The Danish Pesticide Leaching Assessment Programme

Monitoring results May 1999–June 2002 Third report

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Preface

In 1998, the Danish Government initiated the Danish Pesticide Leaching Assessment Programme (PLAP), an intensive monitoring programme aimed at evaluating the leaching risk of pesticides under field conditions. The first phase of the programme from 1998 to 2001 was funded by the Danish Government, while a two-year prolongation from 2002 to 2003 was funded by the Ministry of the Environment and the Ministry of Food, Agriculture and Fisheries.

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), Marlene Ullum (GEUS), Svend Elsnab Olesen (DIAS), Arne Helweg (DIAS), Ruth Grant (NERI), Betty Bügel Mogensen (NERI), Christian Ammitsøe (Danish Environmental Protection Agency) and Christian Deibjerg Hansen (Danish Environmental Protection Agency).

This report presents the results for the period May 1999–June 2002. Preliminary results covering part of the period (May 1999–June 2001) have been reported previously (Kjær *et al.*, 2002). The present report should therefore be seen as a continuation of that report, with the main focus on the monitoring period July 2001–June 2002.

The report was prepared jointly by Jeanne Kjær (GEUS), Marlene Ullum (GEUS), Preben Olsen (DIAS), Pia Sjelborg (DIAS), Arne Helweg (DIAS), Betty Bügel Mogensen (NERI), Finn Plauborg (DIAS), Ruth Grant (NERI), Inge S. Fomsgaard (DIAS) and Walter Brüsch (GEUS). While all authors contributed to the whole report, the aspects for which each author was mainly responsible are as follows:

- Pesticide and bromide leaching: Jeanne Kjær, Preben Olsen and Walter Brüsch
- Soil water dynamics and water balances: Marlene Ullum, Finn Plauborg and Ruth Grant
- Degradation and sorption parameters: Pia Sjelborg, Inge S. Fomsgaard and Arne Helweg
- Pesticide analysis quality assurance: Betty Bügel Mogensen.

Jeanne Kjær June 2003

Summary

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 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 at levels exceeding the maximum allowable concentration of $0.1 \mu g/l$.

The PLAP includes evaluation of the leaching risk of 27 pesticides at six agricultural sites (ranging from 1.1 to 2.4 ha) representing a wide range of Danish soil and climate conditions. The pesticides were all applied at the maximum permitted rate. Bromide tracer was applied early in the monitoring period and 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 for the six agricultural sites during the monitoring period May 1999–June 2002. The report is preliminary as the monitoring period is too short to fully evaluate the leaching risk of all applied pesticides. A more complete evaluation integrating the monitoring data with both sorption and degradation studies and modelling of pesticide transport will be made once a more comprehensive data set covering the entire leaching period of more pesticides becomes available. The results hitherto obtained preliminary findings are that:

- Nearly half of the applied pesticides (11 of 27) did not leach during the current monitoring period.
- The monitoring data indicate unacceptable leaching of two of the applied pesticides or their degradation products. Thus glyphosate and its degradation product AMPA and two degradation products of metribuzin leached from the root zone (1 m b.g.s.) in average concentrations exceeding the maximum allowable concentration of 0.1 μ g/l.
- At the two sandy sites, previous application of pesticides has caused marked groundwater contamination with degradation products of metribuzin. These appear to be relatively stable, and both leached throughout the entire monitoring period, thus indicating continuation of leaching as long as three years after application. There was evidence that the degradation products may persist in the groundwater several years after application.
- Finally, the monitoring data indicate leaching of a further 14 pesticides. The levels of leaching hitherto detected were not unacceptable, however. Although the concentration in several samples exceeded 0.1 μ g/l, the average concentration did not.

The monitoring data were supported by hydrological modelling (MACRO version 4.2) providing an overall water balance for each of the six sites. The model was parameterized using measured data or literature/default values, but has not yet been calibrated except for the sandy sites Tylstrup and Jyndevad. The uncalibrated models performed surprisingly well when comparing simulated and observed time series for groundwater table, soil water content and drainage flow. Sorption and degradation parameters were determined on various combinations of pesticides and soil types representative of the PLAP. The results suggest that:

- Microbial activity, sorption and degradation rates are low, as is generally the case in subsoil.
- Both degradation rates and sorption differed markedly between soils, thus stressing the importance of having site-specific parameters when modelling the leaching of pesticides.
- The degradation rates were in some cases better described by a two-compartment 1st + 1st order model than by the usual 1st order model. Degradation often encompasses an initial fast degradation rate with a short half-life followed by slower degradation rates with longer half-lives. An error is thus introduced if the simple 1st order half-life is used in the evaluation of pesticide persistence. Further analysis of the significance of the introduced error for risk assessment of pesticide leaching is thus required.

The quality of the pesticide analyses was evaluated continuously using an intensive quality assurance (QA) system. This consisted of internal control samples prepared by the analysis laboratory as part of their standard method of analysis and both blank and spiked samples prepared in the field and analysed in the laboratory together with the routine samples. The overall quality of the pesticide analysis was considered satisfactory:

- Reproducibility of the pesticide analyses was good, with standard deviation generally being in the range 0.003–0.025 μg/l.
- Reproducibility of the degradation products was slightly poorer than that of the mother compounds, standard deviation being 0.004–0.029µg/l.
- Recovery was generally good (>70%) in the case of spiked samples. Exceptions are fenpropimorph, desmedipham, glyphosate, phenmedipham and pirimicarb at single sites.
- Variation in recovery of the same compound in spiked samples from all field sites indicate uncertainties in analysis caused by differences in matrix composition.
- Contamination of samples rarely occurred during collection, storage and analysis.

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. Under the Danish National Groundwater Monitoring Programme (GRUMO), pesticides and their degradation products have so far been detected in 40% of all screens monitored (Jørgensen, 2002).

The increasing detection of pesticides in groundwater over the past 10 years has raised doubts as to the adequacy of the existing approval procedure for pesticides. 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 laboratory or lysimeter studies. However, these types of data may not suffice to adequately characterize the leaching that may occur under actual field conditions. A major limitation is that the 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 potentially may leach to the groundwater are required to be included in field studies as part of the registration procedure. Over the past decade 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 to the groundwater in unacceptable concentrations. The programme focuses on pesticides used in arable farming, and monitors leaching at six 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. The specific aim is to analyse whether pesticides applied in accordance with current regulations leach to the ground-water 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, 27 pesticides and 17 of their degradation products are included in the PLAP. All the compounds analysed are listed in Appendix 1. The reasons for selecting the specific pesticides are detailed in Lindhardt *et al.* (2001).

Soil type and climatic conditions are considered to be some of the most important parameters controlling pesticide leaching. The PLAP therefore encompasses six test sites representative of the dominant soil types and the climatic conditions in Denmark (Figure 1). The groundwater table at all six sites is shallow, thereby enabling a rapid groundwater response



Figure 1. Location of the six PLAP sites Tylstrup, Jyndevad, Silstrup, Estrup, Faardrup and Slaeggerup.

to pesticide leaching (Table 1). Cultivation of the PLAP sites is in line with conventional agricultural practices 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. During 1999, the six test sites were selected and established. Monitoring was initiated in 1999 at Tylstrup, Jyndevad and Faardrup, and in 2000 at Silstrup, Estrup and Slaeggerup (See Table 1).

