leaching concentration (1 m b.g.s.) did not. This is summarized in Table 18, which shows the number of samples in which the various pesticides were detected at each site and the maximum concentration. Apart from the sandy soil site at Tylstrup, where slight leaching of ETU was observed (Kjær *et al.*, 2002), leaching within this group of pesticides was only observed at the loamy soil sites, where leaching was associated with pronounced macropore transport resulting in very rapid movement of pesticides through the unsaturated zone.

Seven of the 29 pesticides applied – about 24% – did not leach during the monitoring period. This group includes the four different sulfonylureas – amidosulfuron, metsulfuron-methyl, triasulfuron and tribenuron methyl – that were applied at several sites. For example, tribenuron methyl was applied at four different sites under different hydrological conditions with percolation (1 m b.g.s.) during the first month after application ranging from 0 to 114 mm. The monitoring results provide no evidence of leaching of any of the applied compounds or their degradation products, including triazinamin and triazinamin-methyl. It should be noted, though, that the leaching risk associated with the late autumn application of tribenuron methyl has not yet been evaluated for the loamy soils. Moreover, the findings regarding amidosulfuron are of very limited use since its degradation products – with which the leaching risk is mainly associated – are not included as methods for their analysis are not yet available.

The difference between the five field sites is further illustrated in Figure 36, which shows the percentage of analysed samples containing one or more pesticides. At the sandy sites the predominant pesticides detected were the degradation products of metribuzin (Figure 36 A). Excluding these degradation products from the analysis (Tylstrup-II and Jyndevad-II) revealed that very few samples from Tylstrup contained other pesticides (Figure 36B). At Jyndevad the percentage of samples containing pesticides/degradation products was slightly higher due to the incipient leaching of desethylterbutylazine (degradation product of terbutylazine), PPU and PPU-desamido (degradation products of rimsulfuron).

The number of samples containing pesticides/degradation products tends to be higher at the loamy sites than at the sandy sites. At present, the differences between loamy and sandy soils are not necessarily due to the sandy soil being less vulnerable to pesticide leaching than the loamy soil, but should be seen in relation to differences in the pesticides applied to the different sites. Thus some of the pesticides that leached on the loamy soils have not yet been tested on the sandy soils (Table 17). The differences should also be seen in relation to the different ways of examining root zone leaching. At the loamy sites the drainage system provides frequent, integrated water samples that continuously capture water infiltrating

during the drainage season. This sampling procedure allowed all major storm events to be captured in separate samples (Appendix 2). At the sandy sites, in contrast, the use of groups of suction cups provides less frequent sampling in the form of discrete samples taken once a month and collected for analysis within a week.

Comparing the loamy sites, the number of samples containing pesticides/degradation products were markedly higher at Silstrup and Estrup than at Faardrup. This is largely attributable to the differences in the hydrological conditions, precipitation and subsequent infiltration being markedly higher at Silstrup and Estrup than at Faardrup (Figure 36B). Moreover, the amount of percolation occurring within the first month after application was generally higher at Silstrup and Estrup than at Faardrup (Table 8, Table 11 and Table 13).



Figure 36. A: Percentage of all analysed samples containing one or more pesticides. In Tylstrup-II and Jyndevad-II, metribuzin-diketo and metribuzin-desamino-diketo have been excluded from the analyses. B: Infiltration apportioned as estimated groundwater recharge and measured drainage runoff (loamy soils).

At the loamy sites, several pesticides were frequently detected in the drainage system, whereas the amount of pesticide reaching the monitoring screens situated beneath the drainage system is limited and varies considerably among the three sites (Figure 37). These differences should be seen in relation to the different sampling procedures applied. The drainage system provides frequent, integrated water samples that continuously capture water infiltrating during the drainage runoff season. On the other hand, the monitoring screens situated beneath the drainage systems were sampled less frequently (monthly basis from a limited number of the monitoring screens; Appendix 2). It should also be noted that the frequencies shown in Figure 37 are based on the entire monitoring period and the time that the different pesticides have been included in the programme, and the number of analysed samples thus vary considerably among the different pesticides.



Figure 37. Frequency of detection in samples from the drainage system (left) and groundwater monitoring screens located deeper than the drainage system (right) at the loamy soils Silstrup (A, B), Estrup (C, D) and Faardrup (E, F). Frequency is estimated for the entire monitoring period and the time that the different pesticides have been included in the programme and the number of analysed samples thus vary considerably among the different pesticides. The figure only includes the ten most frequently detected pesticides. Pesticides monitored for less than two years are indicated by an asterisk and pesticides monitored for less than one year are not included.

Nevertheless, evidence of pesticide leaching was frequently found in selected monitoring screens at Faardrup (Kjær *et al.*, 2003) and in particular at Silstrup, where the highest concentrations were detected. On the other hand, pesticide leaching at Estrup has hitherto mainly been confined to the depth of the drainage system. Apart from eight samples containing glyphosate, pesticides have only sporadically been detected in monitoring screens located deeper than the drainage system. Again, these differences are largely attributable to the hydrological conditions. The amount of leached pesticide leaving the system through drainage runoff is much higher at Estrup than for example at Silstrup, since the amount of percolation leaving the system through drainage runoff is far higher at Estrup than at Silstrup (Figure 36). Compared to Silstrup and Faardrup, moreover, the C horizon (situated beneath the drainage depth) at Estrup was less permeable with a lower degree of preferential flow occurring through macropores (Section 5.2.3). Water and solute transport may therefore be slower at Estrup, thereby allowing dispersion, dilution, sorption and degradation to reduce the deeper transport.

The occurrence of pesticides/degradation products in the monitoring screen was often related to rapid macropore transport occurring shortly after pesticide application. Evidence of a single rain event transporting applied pesticide to both the drainage system and the deeper-lying monitoring screens was observed at both Silstrup and Faardrup. In most cases the concentration decreased to a low level shortly thereafter, and low concentrations of pesticides were typically detected 2-12 months following pesticide application (example shown in Figure 38). Evidence of degradation products leaching beneath the drainage system over a long time period was also observed for mobile degradation products such as desethylterbutylazine. This is illustrated in Figure 39, which also shows the leaching pattern of AMPA for comparison. Both compounds leached over a long period of time at concentrations around 0.1 µg/l in the drainage water 1 m b.g.s. Desethylterbutylazine was continuously detected beneath the drainage system over a two-year period, while AMPA was only detected on a few occasions in much lower concentrations. These differences are probably attributable to the different sorption characteristics of the two compounds as the slower water transport that typically occurs beneath the drainage system probably promotes retention of the strongly sorbing compound AMPA, whereas the more weakly sorbing compound desethylterbutylazine will not be retained to the same extent.



Figure 38. Simulated percolation (secondary axis) together with the concentration of metamitron and terbutylazine (primary axis) in water sampled from the drainage system and monitoring screens at Silstrup. The green vertical lines indicate the dates of application. Open symbols indicate concentrations below the detection limit of 0.01 μ g/l.



Figure 39. Concentration of desethylterbutylazine and AMPA in water sampled from the drainage system and monitoring screens at Silstrup. The green vertical lines indicate the dates of application. Open symbols indicate concentrations below the detection limit of $0.01 \mu g/l$.