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 2002. Preliminary results covering part of the monitoring period (May 1999–June 2001) have been published previously (Kjær *et al.*, 2002). The present report should therefore be seen as a continuation of the latter report, with the main focus on the last year of the monitoring period (July 2001–June 2002). For detailed description of the first part of the monitoring period (May 1999–June 2001), see Kjær *et al.* (2001) and Kjær *et al.* (2002).

	Tylstrup	Jyndevad	Silstrup	Estrup	Faardrup	Slaeggerup
Location	Brønderslev	Tinglev	Thisted	Vejen	Slagelse	Roskilde
Precipitation ¹⁾ (mm/y)	668	858	866	862	558	585
Pot. evapotransp. ¹⁾ (mm/y)	552	555	564	543	585	572
W x L (m)	70 x 166	135 x 184	91 x 185	105 x 120	150 x 160	130 x 165
Area (ha)	1.1	2.4	1.7	1.3	2.3	2.2
Tile drain	No	No	Yes	Yes	Yes	Yes
Monitoring initiated	May 1999	Sep 1999	Apr 2000	Apr 2000	Sep 1999	Apr 2000
Geological characteristics						
- Deposited by	Saltwater	Meltwater	Glacier	Glacier/meltwater	Glacier	Glacier
– Sediment type – DGU symbol	Fine sand YS	Coarse sand TS	Clayey till ML	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	5-9	1.3	$1-4^{(2)}$	1.5	0.7
matrix (m b.g.s.)	>12	10-12	5	>3 *	4.2	3.7
– Max. fracture depth $^{3)}(m)$	-	-	4	>6.5	8	4.7
 Fracture intensity 3–4 m depth (fractures m⁻¹) Ks in C horizon (m/s) 	- 2 0·10 ⁻⁵	_ 1 3·10 ⁻⁴	<1 3 4·10 ⁻⁶	11 8 0·10 ⁻⁸	4 7 2·10 ⁻⁶	11 3 1·10 ⁻⁶
Topsoil characteristics	2.0 10	1.0 10	0.1.10	0.0 10	,. <u> </u>	0.1 10
– DK classification	JB2	JB1	JB7	JB5/6	JB5/6	JB7
- Classification	Loamy sand	Sand	Sandy clay loam/	Sandy loam	Sandy loam	Loam/ sandy loam
- Clay content (%)	6	5	18–26	10-20	14–15	20–24
- Silt content (%)	13	4	27	20-27	25	25-33
- Sand content (%)	78	88	8	50-65	57	41–54
– pH	4-4.5	5.6-6.2	6.7–7	6.5-7.8	6.4–6.6	6-6.3
– TOC (%)	2.0	1.8	2.2	1.7-7.3	1.4	1.4

Table 1. Characteristics of the six PLAP sites (modified from Lindhardt et al., 2001).

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

Within the PLAP, the evaluation of pesticide leaching risk is based upon 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. A more complete evaluation of the data, including model simulation of the pesticide transport and transformation processes, will thus be made once a more comprehensive data set covering the entire leaching period becomes available.

Hydrological modelling of the unsaturated zone at each PLAP site supported the monitoring data. The MACRO model (version 4.2) was used to describe the soil water dynamics at each site during the full monitoring period July 1999–June 2002. In addition, bromide transport was simulated at the two sandy sites Tylstrup and Jyndevad.

The risk of pesticide leaching is highly dependent on the degradation and sorption processes occurring in the root zone. To improve interpretation of the data, sorption and degradation studies have been conducted on selected combinations of pesticides and soil types representative of the PLAP. The methodology and results are presented in Section 8.

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 9.

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

The 1999 crop was potato for starch production. The cultivar used was Dianella, which is a commonly used variety. During the growing season the field was sprayed with the herbicides linuron and metribuzin and with the fungicide mancozeb. Potassium bromide tracer was applied on 27 May. The potatoes were harvested on 20 October. The yield of tubers was 475 hkg/ha (24% dry matter), which is somewhat less than the average for the location. During the autumn of 1999 the field was disc harrowed several times in order to reduce problems of waste potatoes in the subsequent crop.

The 2000 crop was spring barley (cv. Bartok), which emerged on 10 April. On 13 May, when the crop had 3 tillers, it was sprayed with the herbicide triasulfuron. Stem elongation and heading began in mid May and June, respectively. Combined fungicide and insecticide spraying was carried out on 19 June, in the middle of heading, using propiconazole, fenpropimorph and pirimicarb. The crop was harvested on 21 August yielding 73.3 hkg/ha of grain (85% dry matter) – somewhat above the average for that year and location.

The 2001 crop was winter rye (cv. Dominator), which emerged on 7 October. On 2 November, when the crop had 2 leaves, it was sprayed with the herbicides tribenuron methyl and pendimethalin. Spraying of fungus was done twice on 14 May and 13 June using propiconazole and fenpropimorph. At harvest on 28 August the grain yield was 63.6 hkg/ha. The winter rye was harvested later than usual due to rainy conditions in August.

The 2002 crop was winter rape (cv. Artus). Due to the rainy conditions in August, sowing had to be postponed until the 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. 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 the 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. Management practice at the site is detailed in Appendix 3, Table A3.1.



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).



Figure 3. NE-SW cross section based on wells at the Tylstrup site (Lindhardt *et al.*, 2001). The location of the wells is indicated in Figure 2.

2.1.3 Model set-up and calibration

The MACRO model was 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 was used to simulate the water and bromide transport in the unsaturated zone during the full monitoring period May 1999–June 2002.

The model was calibrated to the observed groundwater table measured in the piezometers located in the buffer zone, as well as to measured time series of soil water content at three different depths (25, 60 and 110 cm b.g.s.) from the two profiles S1 and S2 (see Figure 13) and to the bromide concentration measured in the suction cups located 1 and 2 m b.g.s. The calibration procedure involved adjustment of the empirical BGRAD parameter regulating the boundary flow and selected crop and hydraulic parameters. The parameter ASCALE, which is related to the solute exchange between matrix and macropores, was also calibrated, but this had very little effect on the results. Dispersive parameters were not adjusted. For a detailed description of data acquisition, model set-up and calibration procedures, see Kjær *et al.* (2002).

In recent years there has been some discussion in Denmark regarding field and catchment scale water balance calculations following several investigations that revealed problems with the water balance. Plauborg *et al.* (2002) examined the problem focussing on precipitation correction factors and calculation of potential evapotranspiration. Based on their recommendations, we made a thorough analysis of the precipitation correction factors used in the PLAP. It was concluded that the precipitation correction factors suggested by Allerup and Madsen (1979) were the most representative for the rain gauges at the PLAP sites. The precipitation corrections applied in Kjær *et al.* (2002) were therefore replaced by the monthly corrections of Allerup and Madsen (1979). These changes slightly increased the precipitation input, resulting in minor changes in the water balance as compared to the 2001 PLAP report.