9 References

Allerup, P. and Madsen, H. (1979): Accuracy of point precipitation measurements. Danish Meteorological Institute, *Climatological Papers No. 5*, Copenhagen, 84 pp.

Aslyng, H. C. and Hansen, S. (1982): Water balance and crop production simulation. Hydrotechnical Laboratory, The Royal Veterinary and Agricultural University, Copenhagen, 200 pp.

Boesten, J. J. T. I. From laboratory to field: uses and limitations of pesticide behaviour models for the soil/plant system. *Weed Res.* 2000, *40*, 123–138.

Danish EPA (1997): Bekendtgørelse nr. 637 af 30. juni 1997, Miljø- og Energiministeriet 1997.

EEC (1971): Directive 71/250/EEC of 15 June 1971 establishing Community methods of analysis for the official control of feeding-stuffs, *Official Journal L 155, 12/07/1971 pp. 0013–0037.* Information is also available on: http://www.seas.upenn.edu/courses/belab/LabProjects/1997/BE210S97R4R01.htm

Funk, W, Dammann, V. and Donnevert, G. (1995): Quality assurance in analytical chemistry, VCH Verlagsgesellschaft GmbH, Weinheim.

Jarvis, N. J. (2000): The MACRO model (Version 4.2), Technical description. <u>ftp://www.mv.slu.se/macro/doc/MACRO42.doc</u>, Department of Soil Sciences, Swedish University of Agricultural Sciences, Uppsala, Sweden.

Jørgensen, L. F. (2005): Groundwater monitoring 2003, Geological Survey of Denmark and Greenland, December 2005. Available on: <u>www.grundvandsovervaagning.dk</u><a>www.grundvandsovervaagning.dk

Kjær, J., Ullum, M., Olsen, P., Sjelborg, P., Helweg, A., Mogensen, B., Plauborg, F., Jørgensen, J. O., Iversen, B. O., Fomsgaard, I. and Lindhardt, B. (2002): The Danish Pesticide Leaching Assessment Programme: Monitoring results, May 1999–July 2001, Geological Survey of Denmark and Greenland, 2002.

Kjær, J., Ullum, M., Olsen, P., Sjelborg, P., Helweg, A., Mogensen, B., Plauborg, F., Grant, R., Fomsgaard, I. and Brüsch, W. (2003): The Danish Pesticide Leaching Assessment Programme: Monitoring results, May 1999–July 2002, Geological Survey of Denmark and Greenland, 2003.

Kjær, J., Olsen, P., Barlebo, H. C., Juhler, R. K., Plauborg, F., Grant, R., Gudmundsson, L. and Brüsch, W. (2004): The Danish Pesticide Leaching Assessment Programme: Monitoring results, May 1999–July 2003, Geological Survey of Denmark and Greenland, 2004. Kjær, J., Olsen, P., Ullum, M. and Grant, R. (2005a): Leaching of glyphosate and aminomethylphosphonic acid from Danish agricultural field sites, J. Environmental Quality, 34, 608–630.

Kjær, J., Olsen, P., Henriksen, T. and Ullum, M. (2005b): Leaching of metribuzin metabolites and the associated contamination of a sandy Danish aquifer, Accepted for publication in ES&T.

Kördel, von W. (1997): Feldversuche zum Austrag von Pflanzenschutzmitteln über Drainage – Abschätzung der Belastung aquatischer Ökosysteme, *Gesunde Pflanzen, 49 (5): 163–170 (in German).*

Larsbo, M. and Jarvis, N. (2003): Macro 5.0. A model of water flow and solute transport in macroporous soil. Technical description. Swedish University of Agricultural Sciences, Department of Soil Sciences, Uppsala, pp. 52, http://www.mv.slu.se/bgf/.

Lindhardt, B., Abildtrup, C., Vosgerau, H., Olsen, P., Torp, S., Iversen, B.V., Jørgensen J. O., Plauborg, F., Rasmussen, P. and Gravesen, P. (2001): The Danish Pesticide Leaching Assessment Programme: Site characterization and monitoring design, Geological Survey of Denmark and Greenland, 2001.

Miller, J. N. and Miller, J. C. (2000): Statistics and chemometrics for analytical chemistry, Pearson, Essex.

Pedersen, C. Aa. (ed) (2004). Oversigt over Landsforsøgene: Forsøg og undersøgelser i de landøkonomiske foreninger. Dansk Landbrugsrådgivning, Landscentret, Planteavl. 395 pp.

Soil Survey Staff (1999): Soil Taxonomy. A basic system for soil classification for making and interpreting soil surveys, *Agricultural Handbook Number 436, Second Edition, United States Department of Agriculture, New York.*

U.S. Environmental Protection Agency (1998): Guidance for prospective groundwater monitoring studies. Environmental Fate and Effects Division, Office of Pesticide Programs, U.S. Environmental Protection Agency, September 16, 1998.

Wilson, A.L. (1970): The performance characteristics of analytical methods II, Talanta 17(1), 31–44.

Parameter	Systematic chemical nomenclature
AIBA*	2-amino-N-isopropyl-benzamid
AMPA	Amino-methylphosphonic acid
Amidosulfuron	N-[[[[(4,6-dimethoxy-2-pyrimidinyl)amino]carbonyl]-amino]sulfonyl]-N-
	methylmethanesulfonamide
Bentazone	3-(1-methylethyl)-1H-2,1,3-benzothiadiazin-4(3H)-one 2,2 dioxide
Bromoxynil	3,5-dibromo-4-hydroxybenzonitrile
Clomazone	2-[(2-chlorphenyl)methyl]-4,4-dimethyl-3-isoxazolidione
Desethylterbutylazine *	6-chloro-N-(1,1-dimethylethyl)-1,3,5,triazine-2,4-diamine
Desisopropylatrazine *	6-chloro-N-ethyl-1,3,5,triazine-2,4-diamine
Desmedipham	Ethyl 3-(phenylcarbamoyloxy)phenylcarbamate
Dimethoate	O,O-dimethyl S-methylcarbamoylmethyl-phosphorodithioate
EHPC^*	Ethyl 3-hydroxy-phenylcarbamate
Ethofumesate	(±)-2-ethoxy-2,3-dihydro-3,3-dimethylbenzofuran-5-yl-methanesulfonate
ETU*	Ethylenethiourea
Fenpropimorph	Cis-4-[3-[4-(1,1-dimethylethyl)-phenyl]-2-methylpropyl]-2,6-
	dimethylmorpholine
Fenpropimorphic acid*	Cis-4-[3-[4-(2-carboxypropyl)-phenyl]-2-methylpropyl]-2,6-
*	dimethylmorpholine
Flamprop (free acid)	N-benzoyl-N-(3-chloro-4-flourophenyl)-D-alanine
Flamprop-M-isopropyl	Isopropyl N-benzoyl-N-(3-chloro-4-flourophenyl)-D-alaninate
Fluazifop-P-butyl	Butyl (R)-2-[4-(5-trifuoromethyl-2-pyridyloxy)phenoxy]propionate
Fluazifop-P (free acid)*	(R)-2-[4-(5-trifluoromethyl-2-pyridyloxy)phenoxy]propanoic acid
Fluroxypyr	(4-amino-3,5-dichloro-6-fluro-2-pyridinyl)oxy]acetic acid
Glyphosate	N-(phosphonomethyl)glycine
Hydroxyterbutylazine*	6-hydroxy-N-(1,1-dimethylethyl)-N'-ethyl-1,3,5,triazine-2,4-diamine
Hydroxydesethylterbutylazine*	6-hydroxy-N-(1,1-dimethylethyl)-1,3,5,triazine-2,4-diamine
PPU-desamido*	N-((3-(ethylsulfonyl)-2-pyridyl)-4,6 dimethoxy-2 pyrimidinamine (IN70942)
PPU*	N-(4,6-dimethoxy-2-pyrimidinyl-N-((3-ethylsulfonyl)-2-pyridinyl)urea
Ioumil	(IN/0941) A hydroxy 2.5 dijodobonzonitrilo
Linuron	4-inydroxy-5,5-diloddobenzoniu ne 2 (2 4 dichlorophenyl) 1 methoxy 1 methylurea
	(4. alore 2. mathylphonoxyl)acatic acid
Metamitron	4 amino 4.5 dihydro 3 mathyl 6 nhanyl 1.2.4 triazin 5 ona
Metamitron desemine [*]	4 5 dibudro 3 mathyl 6 nhanyl 1.2.4 triazin 5 one
Metribuzin	4, J-uniyuro-J-memyi-o-phenyi-1,2,4-una2111-J-one
Metribuzin desemine dikete*	6 tert butyl 4.5 dibydro 3 methylthio 1.2.4 triazin 3.5 diana
wieu iouzin-desamino-diketo	0-1011-001191-4,3-01119010-5-111e011910110-1,2,4-01a2111-5,3-010fte

Table A1.1 Systematic chemical nomenclature for the pesticides and degradation products encompassed by the PLAP.

* Degradation product

Parameter	Systematic chemical nomenclature
Metribuzin-diketo*	4-amino-6-tert-butyl-4,5-dihydro-1,2,4-triazin-3,5-dione
Metsulfuron-methyl	Methyl2-[[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]=carbonyl]amino]-
	sulfonyl]benzoic acid
MHPC [*]	Methyl-N-(3-hydoxyphenyl)-carbamate
Pendimethalin	N-(1-ethyl)-2,6-dinitro-3,4-xynile
Phenmedipham	3-[(methoxycarbonyl)amino]phenyl (3-methylphenyl)carbamate
PHCP*	3-phenyl-4-hydroxy-6-chloropyridazine
Pirimicarb	2-(dimethylamino)-5,6-dimethyl-4-pyrimidinyldimethylcarbamate
Pirimicarb-desmethyl*	2-(dimethylamino)-5,6-dimethyl-4-pyrimidinylmethylcarbamate
Pirimicarb-desmethyl-	2-methylformamido-5,6-dimethylpyrimidine-4-yl dimethylcarbamate
formamido [*]	
Propanamide-clomazone*	(N-[2- chlorophenol)methyl] -3-hydroxy-2,2- dimethyl propanamide
Propiconazole	1-[[2-(2,4-dichlorophenyl)-4-propyl-1,3-dioxolan-2-yl]methyl]-1H-1,2,4-triazole
Rimsulfuron	N-[[(4,6-dimethoxy-2-pyrimidinyl)amino]carbonyl]-3-(ethylsulfonyl)-2-
	pyridinesulfonamide
Terbutylazine	6-chloro-N-(1,1-dimethylethyl)-N-ethyl-1,3,5,triazine-2,4-diamine
Triasulfuron	1-[2-(2-chloroethoxy)phenylsulfonyl]-2-(4-methoxy-6-methyl-1,3,5-triazin-2-yl)-urea
Triazinamin	4-methoxy-6-methyl-1,3,5-triazin-2-amin
Triazinamin-methyl*	1,3,5-triazin-2-2-amine 4-methoxy-N, 6-dimethyl

 Table A1.1 (continued)
 Systematic chemical nomenclature for the pesticides and degradation products encompassed by the PLAP.

* Degradation product

From each of the PLAP sites, samples were collected of groundwater, drainage water and soil water in the unsaturated zone. A full description of the monitoring design is provided in Lindhardt *et al.* (2001). The sampling procedures are briefly summarized below:

Groundwater samples are collected monthly from vertical and horizontal monitoring wells. To facilitate sample collection from the vertical monitoring wells, a whale pump was permanently installed in each screen. Sampling from the horizontal monitoring wells was performed using a peristaltic pump. At the two sandy sites (Tylstrup and Jyndevad), each well was purged by removing a volume of water equivalent to three times the volume of the saturated part of the well prior to water sampling. At the four clayey sites, the well was purged by emptying it the day before sampling.

Soil water samples are collected monthly using 16 Teflon suction cups each connected via a single length of PTFE tubing to a sampling bottle located in a refrigerator in the instrument shed. The soil water was extracted by applying a continuous vacuum (of about 0.8 bar) to each of the suction cups one week prior to sampling. The 16 suction cups were clustered in four groups installed 1 m b.g.s. and 2 m b.g.s. at locations S1 and S2. Each group of suction cups consists of four individual cups covering a horizontal distance of 2 m. The chemical analysis for each group was performed on a single, pooled water sample.

Drainage water samples are collected using ISCO 6700 samplers equipped with eight 1,800-ml glass bottles (boron silicate), teflon suction tubes and intakes of stainless steel. The intakes are located a few centimetres into the inlet of the drainpipe to ensure sampling of flowing drain water and particulate matter. Two samplers are used at each site – one for time-proportional sampling and one for flow-proportional sampling:

- The time-proportional sampler is equipped with seven refrigerated bottles such that the water samples can be collected over a 7-day period. Hence during the period of continuous drainage runoff, a 70-ml sample is collected every hour independent of flow rate. 24 samples are collected per bottle giving 1,680 ml per day. Pesticides and inorganic chemicals (Br, Cl, K, Ca, Mg, Mn, Na, NO₃, PO₄, total-N, PO₄, total-P, dissolved total-P and suspended matter) are then analysed on a weekly basis on a pooled sample derived from the seven bottles.
- The flow-proportional sampler is only activated during storm events and sampling is carried out for 1–2 days depending on the intensity of the event. Hence each flow event is activated by a predefined rise in water level/runoff within the preceding 12-hour period. Sampling is controlled by the flow rate, where collection of each sample is initiated when the accumulated flow rate exceeds a predefined level depending on the month of the year. Levels of predefined rise and accumulated flow rate are set/adjusted individually for each site by experience. Each sample volume is 200 ml yielding nine samples per bottle and a maximum of 72 samples per storm event. For each storm event, analysis of pesticides and inorganic chemicals (Br, Cl, K, NO₃, DOC, PO₄, total-N, PO₄, total-P, dissolved total-P and suspended matter) is performed on pooled water samples deriving from all seven bottles. In addition, tracer analysis (Br, Cl, Ca and K) is performed on additional water samples deriving from each of the seven individual bottles.