2.2 Results and discussion

2.2.1 Soil water dynamics and water balances

In general the model simulations were consistent with the observed data, thus indicating a good model description of the overall soil water dynamics in the unsaturated zone. The calibrated model provides a good simulation of the measured fluctuations in the groundwater table. The dynamics is captured, whereas the amplitude of the fluctuations is less well described. The overall trends in soil water content could be modelled successfully, with the model capturing soil water dynamics at all depths (Figure 4E).

An annual water balance is determined for each monitoring year (July to June; Table 2). Because monitoring at the Tylstrup site was initiated in May 1999, the two months preceding the monitoring year are included as a separate period.



Figure 4. Soil water dynamics at Tylstrup: Locally measured precipitation 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 2).

	Normal Precipitation ²⁾	Precipitation	Irrigation	Actual evapotranspiration	Groundwater recharge ³⁾
1.5.99–30.6.99 ¹⁾	120	269	0	123	145
1.7.99-30.6.00	773	1073	33	511	595
1.7.00-30.6.01	773	891	75	486	479
1.7.01-30.6.02	773	906	80	550	436

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

All 3 monitoring periods (July–June) were wet at Tylstrup, with precipitation input exceeding the yearly normal by 15–39%. Except for the first exceptionally wet year, the precipitation input was counterbalanced by the actual evapotranspiration during the summer months (Figure 4A). Generally, percolation 1 m b.g.s is continuous from September to May.

2.2.2 Bromide leaching

In the unsaturated zone the breakthrough of bromide at 1 m b.g.s. started in August 1999, three months after application. The bromide concentration peaked in September, and the leaching continued throughout the whole winter period until March 2000 (Figure 5). As expected, the breakthrough of bromide at 2 m b.g.s. was delayed by a few months, and the concentration profile at this depth was somewhat wider due to hydrodynamic dispersion.

The model is generally able to satisfactorily simulate the bromide transport, and hence also the percolation. In terms of timing and concentration level of the breakthrough curves the bromide transport was well captured by the model. The simulated breakthrough at 1 m b.g.s. is initiated too soon, however. Attempts have been made to delay this initial breakthrough, but without success. The accelerated breakthrough is probably due to the wet months of May and June 1999, and resultant overestimation of percolation deeper than 1 m b.g.s. and therefore of transport of the bromide to this depth. At 1 m b.g.s. bromide is detected 2–3 months longer than simulated by the model. Improved modelling of the latter would necessitate thorough calibration of the dispersivity and mixing layer. The pulse at 2 m b.g.s. is very well described.

A mass balance for the applied bromide tracer based on daily, simulated values of water flux and bromide concentration revealed that by the end of December 1999, 99% of the applied bromide had leached from the root zone (1 m b.g.s.). Considering the measured bromide concentrations (Figure 5), the tail of the main pulse continued throughout January and February 2000, and small amounts of bromide continued to leach as late as autumn 2000. These findings indicate that a minor part of the bromide had diffused into less accessible pore water, which cannot be described by the MACRO model. The overall conclusion, though, is that the applied bromide leached out of the root zone (1 m b.g.s.) within a year of application.

In the saturated zone, marked breakthrough of bromide was detected in all downstream monitoring wells, although the temporal evolution varied markedly within the various monitoring wells (Figure 6). A rapid breakthrough of bromide occurred in monitoring well M4, where an elevated bromide concentration was detected just 6 months after application.



Figure 5. Simulated (solid line) and measured (crosses) 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 line indicates the date of bromide application.

The breakthrough in the other monitoring wells occurred much later, thus indicating a much slower bromide transport, especially in the northern part of the field site. The bromide transport to M2 was thus delayed about a year as compared to M4 (Figure 6). The difference between the various monitoring wells demonstrates the marked heterogeneity within the test field. Silt lenses identified in the northern part of the area probably cause heterogeneous water flow (Kjær *et al.*, 2002; Lindhardt *et al.*, 2001). Slightly elevated bromide concentrations were detected in monitoring well M1. As M1 is located about 3 m upstream of the treated area, the tracer bromide was not expected to reach it. However, the silt lenses might have deflected the vertical transport through the unsaturated zone, enabling bromide to reach this upstream monitoring well.

During the 3-year monitoring period the majority of the applied bromide seems to have passed the downstream monitoring wells. Other than at M2, decreasing bromide concentrations were observed at the end of the monitoring period in all the downstream monitoring wells. The overall transport time from field application until the majority of the bromide has passed the monitoring wells ranges from 1.5 to 3 years in M4, M3 and M5, respectively.

Bromide concentration measured 6–7, 7–8 and 8–9 m b.g.s. derives from three additional screens installed near M4 and M5 in August 2001 (Figure 6). Finally, it should be noted that based on the bromide concentration detected during the period 1 May 1999–1 November 1999, the background concentration of bromide at Tylstrup was 0.23 ± 0.06 mg/l.



Figure 6. 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 line indicates the date of bromide application.

2.2.3 Pesticide leaching

At Tylstrup, the monitoring encompassed 11 different pesticides and several degradation products applied throughout four growing seasons as indicated in Table 3 and Figure 7. 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 mother compounds that are monitored in the PLAP (Table 3).

Table 3. Pesticides analysed at Tylstrup with the product used shown in parentheses. Degradation products are in italics. Precipitation and percolation are accumulated from the date of first application (App. date) until 1 July 2002. 1^{st} month percolation refers to accumulated percolation within the first month after application. C_{mean} refers to average leachate concentration at 1 m b.g.s. The number of pesticide-positive samples is indicated in parentheses.

Crop and analysed pesticides	App. date	Precipitation	Percolation	1 st month percolation	C_{mean}
Potatoes 1999		(11111)	(11111)	(11111)	(µg/1)
Linuron (Afalon)	May 99	2527 ¹⁾	1208 ¹⁾	81	< 0.01 (0)
- ETU^{2} (Dithane DG)	Jun 99	2358 ¹⁾	1129 ¹⁾	66	< 0.01(8)
Metribuzin (Sencor WG) - metribuzin-diketo - metribuzin-desamino - metribuzin-desamino-diketo	Jun 99	3258	1621	80	$\begin{array}{c} < 0.01 \ (3) \\ 0.05 - 0.27^* \ (352) \\ < 0.02 \ (0) \\ 0.14 - 0.97^* \ (238) \end{array}$
Spring barley 2000					
Triasulfuron (Logran 20 WG) - <i>triazinamin</i>	May 00	2100	907	7	<0.01 (0) <0.01 (0)
Propiconazole (Tilt Top)	Jun 00	1983	891	13	< 0.01 (0)
Fenpropimorph (Tilt Top) - <i>fenpropimorphic acid</i>	Jun 00	1983	891	13	<0.01 (0) <0.01 (0)
Pirimicarb (Pirimor G) - pirimicarb-desmethyl - pirimicarb-desmethyl-for- mamido	Jun 00	1982	889	19	<0.01 (0) <0.01 (0) <0.01 (0)
Winter rye 2001					
Pendimethalin (Stomp SC) <i>Triazinamin-methyl³⁾</i> (Express) Propiconazole (Tilt Top) Fenpropimorph (Tilt Top) - fenpropimorphic acid	Nov 00 Nov 00 May 01 May 01	1631 1631 1182 1182	839 839 461 461	114 114 18 18	$\begin{array}{c} < 0.01 \ (0) \\ < 0.01 \ (0) \\ < 0.01 \ (0) \\ < 0.01 \ (0) \\ < 0.01 \ (0) \end{array}$
Winter rape 2002 Clomazone (Command CS) - propanamide-clomazone Clopyralid (Matrigon)	Sep 01 Oct 01	834 696	428 397	13 35	<0.01 (0) <0.01 (0) <0.01 (2)

Chemical Abstracts nomenclature for the analysed pesticides is given in Appendix 1

¹⁾ Accumulated from date of application until monitoring ceased on 1 July 2001(ETU) or 1 October 2001(linuron)

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

³⁾ Degradation product of tribenuron methyl. The parent compound degrades too rapidly to be detected by monitoring

*) Average concentration refers to the first year after application (See text for further explanation)



Figure 7. Pesticide application, precipitation and irrigation (primary axis) together with simulated percolation 1 m b.g.s. (secondary axis) at Tylstrup. Pesticides applied later than April 2002 are not included.

The leaching risk of pendimethalin, triazinamin-methyl (degradation product of tribenuron methyl), clomazone and clopyralid, which were applied in 2001/2002, will not be evaluated until the 2003 monitoring results become available, i.e. when two years of monitoring data have been collated. It should be noted, though, that apart from two samples containing 0.016 and 0.72 μ g/l of clomazone, none of these three pesticides or their degradation products listed in Table 3 have yet been detected in any of the water samples analysed.

None of the pesticides triasulfuron, pirimicarb, propiconazole, fenpropimorph or their degradation products listed in Table 3 were detected in any of the water samples. All the pesticides were applied in summer 2000, during which time precipitation input was close to normal and was almost counterbalanced by actual evapotranspiration, resulting in little percolation during the first month after application (Figure 7 and Table 3). Monitoring of propiconazole and fenpropimorph has not yet been completed, however, but will continue throughout the next monitoring period, thereby providing two years of monitoring data for evaluation of both applications.

With ETU (degradation product of mancozeb) and linuron, the leaching risk was found to be negligible at the Tylstrup site. Linuron was not detected in any of the water samples, whereas ETU was detected in just six samples taken from the unsaturated zone (Kjær *et al.*, 2001) and two samples from the saturated zone in concentrations of 0.02 μ g/l. For further information see Kjær *et al.* (2002).

Metribuzin was only detected in concentrations of $0.01-0.02 \ \mu g/l$ in three water samples. However, two degradation products of metribuzin leached from the root zone (1 m b.g.s.) in average concentrations exceeding 0.1 $\mu g/l$. Leaching was most pronounced with metribuzin-desamino-diketo, reaching an annual average concentration of 0.9 $\mu g/l$ in suction cup S1. Metribuzin-diketo, the other degradation product of metribuzin, also leached, in this case reaching an average concentration of 0.3 $\mu g/l$. Both compounds leached throughout the entire monitoring period, and average concentrations exceeding 0.1 $\mu g/l$ were detected as long as three years after application. Over the 3-year period as much as 11-13% and 4-6% of the applied dosage leached as metribuzin-desamino-diketo and metribuzin-diketo, respectively (Table 4 and Figure 8).

	Metribuzin-	desamino-diketo	Metribuzin-diketo		
	Suction cup – S1	Suction cup – S2	Suction cup – S1	Suction cup – S2	
1.7.99-30.6.00	0.87—0.97	0.14-0.27	0.26-0.36	0.05-0.11	
1.7.00-30.6.01	0.33	0.33	0.13	0.12	
1.7.01-30.6.02	0.06	0.19	0.11	0.09	
Leached mass ¹⁾	13%	11%	6%	4%	

Table 4. Estimated average concentration (μ g/l) of metribuzin-desamino-diketo and metribuzin-diketo 1 m b.g.s. at Tylstrup. Leached mass refers to the total mass (% of applied metribuzin) leached during the entire monitoring period (1.7.99–30.6.02). The primary data are given in Appendix 5.

¹⁾ Expressed as metribuzin equivalent



Figure 8. Bromide and pesticide concentrations 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 red vertical line indicates the date of bromide application.

The average concentration of pesticides (Table 4) was estimated using the measured pesticide concentration and estimated percolation on a monthly basis. Measured pesticide concentrations were thus assumed to be representative for each sample period, and accumulated percolation rates calculated using the MACRO model were assumed to be representative for both suction cups S1 and S2. It should also be noted that for 1999/2000 the average concentration is given as a range due to the high level of uncertainty that characterized the first analyses in 1999. The primary data and further information concerning the calculation methods are given in Appendix 5.

In the saturated zone, elevated concentrations of metribuzin-diketo were detected in M1, M3 and M4, while the pesticide concentration in the other wells (M5, M6) could not be distinguished from the background level (Figure 9– Figure 11). At Tylstrup, pesticide application prior to the monitoring period has thus resulted in marked groundwater contamination with the degradation products of metribuzin.

Evidence of previous contamination is provided by the initial screening analysis. The degradation products were present in the groundwater before the monitoring started in May 1999 (Kjær *et al.*, 2002). In M3 and M5, both degradation products were detected long before the bromide had reached the monitoring wells. Bromide was not detected in M6, and the marked contamination was thus due to prior application of the pesticide on the neighbouring field located just south of the test site or on the fields located upstream of M6 (Kjær *et al.*, 2002). The two degradation products of metribuzin were also detected in M1. In view of the slightly elevated bromide concentration detected in M1 (Section 2.2.2), part of the water infiltrating the test site might reach M1. Moreover, metribuzin was applied to the neighbouring field located upstream of the test site in 1999 concomitantly with application on the test site. The elevated concentration of degradation products detected in M1 may thus derive from the test site or the upstream neighbouring field. Previous application of pesticides at the test site and neighbouring upstream fields is detailed in Kjær *et al.* (2002).

The high background concentration found in all monitoring wells makes it difficult to determine whether the elevated concentrations observed in downstream monitoring wells are due to the metribuzin applied during the PLAP or to metribuzin applied on the test site or on the "upstream" fields prior to the PLAP. Consequently it is not possible to fully verify the impact of the metribuzin applied during the PLAP on the quality of the groundwater. It should be noted, though, that the average concentration of metribuzin-diketo in the Tylstrup groundwater was 0.15 µg/l, and that the average concentration exceeded the maximum allowable concentration (0.1 µg/l) at 81% of the screens analysed. High concentrations were also detected in the deep screens installed in August 2001 near M4 and M5 (Section 2.2.1). In fact, the average concentration in the deepest screen located 8–9 m b.g.s. was 0.32 µg/l in M4 and 0.22 µg/l in M5 (Figure 10–Figure 11).

Metribuzin-desamino-diketo was also detected in 57% of the analysed groundwater samples. Apart from one sample reaching 0.14 μ g/l concentrations never exceeded 0.1 μ g/l.