The weighted average concentration of pesticides in the drainage water was calculated according to the following equation:

$$C = \frac{\sum_{i=1}^{n} M_i}{\sum_{i=1}^{n} V_i}$$

 $M_i = Ct_i \cdot V_i$ If no flow event occurs within the *i*'te week $M_i = Cf_i \cdot Vf_i$ If a flow event occurs within the *i*'te week and if $Cf_i \cdot Vf_i > Ct_i \cdot V_i$

where:

n = Number of weeks within the period of continuous drainage runoff

V_i = Weekly accumulated drainage runoff (mm/week)

 Vf_i = Drainage runoff accumulated during a "flow event" (mm/storm event)

 Cf_i = Pesticide concentration in the "event samples" collected by means of the flow-proportional sampler (µg/l)

 Ct_i = Pesticide concentration in the weekly samples collected by means of the time-proportional sampler (µg/l)

The monitoring programme encompasses the analysis of both inorganic parameters and selected pesticides:

Inorganic analysis is performed monthly on water samples derived from all monitoring wells and from the suction cups located at 1 m b.g.s. and 2 m b.g.s. Br, Cl, K, Ca, NO₃, NO₂, PO₄, SO₄, pH and conductivity are measured monthly. Until March 2002, HCO₃, Fe, Mg, Mn, DOC, Na, NO₃, NO₂, PO₄, total-P, dissolved total-P, suspended matter and SO₄ were measured four times a year. At the loamy sites the inorganic analysis is also performed on drainage water samples.

Until March 2002, pesticide analysis was performed monthly on water samples from the suction cups located both 1 m b.g.s. and 2 m b.g.s., from two screens of the horizontal monitoring wells and from two of the downstream vertical monitoring wells. In addition, more intensive monitoring encompassing all four groups of suction cups, six screens of the horizontal monitoring wells and five monitoring wells was performed every fourth month (Kjær *et al.*, 2002). At the loamy sites, the pesticide analysis was also performed on drainage water samples. The monitoring programme was revised in March 2002 and the number of pesticide analyses was reduced. At the loamy sites, pesticide analysis of water sampled from the suction cups was ceased, and the monthly monitoring was restricted to just one monitoring well. At Jyndevad, pesticide analysis of the suction cups located 2 m b.g.s. was ceased and the interval for the intensive monitoring encompassing the larger number of monitoring screens was extended to six months except for the suction cups 2 m b.g.s. at Tylstrup, where the four-month interval was retained (Kjær *et al.*, 2004).

Date	Management practice
03.09.01	Winter rape sown – cultivar Artus
05.09.01	Herbicide – 0.25 l/ha Command CS (clomazone)
16.10.01	Herbicide – 1.0 l/ha Matrigon (clopyralid)
22.03.02	Fertilization – 155 kg N/ha, 20 kg P/ha and 72 kg K/ha
24.04.02	Irrigation – 24 mm/ha
16.05.02	Irrigation – 22 mm/ha
31.05.02	Irrigation – 34 mm/ha
27.07.02	Winter rape harvested (seed yield 25.9 hkg/ha; 91% dry matter)
12.08.02	Disk harrowed – 6 cm depth
19.09.02	Winter wheat sown – cultivar Solist
09.10.02	Herbicide – 3.0 l/ha Boxer EC (prosulfocarb) + 1.0 l/ha Oxitril (ioxynil+bromoxynil)
17.03.03	Tracer application – 30 kg/ha potassium bromide
17.03.03	Fertilization – 61.1 kg N/ha, 8.7 kg P/ha and 29.1 kg K/ha
08.05.03	Herbicide application – 0.8 l/ha Starane 180 (fluroxypyr)
13.05.03	Fertilization – 76.4 kg N/ha, 10.9 kg P/ha and 36.4 kg K/ha
15.05.03	Herbicide – 3.0 l/ha Barnon Plus (flamprop-m-isopropyl)
28.05.03	Fungicide – 0.25 l/ha Tilt 250 EC (propiconazole)
17.06.03	Fungicide – 0.25 l/ha Tilt 250 EC (propiconazole)
24.06.03	Irrigation – 23 mm/ha
08.07.03	Insecticide – 0.6 l/ha Perfekthion 500 S (dimethoate)
20.08.03	Winter wheat harvested (grain yield 54.5 hkg/ha, 85% dry matter. Straw yield 35.0 hkg/ha,
	100% dry matter)

Table A3.1 Management practice at Tylstrup during the 2002 and 2003 growing seasons. The active ingredients of the various pesticides are indicated in parentheses.

Table A3.2 Management practice at Jyndevad during the 2003 and 2004 growing seasons. The active ingredients of the various pesticides are indicated in parentheses.

Date	Management practice
01.04.02	Ploughed – 20 cm depth
20.04.02	Seed bed preparation – 15 cm depth
22.04.02	Potatoes planted – cultivar Oleva
13.05.02	Herbicide – 0.2 kg/ha Sencor WG (metribuzin)
23.05.02	Herbicide – 30 g/ha Titus (rimsulfuron)
01.06.02	Fertilization – 30 kg N/ha
13.06.02	Irrigation – 20 mm/ha
18.06.02-05.08.02	Eight fungicide applications – each comprising 0.2 l/ha Shirlan (fluazinam)
24.09.02	Potatoes harvested (tuber yield 515.8 hkg/ha; 23.0% dry matter)
01.10.02	Stubble harrowed – 12 cm depth
12.03.03	Tracer application – 30.0 kg/ha potassium bromide
07.04.03	Ploughed – 20 cm depth (furrow packed)
08.04.03	Fertilization – 128 kg N/ha, 19 kg P/ha and 64 kg K/ha
09.04.03	Spring barley sown – cultivar Otira
06.05.03	Herbicide – 0.020 kg/ha Ally (metsulfuron-methyl)
03.06.03	Herbicide – 2.0 l/ha Metaxon (MCPA)
06.06.03	Fungicide – 0.25 l/ha Tilt 250 EC (propiconazole)
07.06.03	Irrigation – 26 mm/ha
25.06.03	Insecticide – 0.6 l/ha Perfekthion 500 S (dimethoate)
25.06.03	Fungicide – 0.25 l/ha Tilt 250 EC (propiconazole)
04.08.03	Spring barley harvested (seed yield 73.3 hkg/ha; 85% dry matter. Straw yield 26.5
	hkg/ha; 100% dry matter)

Table A3.3 Management practice at Silstrup during the 2002, 2003 and 2004 growing seasons. The active ingredients of the various pesticides are indicated in parentheses.

Date	Management practice
25.04.02	Seedbed preparation – 8 cm depth
25.04.02	Maize sown – cultivar Loft
19.05.02	Herbicide – 1.5 l/ha Lido (terbutylazine + pyridate)
03.06.02	Herbicide – 1.5 l/ha Lido (terbutylazine + pyridate)
19.06.02	Herbicide – 1.5 l/ha Matrigon (clopyralid)
23.09.02	Maize harvested (total yield 134.3 hkg/ha; 100% dry matter. Left on field 27.5 hkg/ha in stubble)
08.10.02	Stubble harrowed – 5 cm depth
11.11.02	Ploughed – 24 cm depth
07.04.03	Fertilization – 8.7 kg P/ha and 45.4 kg K/ha
07.04.03	Seedbed preparation – 3 cm depth
14.04.03	Peas sowing – cultivar Attica
17.05.03	Herbicide – 1.0 l/ha Basagran 480 (bentazone) + 1.5 l/ha Stomp SC (pendimethalin)
10.08.03	Peas harvested (seed yield 39.8 hkg/ha; 86% dry matter. Straw yield 30.0 hkg/ha; 100% dry matter)
15.09.03	Herbicide – 4.0 l/ha Roundup Bio (glyphosate)
26.09.03	Ploughed
26.09.03	Winter wheat sown – cultivar Deben
29.10.03	Herbicide – 4.0 l/ha Boxer EC (prosulfocarb)
31.03.04	Fertilization 67.0 N, 8.5 P and 37.4 K kg/ha
10.05.04	Fertilization 100.1 N, 12.6 P and 55.9 K kg/ha
12.05.04	Herbicide – 2.0 l/ha Metaxon (MCPA)
14.06.04	Fungicide – 1.0 l/ha Amistar (azoxystrobin)
20.07.04	Insecticide – 0.25 kg/ha Pirimor G (pirimicarb)
23.08.04	Winter wheat harvested (grain yield 97.6 hkg/ha 85% dry matter, straw yield 40.8 hkg/ha 100% dry
	matter)

Table A3.4 Management practice at Estrup during the 2002 and 2003 growing seasons. The active ingredients of the various pesticides are indicated in parentheses.

Date	Management practice
19.10.01	Winter wheat sown – cultivar Ritmo
20.11.01	Herbicide – 1.0 l/ha Oxitril CM (ioxynil + bromoxynil)
22.03.02	Fertilization – 73.5 kg N/ha, 10.5 kg P/ha and 35 kg K/ha
24.04.02	Fertilization – 73.5 kg N/ha, 10.5 kg P/ha and 35 kg K/ha
25.04.02	Herbicide – 20 g/ha Gratil 75 WP (amidosulfuron)
13.05.02	Herbicide – 2.0 l/ha Metaxon (MCPA)
27.05.02	Fungicide – 0.25 l/ha Tilt 250 EC (propiconazole)
17.06.02	Fungicide – 0.25 l/ha Tilt 250 EC (propiconazole)
24.06.02	Insecticide – 0.25 kg/ha Pirimor G (pirimicarb)
09.08.02	Winter wheat harvested (grain yield 69.4 hkg/ha; 85% dry matter)
19.08.02	Straw removed (straw yield 41.4 hkg/ha; 100% dry matter)
02.09.02	Herbicide – 4.0 l/ha Roundup Bio
14.04.03	Cattle slurry - 60.8 tonnes/ha: 265.7 kg Total-N/ha, 60.2 kg P/ha, 266.3 kg K/ha and
	169.0 kg NH ₄ -N/ha
15.04.03	Ploughed -20 cm depth
16.04.03	Seedbed preparation – 5 cm depth
16.04.03	Fodder beet sown – cultivar Magnum,
08.05.03,	Herbicide - 1.0 l/ha Goltix SC700 + 1.0 l/ha Betanal Optima (metamitron, phenmedi-
22.05.03 & 16.06.03	pham, desmedipham and ethofumesate)
28.07.03	Insecticide – 0.3 kg/ha Pirimor G (pirimicarb)
22.10.03	Fodder beet harvested (root yield 18.95 t/ha and top yield 3.42 t/ha, 100% dry matter)
25.10.03	Ploughed – depth 20 cm

Date	Management practice
27.03.02	Fertilization – 95 kg N/ha, 13 kg P/ha and 35 kg K/ha
28.03.02	Spring barley sown – cultivar Barke
07.05.02	Herbicide – 15 g/ha Express (tribenuron methyl)
22.05.02	Herbicide – 2.0 l/ha Metaxon (MCPA)
25.05.02	Herbicide – 3.0 l/ha Barnon Plus (flamprop-M-isopropyl)
04.06.02	Insecticide – 0.4 l/ha Perfekthion 500 S (dimethoate)
04.06.02	Fungicide – 0.5 l/ha Tilt 250 EC (propiconazole)
09.08.02	Spring barley harvested (grain yield 65.6 hkg; 85% dry matter. Straw yield 60.2 hkg/ha;
	100% dry matter)
19.08.02	Ploughed – 25 cm depth
20.08.03	Fertilization – 30 N kg/ha
22.08.03	Winter rape sown – cultivar Canberra
23.08.03	Herbicide – 0.33 l/ha Command CS (clomazone)
25.09.02	Herbicide – 1.0 l/ha Matrigon (clopyralid)
24.03.03	Fertilization – 145 kg N/ha, 20 kg P/ha and 53 kg K/ha
24.04.03	Insecticide – 0.5 l/ha Fastac (alpha-cypermethin)
28.07.03	Winter rape harvested (seed yield 28.7 hkg/ha; 9% dry matter. Straw yield 38.9 hkg/ha;
	100% dry matter).
12.08.03	Rotary cultivated. Depth 5 cm
19.09.03	Ploughed and packed. Depth 25 cm
19.09.03	Winter wheat sown – cultivar Galicia
17.10.03	Herbicide – 4.0 l/ha Boxer (prosulfocarb)
29.03.04	Fertilization – 70.4 N, 9.6 P and 25.6 K kg/ha
30.04.04	Fertilization – 83.6 N, 11.4 P and 30.4 K kg/ha
03.06.04	Herbicide – 2.0 l/ha Metaxon (MCPA)
03.06.04	Fungicide – 1.0 l/ha Amistar (azoxystrobin)
07.09.04	Winter wheat harvested (grain yield 89.3 hkg/ha 85% dry matter. Straw yield 69.3 hkg/ha
	100% dry matter)

Table A3.5 Management practice at Faardrup during the 2002, 2003 and 2004 growing seasons. The active ingredients of the various pesticides are indicated in parentheses.

The MACRO model is a one-dimensional physically based numerical model for water flow and reactive solute transport in structured soils, Jarvis (2000). The model describes coupled unsaturated-saturated non-steady state water flow in cropped soils including lateral flow to field drains. The model is a dual-permeability model dividing the flow field into two separate domains: a high-conductivity/low porosity macropore domain is coupled to a lowconductivity/high porosity domain representing the soil matrix. Mass exchange between the domains is calculated with approximate, physically-based, first-order expressions. The model structure therefore enables quantitative evaluation of the impact of macropore flow on solute transport in structured soils. The model is further described in Larsbo and Jarvis (2003). A brief summary of some of the more important processes in the model is presented in Table 4A.1 (Larsbo and Jarvis, 2003).

Process	Treatment
Unsaturated water flow	Richards' equation in micropores, gravity flow in
	macropores
Root water uptake	Empirical sink term, water preferentially extracted
	from macropores
Seepage to drains and groundwater	Seepage potential theory. Sink term in vertical water
	flow equations
Solute transport	Convection/dispersion equation in the micropores,
	mass flow only in the macropores
Mass exchange	Approximate first-order rate equations for mass ex-
	change of both solute and water
Sorption	Instantaneous equilibrium/kinetic sorption according
	to the "two-site" model, Freundlich isotherm, sorption
	partitioned between micro- and macropores
Degradation	First-order kinetics, separate rate coefficients for four
	pools (solid and liquid, micro- and macropores)
Soil temperature	Heat conduction equation

Table A4.1 Treatment of flow and transport processes in the MACRO model.

The model has been applied to each of the five field sites, covering the soil profile to a depth of 5 m b.g.s. including the groundwater table at all times. Field and laboratory observed data on physical and hydraulic properties characterizing the sites were used as input to the model to the largest extent possible. Literature values were used for the remaining parameters, which primarily concerned the mass transfer coefficient and crop-related parameters.