Figure 9. Bromide and pesticide concentrations in the groundwater at Tylstrup. The data derive from monitoring wells M1 (A,B,C) and M3 (D,E,F). Screen depth is indicated in m b.g.s. The green vertical line indicates the date of application.



Figure 10. Bromide and pesticide concentrations in the groundwater at Tylstrup. The data derive from monitoring well M4. Screen depth is indicated in m b.g.s. The green vertical line indicates the date of application.



Figure 11. Bromide and pesticide concentrations in the groundwater at Tylstrup. The data derive from monitoring well M5. Screen depth is indicated in m b.g.s. The green vertical line indicates the date of application.



Figure 12. Bromide and pesticide concentrations in the groundwater at Tylstrup. The data derive from monitoring well M6. Screen depth is indicated in m b.g.s. The green vertical line indicates the date of application.

2.3 Summary

The risk of pesticide leaching at Tylstrup can be summarized as follows:

- With triazinamin-methyl (degradation product of tribenuron methyl), fenpropimorph, propiconazole, pendimethalin, clomazone and clopyralid the leaching risk will not be evaluated until the 2003 monitoring results become available, i.e. when a total of two years of monitoring data have been collated. It should be noted, though, that none of these pesticides or the degradation products fenpropimorphic acid, propanamide-clomazone, pirimicarb-desmethyl or pirimicarb-desmethyl-formamido have yet been detected in any of the water samples analysed.
- With triasulfuron, pirimicarb, ETU (degradation product of mancozeb) and linuron, the leaching risk was found to be negligible.
- Two degradation products of metribuzin (metribuzin-desamino-diketo and metribuzindiketo) were found to leach from the root zone (1 m b.g.s.) in average concentrations exceeding 0.1 μ g/l. The estimated leachate concentrations of metribuzin-desaminodiketo and metribuzin-diketo reached 0.9 μ g/l and 0.3 μ g/l, respectively.
- The monitoring results indicate marked groundwater contamination with the degradation products of metribuzin. The average concentration of metribuzin-diketo was 0.15 μ g/l, and in 81% of the screens analysed the average concentration exceeded the maximum allowable concentration (0.1 μ g/l). Metribuzin-desamino-diketo was also detected in 57% of the analysed groundwater samples. Apart from one sample, the concentration never exceeded 0.1 μ g/l. Whether or not the observed groundwater contamination is due to the metribuzin applied during the PLAP or prior to the monitoring period cannot be determined.

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 13). 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. The geological description points to a rather homogeneous aquifer of meltwater sand, with local occurrence of thin clay and silt beds (Figure 14). 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

The field was sprayed with glyphosate on 22 September 1999 prior to the sowing of winter rye (cv. Dominator) on 13 October. Weeds were sprayed on 12 November using tribenuron methyl. At the same time, potassium bromide tracer was applied. Fungicide spraying was carried out twice on 5 May and 7 June, each time using propiconazole and fenpropimorph. On 6–7 May the site was irrigated with 29 mm/ha. The winter rye was harvested on 9 August, yielding 56.2 hkg/ha of grain (water content 15%), approximately 5 hkg/ha less than average for the location.

On 24 April 2001, 49 tonnes/ha of cattle slurry was spread and incorporated. The field was ploughed two days later and sown with maize (cv. Loft) on 30 April. Herbicide spraying with terbuthylazine + pyridate was carried out on 14 May and on 30 May. The site was irrigated twice with 31 mm/ha on 4–5 July and 30 mm/ha on 23–24 July. The maize was harvested on 1 October yielding 151.4 hkg/ha (100% dry matter) cobs and stalks.

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. Management practice at the site is detailed in Appendix 3, Table A3.2.



Figure 13. 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).



Figure 14. Geological description of the Jyndevad site (Lindhardt et al., 2001).

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Screen

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 2002.

The model was calibrated to the observed groundwater table measured in the piezometers located in the buffer zone, as well as to measured time series of soil water content at three different depths (25, 60 and 110 cm b.g.s.) from the two profiles S1 and S2 (see Figure 13) and to the bromide concentration measured in the suction cups located 1 m b.g.s. The calibration procedure is briefly described in Section 2.1.3. For a detailed description of data acquisition, model set-up and calibration procedures, see Kjær *et al.* (2002).

3.2 Results and discussion

3.2.1 Soil water dynamics and water balances

The model simulations were generally consistent with the observed data, thus indicating a good model description of the overall soil water dynamics in the unsaturated zone. The model provides a good simulation of the fluctuations in the measured groundwater table well. The dynamics of the measured soil water saturation was improved during calibration, especially 0.6 m b.g.s. (Figure 15D). The model still has some difficulty in capturing the degree of the soil water saturation 1.1 m b.g.s., however (Figure 15E). One explanation could be the large inter-probe variation in this horizon (data not shown), probably due to local variations in the texture of the sand in which the probes are installed.

Table 5. Annual water balance for Jyndevad (mm/yr)	Precipitation is corrected to the soil surface according
to the method of Allerup and Madsen (1979).	

	Normal			Actual evapotranspira-	Groundwater
	precipitation ¹⁾	Precipitation	Irrigation	tion	recharge ²⁾
1.7.99-30.6.00	995	1053	29	549	533
1.7.00-30.6.01	995	810	0	447	363
1.7.01-30.6.02	995	1287	20	508	799

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

 $\label{eq:constraint} \textit{2) Groundwater recharge is calculated as precipitation + irrigation - actual evapotranspiration \\$

At Jyndevad the three monitoring years differed as regards annual water balance, the first year being normal, the second dry and the third wet. The simulated actual evapotranspiration varies only slightly compared to the precipitation input, thus resulting in large variation in the modelled groundwater recharge. During the summer months the actual evapotranspiration usually counterbalances the precipitation, but periods with heavy precipitation events might result in percolation to 1 m b.g.s., thus minimizing the periods without percolation.



Figure 15. Soil water dynamics at Jyndevad: Locally measured precipitation 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 13).

3.2.2 Bromide leaching

The autumn application of bromide was followed by high autumn precipitation with a resultant high level of infiltration and rapid leaching of bromide. The bromide concentration 1 m b.g.s. thus increased rapidly just one month after application. All of the bromide had leached from the uppermost metre of the soil about four months after application (Figure 16). The model was able to satisfactorily simulate the bromide transport at 1 m b.g.s. Both the timing and the concentration level, as indicated by the measurements, were well captured by the model (Figure 16). The model predicts a high peak concentration between the measurements in the breakthrough curve, but no monitoring data are available to confirm this.

As the suction cups located 2 m b.g.s. are mostly in the saturated zone during the winter, no attempt has been made to calibrate the model towards the measured bromide concentrations at this depth. Nevertheless, the breakthrough of bromide at 2 m b.g.s. was detected in both suction cups two months after application. The bromide concentration remained elevated until January 2002, indicating an overall transport time of 27 months from field application until the majority of the bromide had passed the suction cups (2 m b.g.s.).

Marked breakthrough of bromide was also detected in all downstream monitoring wells, with the results indicating rather homogeneous groundwater flow. Elevated bromide concentrations were thus detected in all downstream monitoring wells around July, with the temporal evolution being somewhat similar (Figure 17). The area around M3 was characterized by a more heterogeneous flow pattern, however. The bromide concentration in the upper screen of M3, located 2–3 m b.g.s., was thus only slightly elevated, while transport of the majority of the bromide took place at lower depths. Silt and clay lenses located in the upper three meters of M3 (Figure 14) may determine the flow pattern. At the end of the monitoring period the bromide concentration in the deepest filter at M5 was slightly elevated, possibly due to the groundwater flow turning slightly northwards during the last part of the monitoring period.


Figure 16. Simulated (red line) and measured (blue and green crosses) 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 13). The green vertical line indicates the date of bromide application.



Figure 17. 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 line indicates the date of bromide application.

3.2.3 Pesticide leaching

At Jyndevad, the monitoring encompassed seven different pesticides and several degradation products applied during three growing seasons as indicated in Figure 18 and Table 6. It should be noted that precipitation in Table 6 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, triazinaminmethyl and PHPC. For the same reasons it is the degradation products and not the parent compounds that are monitored in the PLAP (Table 6).

Table 6. Pesticides analysed at Jyndevad with the product used shown in parentheses. Degradation products are in italics Precipitation and percolation are accumulated from the date of first application (App. date) until 1 July 2002. 1^{st} month percolation refers to accumulated percolation within the first month after application. C_{mean} refers to average leachate concentration at 1 m b.g.s. The number of pesticide-positive samples is indicated in parentheses.

Analysed pesticides	App. date	Precipitation	Percolation	1 st month percolation	C _{mean}
		(mm)	(mm)	(mm)	(µg/l)
Winter rye 2000		· ·	· ·		
Glyphosate (Roundup 2000)	Sep 99	3047 1)	1662 1)	149	< 0.01 (0)
- AMPA		1)	1)		<0.01 (3)
<i>Triazinamin-methyl</i> ² (Express)	Nov 99	2821	1495 1)	95	< 0.01 (0)
Propiconazole (Tilt Top)	Apr 00	2303	1094	0	< 0.01 (0)
Fenpropimorph (Tilt Top)	Apr 00	2303	1094	0	<0.01 (2)
Maize 2001					0.01 (0)
Terbuthylazine (Lido)	May 01	1392	692	0	< 0.01 (0)
- desethylterbuthylazine					See text (13)
$PHPC^{3}$ (Lido)	May 01	1392	692	0	< 0.01 (0)
Potatoes 2002	•				
Rimsulfuron (Titus)	May 02	181	35	26	- (0)
- DEPU					- (0)
- DPEUP-desamido					- (0)

Chemical Abstracts nomenclature for the analysed pesticides is given in Appendix 1

¹⁾ Accumulated from date of application until monitoring ceased in February 2002 (glyphosate) or April 2002 (triazinamin-methyl)

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

³⁾ Degradation product of pyridate. The parent compound degrades too rapidly to be detected by monitoring

With propiconazole, fenpropimorph, triazinamin-methyl (degradation product of tribenuron methyl) and glyphosate, the leaching risk was found to be negligible at the Jyndevad site. Apart from two samples containing $0.03-0.04 \mu g/l$ of fenpropimorph, and three containing $0.01-0.02 \mu g/l$ of AMPA, none of these compounds or the degradation products listed in Table 6 have yet been detected.



Figure 18. Pesticide application, precipitation and irrigation (primary axis) together with simulated percolation 1 m b.g.s. (secondary axis) at Jyndevad. Pesticides applied later than April 2002 are not included.

The leaching risk of glyphosate and triazinamin-methyl should be viewed in relation to the rather wet monitoring period, with percolation occurring shortly after application of both pesticides (Figure 18). Percolation within the first month after application was 149 mm for glyphosate and 95 mm for triazinamin-methyl (Table 6.). For further information, see Kjær *et al.* (2002). In contrast, fenpropimorph and propiconazole were applied during summer 2000, when precipitation input was nearly normal (Appendix 4). During this period precipitation input was almost counterbalanced by actual evapotranspiration such that no percolation occurred during the first month after application (Table 6 and Figure 18).

The leaching risk of terbuthylazine, PHPC (degradation product of pyridate) and rimsulfuron will not be evaluated until the 2003 monitoring results become available, i.e. when two years of monitoring data have been collated. It should be noted, though, that apart from desethylterbuthylazine, none of these compounds or their degradation products listed in Table 6 have yet been detected in any of the water samples analysed.

Desethylterbuthylazine (degradation product of terbuthylazine) did leach during the current monitoring period. In mid October 2001, about five months after application, desethylterbuthylazine was detected in elevated concentrations in the S1 suction cups located 1 m b.g.s. The average concentration has not yet been calculated, though, as the monitoring period does not fully cover the leaching period. The highest concentration $(0.06 \ \mu g/l)$ was detected at the very end of the current monitoring period, thus indicating that leaching of the compound from the uppermost metre of the soil has not yet ceased.

The observed leaching should be viewed in relation to the spring application, when hydrological conditions allow the applied compound a relatively long residence time in the root zone. Terbuthylazine was applied in May 2001, when precipitation input was close to normal and counterbalanced by actual evapotranspiration (Appendix 4 and Figure 18). Hence, percolation did not occur until mid July, about 1.5 months after the last application (Figure 19). Desethylterbuthylazine was first detected after 190 mm of percolation, equivalent to 1.5 pore volumes.



Figure 19. Measured concentration of desethylterbuthylazine (primary axis) together with accumulated percolation 1 m b.g.s. (secondary axis) at Jyndevad. The measured data derive from suction cups installed 1 m b.g.s. at location S1 (see Figure 13). Percolation is simulated (see Section 3.2.1.). The red vertical lines indicate date of pesticide application. Concentrations below detection limits are indicated with open squares.

Desethylterbuthylazine has not been detected in either the S2 suction cups or the downstream monitoring wells. In the monitoring well M7 located upstream of the test site, however, desethylterbuthylazine was detected in 8 of 9 analysed samples in concentrations ranging from 0.01–0.02 μ g/l due to prior application of terbuthylazine on the neighbouring field located upstream of the PLAP site. This was detected in the initial screening analysis, indicating that desethylterbuthylazine was present in M7 before the monitoring started in September 1999 (Kjær *et al.*, 2001).

It should also be noted that pesticide application prior to the PLAP has caused marked groundwater contamination with the degradation products of metribuzin. Metribuzin-diketo was detected in concentrations as high as 1.37 μ g/l and exceeded 0.1 μ g/l in 73% of the 26 water samples analysed. Metribuzin-desamino-diketo was detected in concentrations as high as 1.83 μ g/l and exceeded 0.1 μ g/l in 50% of the 26 water samples analysed. For further information, see Kjær *et al.* (2002).