Discretization: The soil profile is divided into 140 numerical increments covering the three (four at Estrup) main horizons described in the pedological profiles (Lindhardt *et al.*, 2001). The increment thickness range from 30 mm at the surface to 37 cm at the bottom of the profile. Each horizon is characterized by increments having the same soil hydraulic properties.

Meteorological data: The driving variables are daily precipitation, daily maximum and minimum temperatures and daily potential evapotranspiration. The precipitation is measured on site, whereas the temperature data is from DIAS meteorological stations, located 1–3 km from each test site. The potential evapotranspiration is calculated using a modified Makkink equation (Aslyng and Hansen, 1982). The potential evapotranspiration is defined as the evapotranspiration from well-growing short grass adequately supplied with water. Potential evapotranspiration and locally measured precipitation are listed in Appendix 5 on a monthly basis for the monitoring period July 2000 – June 2004.

Initial conditions: The initial conditions in terms of soil water content and soil temperature were assessed from previous simulations. A spin-up period of 5 years was applied before any results were evaluated, leaving the initial conditions less important.

Boundary conditions: The bottom boundary condition is an empirical approach where a deep percolation rate is given as a function of the water table height in the soil profile. This is the boundary condition allowing a fluctuating water table in the profile. The flow is controlled by an empirical coefficient, which seems to be related to the hydraulic conductivity of the soil. This parameter was assessed through calibration.

Dispersive properties: Solute transport parameters (e.g. diffusion coefficient, dispersivity and mixing depth) were initially set to the default values in the model. The parameters were determined through calibration.

Crop parameters: The parameters characterizing the crop development derive from the MACRO crop database available on http://viso.ei.jrc.it/focus/gw/index.html.

Agricultural management: Information about crop type, date of emergence, date of harvest and irrigation were registered at the five fields (Appendix 3). The bromide tracer was applied as an irrigation event with a known high concentration of bromide. The irrigation amount is calculated from the amount of bromide applied at the site and the measured concentration in the applied water.

Drainage parameters: The parameters characterizing the drainage system (drain depth and spacing) are specified for the tree clayey sites. According to Lindhardt *et al.* (2001) drain spacing ranges from 13 to 18 m. Typically the drain depth varies across the field, and it is therefore difficult to represent by one soil column. The drain depth is found by calibration with a resulting depth of 1 to 1.3 m b.g.s.

Soil hydraulic properties: In MACRO in the soil hydraulic properties (soil retention and unsaturated conductivity curves) of each horizon are described by two sets of equations representing the relationships in either the macropores or in matrix. For details on equations see Larsbo and Jarvis (2003).

Each site is represented by one soil column divided into 3–4 horizons. Measurements have been made on several soil samples from each horizon from 2–3 pedological profiles at the sites described in Lindhardt *et al.* (2001). From each horizon measured data on saturated water content, saturated hydraulic conductivity, and soil bulk density, are available. Spatial variability within the field is aggregated and accounted for in effective parameter values assessed from the measured data. In order to retrieve the remaining parameters for describing soil retention and unsaturated conductivity functions measured data of tension, unsaturated conductivity and soil water content were fitted with the parameter-estimating programme RETC (version 6.0). A major change between MACRO version 4.2 used in previous PLAP reports (Kjær *et al.*, 2003) and MACRO version 5.0 used in this report is that the soil retention function is now described by a modified van Genuchten function (Larsbo and Jarvis, 2003) instead of the Brooks and Corey formulation.

The total porosity is in MACRO partitioned into macropores and matrix at a user-defined "breakpoint" or "boundary" pressure head (ψ_b), while a corresponding water content (θ_b) and hydraulic conductivity (K_b) represent the saturated state of the soil matrix (see Figure **A4.1**). The "boundary" pressure head in each horizon was determined through fitting to the data. Measured data and parameterized curves of the hydraulic conductivity function and retention are illustrated in Figure A4.2–A4.6.

The tortuosity factor in matrix is set to 0.5, as suggested by the Mualem (1976) approach. The tortuosity factor/pore size distribution index in the macropores vary from 6 at the sandy soils (representing a soil with a wide macropore size distribution and large tortuosity) to 3-4 at the clayey sites, which have larger and well-structured macropore/fracture systems. The effective diffusion path length controlling the exchange of both water and solute between the two flow domains is determined through model calibration to field data.



Figure A4.1 Example of measured and modelled soil hydraulic conductivity and retention curves.



Figure A4.2 Measured (points) and fitted (solid line) retention and unsaturated conductivity curves in the A, B, and C horizon at Tylstrup. The points represent data from two pedological profiles. Each point in the retention curve represents an average of nine measurements, and error bars indicate their standard deviation.



Figure A4.3 Measured (points) and fitted (lines) retention (left) and unsaturated conductivity curves (right) in the A, B, and C horizon at Jyndevad. The points represent data from three pedological profiles. Each point in the retention curve represents an average of nine measurements, and error bars indicate their standard deviation.


Figure A4.4 Measured (points) and fitted (lines) retention (left) and unsaturated conductivity curves (right) in the A, B, and C horizon at Silstrup. The points represent data from two pedological profiles. Each point in the retention curve represents an average of nine measurements, and error bars indicate their standard deviation.



Figure A4.5 Measured (points) and fitted (lines) retention (left) and unsaturated conductivity curves (right) in the A, BE, Bt, and C horizon at Estrup. The points represent data from three pedological profiles. Each point in the retention curve represents an average of nine measurements, and error bars indicate their standard deviation.



Figure A4.6 Measured (points) and fitted (lines) retention (left) and unsaturated conductivity curves (right) in the A, B, and C horizon at Faardrup. The points represent data from three pedological profiles. Each point in the retention curve represents an average of nine measurements, and error bars indicate their standard deviation.



Figure A5.1. Monthly precipitation (A) and potential evapotranspiration (B) at Tylstrup for the monitoring period May 1999–June 2004. Normal values (1961–1990) compared to locally measured (precipitation) or calculated (evapotranspiration) values.



Figure A5.2. Monthly precipitation (A) and potential evapotranspiration (B) at Jyndevad for the monitoring period May 1999–June 2004. Normal values (1961–1990) compared to locally measured (precipitation) or calculated (evapotranspiration) values.



Figure A5.3. Monthly precipitation (A) and potential evapotranspiration (B) at Silstrup for the monitoring period April 2000–June 2004. Normal values (1961–1990) compared to locally measured (precipitation) or calculated (evapotranspiration) values.



Figure A5.4. Monthly precipitation (A) and potential evapotranspiration (B) at Estrup for the monitoring period June 2000–June 2004. Normal values (1961–1990) compared to locally measured (precipitation) or calculated (evapotranspiration) values.



Figure A5.5. Monthly precipitation (A) and potential evapotranspiration (B) at Faardrup for the monitoring period May 1999–June 2004. Prior to July 2002 precipitation measured at the nearby Flakkebjerg site was used instead of precipitation at Faardrup due to noise in the measurements. Normal values (1961–1990) compared to locally measured (precipitation) or calculated (evapotranspiration) values.

		Suction c	up S1 – 1 m b.g.s.	Suction	cup S2 – 1 m b.g.s.
Date	Perc. (mm)	PPU (µg/l)	PPU-desamido (µg/l)	PPU (µg/l)	PPU-desamido (µg/l)
t _i	Pi	Ci	Ci	Ci	Ci
30.04.02		< 0.01	< 0.01	< 0.01	< 0.01
29.05.02		< 0.01	< 0.01	< 0.01	< 0.01
03.07.02	100	0.022	< 0.01	0.028	< 0.01
06.08.02	33	0.058	0.071	< 0.01	0.041
03.09.02	41	0.21	0.04	0.17	< 0.01
01.10.02	44	0.096	0.044	0.023	0.092
29.10.02	215	0.16	0.037	0.048	< 0.01
03.12.02	70	0.18	0.031	0.075	0.025
08.01.03	79	0.17	0.043	0.086	< 0.01
05.02.03	51	0.16	0.03	0.096	< 0.01
04.03.03	13	0.12	0.026	0.09	< 0.01
02.04.03	0	0.11	0.033	0.11	0.026
06.05.03	2	0.088	0.036	0.11	0.036
03.06.03	1	0.12	0.036	0.11	0.022
16.07.03	1	0.11	0.044	0.14	0.051
22.08.03	1	0.14	0.03	0.2	0.053
16.09.03	0	0.1	0.03	0.048	0
26.10.03	31	0.12	0.04	0.15	0.041
17.11.03	38	0.12	0.03	0.1	0.026
17.12.03	54	0.11	0.043	0.073	0.031
23.01.04	160	0.13	0.042	0.064	0.034
17.02.04	119	0.084	0.044	0.096	0.044
16.03.04	20	0.11	0.035	0.12	0.038
13.04.04	30	0.15	0.034	0.23	0.047
21.05.04	11	0.16	0.036	0.25	0.053
15.06.04	2	0.1	0.043	0.19	0.062
1.7.02-30.6.03	648	0.13	0.03	0.06	<0.02
1.7.03-30.6.04	467	0.12	0.04	0.10	0.04

Table A6.1 Estimated percolation rate (Perc.) and measured concentration of PPU and PPU-desamido at Jyndevad. The estimated average concentrations for each monitoring period are also shown.

The average concentration of pesticides was estimated using the measured pesticide concentration and estimated percolation on a monthly basis. Pesticide concentrations measured in suction cups S1 and S2 were assumed to be representative for each sample period. Moreover, accumulated percolation rates deriving from the MACRO model were assumed to be representative for both suction cup S1 and suction cup S2. For each of the measured concentrations, the corresponding percolation (Perc.) was estimated according to the equation:

$$P_i = \sum\nolimits_{t_1}^{t_2} P_t$$

where

t = sampling date; $t_1 = 0.5(t_{i-1}+t_i)$; $t_2=0.5(t_i+t_{i+1})$ P_t = daily percolation at 1 m b.g.s. as estimated by the MACRO model (mm) The average concentration was estimated according to the equation:

$$C = \frac{\sum C_i \cdot P_i}{\sum P_i}$$

where C_i = measured pesticide concentration in the suction cups located 1 m b.g.s.



Figure A6.1 Comparison of the precipitation pattern for the current monitoring period (marked in red) and that for the preceding ten years (marked in black). The daily precipitation is compared in A, whereas the monthly precipitation in June and July is compared in B and C, respectively. Data from the monitoring period are marked in red. Data from the current monitoring period derive from the Jyndevad test site, whereas data from the preceding ten years derives from the DIAS meteorological station located less than 1 km from the test site. All data refer to precipitation corrected to the soil surface according to Allerup and Madsen (1979).

Table A7.1 Detection of glyphosate and AMPA in groundwater monitoring screens at Silstrup during the pe-
riod from 25.10.01 (date of first application) until 01.07.04 (µg/l). The location of the monitoring installations
is indicated in Figre 13. AMPA and glyphosate were not detected in water sampled from H2 (monitored
monthly) and M4, M6 and M9 (monitored half-yearly).

Monitoring well	$H1.2^1$	H1.3 ²		M5 ¹		M12 ²	M13 ²
Screen depth (m b.g.s.)	3.5	3.5	1.5-2.5	2.5-3.5	3.5-4.5	1.5-2.5	2.5-3.5
AMPA							
06.11.01	<		0.011	0.08	<		
04.12.01	<		<	0.01	<		
08.01.02	0.014		0.012	<	<		
05.02.02	<		<	<	<		
05.03.02	0.01		0.014	<	<		
14.01.03	<	0.011	0.019	<	<	0.012	<
04.02.03	<		0.01	<	<		
03.02.04	<	<	0.021	<	<		
Glyphosate							
09.10.01	<	<	<	<	<		
06.11.01	<		0.01	0.03	<		
04.12.01	<	<	<	0.01	<		
03.07.02	<	<	<	<	<	<	0.014

<: Concentration below the detection limit of 0.01 µg/l, ¹ Monitored monthly, ² Monitored half-yearly

Table A7.2 Detection of PHCP in groundwater monitoring screens at Silstrup during the period from 19.05.02 (date of first application) until 01.07.04 (μ g/l). The location of the monitoring installations is indicated in Figure 13. PHPC was not found in water sampled from H2 (monitored monthly) and M4, M6 and M12 (monitored half-yearly).

Monitoring well	H1.1 ²	H1.2 ¹	H1.3 ²		М	[5 ¹		M9 ²	M13 ²
Screen depth (m b.g.s.)	3.5	3.5	3.5	1.5-2.5	2.5-3.5	3.5-4.5	4.5-5.5	1.5-2.5	1.5-2.5
28.05.02		<		<	<	<			
03.07.02	0.042	0.035	<	0.309	0.197	0.091		0.048	0.041
05.08.02		<		0.11	0.059	0.121			
03.09.02		<			<	0.093			
02.10.02		<			<	0.054	0.059		
29.10.02		<		<	<	0.033			

<: Concentration below the detection limit of 0.01 µg/l, ¹ Monitored monthly, ² Monitored half-yearly

Table A7.3 Detection of bentazone in groundwater monitoring screens at Silstrup during the period from 17.05.03 (date of first application) until 01.07.04 (μ g/l). The location of the monitoring installations is indicated in Figure 13. Bentazone was not found in water sampled from H2 (monitored monthly) and M4, M6, M9, M12 and M13 (monitored half-yearly).

Monitoring well	H1.1 ²	H1.2 ¹	H1.3 ²		М	[5 ¹	
Screen depth (m b.g.s.)	3.5	3.5	3.5	1.5-2.5	2.5-3.5	3.5-4.5	4.5-5.5
03.06.03		<		0.056	0.038	<	
01.07.03		0.44		0.37	0.23	0.1	
05.08.03	0.035	0.081	<		0.048	0.099	
02.09.03		0.035			0.01	0.041	0.036
07.10.03		0.025			<	0.026	0.02
04.11.03		0.015			<	0.014	<

<: Concentration below the detection limit of 0.01 μ g/l, ¹ Monitored monthly, ² Monitored half-yearly

Table A7.4 Detection of desethylterbutylazine in groundwater monitoring screens at Silstrup during the period
from 19.05.02 (date of first application) until 01.07.04 (µg/l). The location of the monitoring installations is
indicated in Figure 13. Desethylterbutylazine was not found in water sampled from H2 (monitored monthly)
and M4, M6, M9, M12 and M13 (monitored half-yearly).