3.3 Summary

The risk of pesticide leaching at Jyndevad can be summarized as follows:

- With terbuthylazine, PHPC (degradation product of pyridate) and rimsulfuron, the leaching risk will be evaluated when the 2003 monitoring results become available, i.e. when two years of monitoring data have been collated. It should be noted, though, that incipient leaching of desethylterbuthylazine (degradation product of terbuthylazine) was detected in the suction cups located 1 m b.g.s. The concentrations detected were all below 0.1 μ g/l. None of the other compounds or their degradation products leached during the current monitoring period.
- With glyphosate and triazinamin-methyl (from tribenuron methyl), fenpropimorph and propiconazole, the leaching risk was found to be negligible.
- Previous application of pesticides has resulted in marked groundwater contamination with degradation products of metribuzin. Metribuzin-diketo was detected in concentrations as high as 1.37 μ g/l, and exceeded 0.1 μ g/l in 73% of the water samples analysed. Metribuzin-desamino-diketo was detected in concentrations as high as 1.83 μ g/l and exceeded 0.1 μ g/l in 50% 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. 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%. 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 (Figure 21). 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

Cattle slurry (36.5 tonnes/ha) was spread on 19 April 2000, whereafter the field was ploughed. Fodder beet (cv. Kyros) was sown on 5 May and emerged unevenly across the field within 1 to 3 weeks. The herbicides metamitron, phenmedipham, desmedipham and ethofumesate were applied on 22 May, 15 June and 12 July. Potassium bromide tracer was applied on 22 May. The field was sprayed with fluazifop-p-butyl on 28 June to combat wild oats and with pirimicarb on 5 July to combat aphids. The crop was harvested on 15 November yielding 134.5 hkg/ha of beet roots (100% dry matter) and 26.3 hkg/ha of beet tops. Taken together, the dry matter yield was at the same level as the normal yield recorded in the area that year.

The field was ploughed in spring 2001. Due to ample precipitation, sowing of the spring barley (cv. Otira) was delayed until 9 May. Crop emergence was recorded 11 days later. The herbicides tribenuron methyl and flamprop-M-isopropyl were sprayed on 9 and 21 June, respectively. The fungicides propiconazole and fenpropimorph were applied on 21 June and 4 July. The insecticide dimethoate was sprayed on 6 July. Despite the very late sowing, grain yield at harvest on 5 September was as high as 88.0 hkg/ha (15% water content). Precipitation prevented the straw being pressed until late October, resulting in a low straw yield of 28.6 hkg/ha (dry matter).



Figure 20. 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).



Figure 21. Geological description of the Silstrup site (Lindhardt et al., 2001).

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 + terbuthylazine 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. Management practice at the site is detailed in Appendix 3 (Table A3.3).

4.1.3 Model set-up and calibration

The MACRO model was 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 was used to simulate the water flow in the unsaturated zone during the full monitoring period April 2000–June 2002 and to establish an annual water balance.

The model was calibrated 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 two profiles S1 and S2 (see Figure 20) as well as to measured drainage flow. A simple calibration procedure was applied that only involved adjustment of the empirical BGRAD parameter regulating the boundary flow and the drain depth, which was determined by the groundwater level during drainage periods. All remaining parameters were based on measured data or literature/default values. The calibration procedure is briefly described in Section 2.1.3. For a detailed description of data acquisition, model set-up and calibration procedures, see Kjær *et al.* (2002).

4.2 Results and discussion

4.2.1 Soil water dynamics and water balances

The model simulations were largely consistent with the observed data, thus indicating a reasonable model description of the overall soil water dynamics in the unsaturated zone. The dynamics and level of the groundwater table were captured well by the model except for the initial rise in the autumn 2000, when percolation and drainage flow were initiated. The delayed rise in the groundwater table resulted in a delayed response in the drainage flow in November 2000. Similarly, the modelled drainage flow is delayed compared to the measured drainage in September 2001 due to the simulated groundwater table being too low (Figure 22B and C).

The overall trends in soil water content could be modelled reasonably well, especially in the A horizon (Figure 22D). In the subsoil the model tends to describe a dryer soil during the summer periods than measured by the deeper TDR probes (Figure 22E and F). Unexpectedly, the measured time series at 60 and 110 cm b.g.s. were not affected by the lower groundwater table during the two summer periods. Measured water saturation ranged from 90 to 110%, with the highest values during the driest periods. According to the measured retention curves the soil water content should have been approximately 80%, as simulated by the model. The quality of the measured time series has been thoroughly analysed. The

unexpected pattern could be related to the use of the general relationship between measured primary TDR data and the calculated soil water content. The use of a calibrated, soil-specific relationship would improve the findings. Another explanation may be the limited applicability of TDR in near-saturated soils and in the heavy clayey and swelling soils in which the probes could have been installed at Silstrup (clay content up to 43%, according to Lindhardt *et al.*, 2001).

Closer examination of measured and modelled drainage flow during the period October 2001 to April 2002 (Figure 23) reveals that the drainage flow pattern at Silstrup is dominated by transient peaks of high flow typically lasting 4–7 days, often separated by no-flow periods. The flow pattern thus seems to be dominated by macropore flow generated during major precipitation events – a finding supported by the rapid occurrence of bromide in the drainage water and suction cups located 1 m b.g.s (Figure 24A and B). The model, which is as yet uncalibrated, could not fully match this flow pattern, but the overall trends and dynamics of the drainage flow are reasonably well simulated.

The resulting water balance is shown in Table 7 (July to June) for the three modelled years. The first and third years were wet years at Silstrup, while the second year was dry. The simulated drainage flow was higher than the measured drainage flow in both of the two monitoring years in which drainage flow was measured, the discrepancy being greatest in the rather wet year of 2001/2002. Despite a difference in precipitation of 138 mm between these two monitoring years the measured drainage flow was similar. Thus the additional precipitation input in the last monitoring year mainly percolated deeper into the soil. Simulated groundwater recharge ranged from 257 to 373 mm/yr. Simulated percolation 1 m b.g.s. is generally continuous from September/October until late spring with precipitation (Figure 22A).

to the method of Al	llerup and Madser	i (1979).				
	Normal precipitation ²⁾	Precipitation	Actual evapotrans- piration	Measured drainage	Simulated drainage	Groundwater recharge ³⁾
$1.7.99 - 30.6.00^{-1}$	976	1175	439	_	479	257 ⁴⁾

393

448

300

373

256

300

217

226

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).

1) The monitoring was started in April 2000

976

976

1.7.00-30.6.01

1.7.01-30.6.02

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

909

1047

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



Figure 22. Soil water dynamics at Silstrup: Locally 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 20).



Figure 23. Simulated and measured drainage flow at Silstrup from October 2000 to April 2002.

4.2.2 Bromide leaching

Two large storm events occurred a few days prior to and after the application of the bromide tracer on 22 May 2000. The first event caused the onset of a minor flow of drainage water, while the second resulted in rapid percolation and breakthrough of bromide to the drainage system, with the concentration reaching 5.1 mg/l on 29 May (Figure 24C). At Silstrup the upper macropore zone extends down to 1.3 m b.g.s. (Lindhardt *et al.*, 2001). The zone is heavily fractured and contains numerous biopores coated with clay and organic matter. When the bromide was applied, the groundwater table was located around 1.25 m b.g.s. (Figure 22B). The presence of macropores and the location of the groundwater at the time of bromide application were reflected in the almost instantaneous occurrence of bromide in the drainage water, suction cups S1 and S2 (Figure 24A, B and C) and in the uppermost filters of all but one of the downstream, vertical wells (Figure 25). The orientation and magnitude of the fractures may also explain why bromide was detected in the lowermost screen of M12, which is located upstream of the test field.