Monitoring well	H1.1 ²	H1.2 ¹	H1.3 ²		М	5 ¹		M9 ²
Screen depth (m b.g.s.)	3.5	3.5	3.5	1.5-2.5	2.5-3.5	3.5-4.5	4.5-5.5	1.5-2.5
28.05.02		<		<	<	<		
03.07.02	0.02	0.018	0.016	0.143	0.051	0.011		0.022
05.08.02		0.028		0.131	0.07	0.038		
03.09.02		0.015			0.05	0.045		
02.10.02		<			0.037	0.045	0.011	
29.10.02		0.026		0.062	0.046	0.043		
03.12.02		0.014		0.046	0.04	0.042		
14.01.03	0.012	0.011	0.013	0.075	0.042	0.045		0.019
04.02.03		0.029		0.064	0.048	0.043		
12.03.03		0.014		0.052	0.054	0.044		
01.04.03		0.017		0.067	0.047	0.047		
05.05.03		0.011		0.056	<	0.049		
03.06.03		0.015		0.066	<	0.051		
01.07.03		0.017		0.068	0.048	0.046		
05.08.03	0.012	0.01	0.011		0.044	0.049		0.021
02.09.03		<			0.038	0.048	0.031	
07.10.03		<			0.049	0.056	0.028	
04.11.03		<			0.034	0.043	0.017	
02.12.03		0.012		0.034	0.027	0.044		
07.01.04	0.013	0.011	0.014	0.032	0.026	0.032		0.01
03.02.04		0.011		0.015	0.033	0.026		
02.03.04		0.011		0.029	0.025	0.024		
30.03.04		0.011		0.032	0.024	0.02		
04.05.04		0.011		0.035	0.025	0.026		
02.06.04		0.012		0.045	0.028	0.032		

<: Concentration below the detection limit of 0.01 μ g/l, ¹ Monitored monthly, ² Monitored half-yearly

Table A7.5 Detection of terbutylazine in groundwater monitoring screens at Silstrup during the period from 19.05.02 (date of first application) until 01.07.04 (μ g/l). The location of the monitoring installations is indicated in Figure 13. Terbutylazine was not found in water sampled from H2 (monitored monthly) and M4, M6, M9, M12 and M13 (monitored half-yearly)

Monitoring well	H1.1 ²	$H1.2^1$	H1.3 ²		М	5 ¹		M9 ²
Screen depth (m b.g.s.)	3.5	3.5	3.5	1.5-2.5	2.5-3.5	3.5-4.5	4.5-5.5	1.5-2.5
28.05.02		<		<	<	<		
03.07.02	0.014	0.011	0.012	0.124	0.03			<
05.08.02		0.011		0.082	0.033			
03.09.02		<			0.022	0.01		
02.10.02		<			0.013	0.011	<	
29.10.02		<		0.025	0.014	<		
03.12.02		<		0.016	0.012	0.011		
14.01.03	<	<	<	0.025	0.011	0.01		<
04.02.03		0.012		0.022	0.014	0.01		
12.03.03		<		0.016	0.013	0.01		
01.04.03		<		0.019	0.01	0.01		
05.05.03		<		0.013	<	<		
03.06.03		<		0.02	0.012	0.012		
01.07.03		<		0.014	<	<		
05.08.03	<	<	<		<	<		<
02.09.03		<			<	<	<	
07.10.03		<			<	<	<	
04.11.03		<			<			
02.12.03		<		<	<	<		
07.01.04	<	<	<	<	<	<		<
03.02.04		<		<	<	<		
02.03.04		<		<	<	<		
30.03.04		<		<	<	<		
04.05.04		<		<	<	<		
02.06.04		<		<	<	<		

<: Concentration below the detection limit of 0.01 µg/l, ¹ Monitored monthly, ² Monitored half-yearly

Table A8.1 Detection of pesticides in groundwater monitoring screens at Estrup during the period from date of pesticide application until 01.07.04 (μ g/l). The location of the monitoring installations is indicated in Figure 23. None of these substances were found in water sampled from the other screens monitored, i.e. M1 and M4 (monitored half-yearly).

Monitoring well		H1.2 ¹	M1 ²	M3	M5 ¹	M5 ¹	M5 ¹	M1 ²	M6 ²
Screen depth (m b.g.s.)		3.5	3.5-4.5	1.5-2.5	2.5-3.5	3.5-4.5	4.5-5.5	1.5-2.5	2.5-3.5
Glyphosate	20.03.02					0.033			
	16.04.02					0.014	0.036		
	18.12.02					0.014	0.013		
	22.01.03								0.015
	19.02.03					0.011			
	13.01.04			0.017					
MCPA	14.05.02				0.019				
Pirimicarb	22.01.03		0.015						
Propiconazole	22.01.03		0.022					0.017	
Triazinamin	16.04.02				0.042				
AIBA	18.09.02	0.026							

¹ Monitored monthly; ² Monitored half-yearly



QA data: 2003-04 Lab 1 2-hydroxy-desethyl-terbuthylazine

Figure A9.1 Quality control data for pesticide analysis by laboratory 1. Internal laboratory control samples are indicated by square symbols and the nominal level is indicated by the solid grey line (*II* IQ measured, — IQ nominal concentration). External control samples are indicated by circles. Open circles indicate the nominal level (O EQ nominal low, O EQ nominal high), and closed circles the observed concentration (O EQ measured low, • EQ measured high).



Figure A9.1 (Continued) Quality control data for pesticide analysis by laboratory 1. <u>Internal laboratory</u> <u>control</u> samples are indicated by square symbols and the nominal level is indicated by the solid grey line (\exists IQ measured, — IQ nominal concentration). <u>External control</u> samples are indicated by circles. Open circles indicate the nominal level (\bigcirc EQ nominal low, \bigcirc EQ nominal high), and closed circles the observed concentration (\bullet EQ measured low, \bullet EQ measured high).

QA data: 2003-04 Lab 1 desisopropylatrazine



Figure A9.1 (Continued) Quality control data for pesticide analysis by laboratory 1. <u>Internal laboratory</u> <u>control</u> samples are indicated by square symbols and the nominal level is indicated by the solid grey line (\exists IQ measured, — IQ nominal concentration). <u>External control</u> samples are indicated by circles. Open circles indicate the nominal level (\bigcirc EQ nominal low, \bigcirc EQ nominal high), and closed circles the observed concentration (\bullet EQ measured low, \bullet EQ measured high).



Figure A9.2 Quality control data for pesticide analysis by laboratory 1. <u>Internal laboratory control</u> samples are indicated by square symbols and the nominal level is indicated by the solid grey line (# IQ measured, — IQ nominal concentration). <u>External control</u> samples are indicated by circles. Open circles indicate the nominal level (\bigcirc EQ nominal low, \bigcirc EQ nominal high), and closed circles the observed concentration (\bigcirc EQ measured high).



QA data: 2003-04 Lab 2 metamitron-desamino

Figure A9.2 (Continued) Quality control data for pesticide analysis by laboratory 1. <u>Internal laboratory control</u> samples are indicated by square symbols and the nominal level is indicated by the solid grey line (μ IQ measured, — IQ nominal concentration). <u>External control</u> samples are indicated by circles. Open circles indicate the nominal level (\bigcirc EQ nominal low, \bigcirc EQ nominal high), and closed circles the observed concentration (\bullet EQ measured low, \bullet EQ measured high).