Total bromide recovery during the two-year monitoring period was 2.1 kg/ha, indicating that only 11% of the applied tracer had leached into the drains. The elevated bromide concentration detected in the suction cups and drainage water in 2002 indicate that bromide continued to leach from the unsaturated zone as long as two years after application. In conclusion, the overall distribution of bromide in the test field indicates that most of the bromide is retained in the upper part of the soil profile, probably in the clay matrix. Continuous, slow leaching of bromide can therefore be expected for a long period of time.



Figure 24. 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 vertical monitoring well M5 (E). The green vertical line indicates the date of bromide application.



Figure 25. 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 began at Silstrup in April 2000 and presently encompasses 12 pesticides and 13 degradation products (Table 8 and Figure 26). 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 PHPC. For the same reasons it is the degradation products and not the parent compounds that are monitored in the PLAP (Table 8).

Table 8. Pesticides analysed at Silstrup with the product used shown in parentheses. Degradation products are in italics. Precipitation and percolation are accumulated from the date of first application (App. date) until 1 July 2002. 1^{st} month percolation refers to accumulated percolation within the first month after application. C_{mean} refers to average concentration in the drainage water. The number of pesticide-positive samples is indicated in parentheses.

Analysed pesticides	App.	Precipitation	Percolation	1 st month	C _{mean} ¹⁾
	date			percolation	((1)
		(mm)	(mm)	(mm)	(µg/I)
Fodder beet 2000					
Metamitron (Goltix WG)	May 00	2049	1083	51	0.05 (68)
- metamitron-desamino					0.06 (60)
Ethofumesate (Betanal Optima)	May 00	2049	1083	51	0.03 (23)
Desmedipham (Betanal Optima)	May 00	2049	1083	51	< 0.01 (1)
- EHPC					< 0.01 (0)
Phenmedipham (Betanal Optima)	May 00	2049	1083	51	< 0.01 (0)
- MHPC					< 0.01 (0)
- 3-aminophenol					< 0.01 (0)
Fluazifop-P-butyl (Fusilade X-tra)	Jun 00	1953	1031	4	< 0.01 (0)
- fluazifop (free acid)					< 0.01 (1)
Pirimicarb (Pirimor)	Jul 00	1943	1029	3	0.01 (17)
- pirimicarb-desmethyl					< 0.01 (1)
- pirimicarb-desmethyl-formamido					< 0.01 (0)
Spring barley 2001					
<i>Triazinamin-methyl</i> ²⁾ (Express)	May 01	1062	546	7	< 0.01 (0)
Flamprop-M-isopropyl (Barnon Plus)	Jun 01	1049	543	6	< 0.01 (13)
- flamprop (free acid)					< 0.01 (7)
Propiconazole (Tilt Top)	Jun 01	1034	540	7	< 0.01 (6)
Fenpropimorph (Tilt Top)	Jun 01	1034	540	7	< 0.01 (0)
- fenpropimorphic acid					< 0.01 (1)
Dimethoate (Perfection 500 S)	Jul 01	1003	538	6	0.02 (2)
Maize 2002					
Glyphosate (Roundup Bio)	Oct 01	608	395	44	0.13 (36)
-AMPA					0.06 (40)
$PHPC^{3}$ (Lido)	May 02	126	24	13	- (0)
Terbuthylazine (Lido)	May 02	126	24	13	- (1)
- desethylterbuthylazine	j = -				- (1)
Clopyralid (Matrigon)	Jun 02	30	11	20	- (1)

Chemical Abstracts nomenclature for the analysed pesticides is given in Appendix 1

¹⁾ Weighted average concentration in the first drainage season after application (See Appendix 2 for calculation methods)

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

³⁾ Degradation product of pyridate. The parent compound degrades too rapidly to be detected by monitoring



Figure 26. Pesticide application, precipitation and irrigation (primary axis) and simulated percolation 1 m b.g.s. (secondary axis) at Silstrup. Desm.: desmedipham; Phenm.: phenmedipham; Fenp.: fenpropimorph; Prop.: propiconazole. Pesticides applied later than April 2002 are not included.

With desmedipham, phenmedipham and fluazifop-P-butyl, the leaching risk was found to be negligible at the Silstrup site. Apart from one sample containing less than 0.1 μ g/l of desmedipham and fluazifop, none of these compounds nor the degradation products listed in Table 8 were detected during the two-year monitoring period. Metamitron, metamitron-desamino, ethofumesate and pirimicarb 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.* (2002).

• Pirimicarb was detected in several drainage water samples, although always at concentrations below 0.1 μ g/l. Pirimicarb was not detected in the suction cups, but was de

tected at a concentration of 0.01 μ g/l in three groundwater samples. Leaching of pirimicarb was confined to a nine-month period ending in April 2001.

- Evidence of ethofumesate leaching was seen at the S2 suction cups located 1 m b.g.s. as well as in the drainage water. Throughout the 2000/2001 leaching period, ethofumesate leached to the drainage system at an average concentration reaching 0.03 μ g/l. The concentration only exceeded 0.1 μ g/l in one sample. In groundwater, ethofumesate was detected at concentrations ranging from 0.01 to 0.02 μ g/l in four samples. Leaching of ethofumesate was confined to a six-month period ending in January 2001.
- Throughout the 2000/2001 leaching period, metamitron and metamitron-desamino leached to the drainage system at average concentrations of 0.05 and 0.06 μ g/l respectively. In addition, both compounds were detected in several samples of groundwater and samples from the suction cups located 2 m b.g.s. In total, only four groundwater samples contained concentrations exceeding 0.1 μ g/l. The maximum concentration detected was 0.17 μ g/l for metamitron and 0.13 μ g/l for metamitron-desamino. Leaching of metamitron was confined to a nine-month period ending in April 2001, whereas metamitron-desamino continued to leach to the drains at low concentrations more than one year after application. During the leaching period 2001/2002, metamitron-desamino was detected in nine samples, the latest of which was a drainage water sample from October 2002. In all instances the concentration was below 0.1 μ g/l.

The leaching risk of the pesticides applied to the spring barley in 2001 and maize in 2002 will not be evaluated until the 2003 monitoring results become available, i.e. when two years of monitoring data have been collated. Nevertheless, no evidence was found to indicate leaching of fenpropimorph and triazinamin-methyl, which were only detected in one sample (fenpropimorphic acid, 0.019 μ g/l; Table 8). In contrast, the other four pesticides applied in 2001 were found to leach from the root zone during the current monitoring period:

- Shortly after dimethoate had been applied in July 2001, a large precipitation event caused rapid leaching through the unsaturated zone (Figure 26). On 24 July, just eight days after application, dimethoate was detected at a concentration of 1.42 μ g/l in the drainage water. This one sample is the reason why the average drainage water concentration of dimethoate is 0.02 μ g/l (Table 8).
- Minor leaching of flamprop-M-isopropyl, flamprop (free acid) and propiconazole was also observed. All three substances were detected in several drainwater samples. Apart from one sample containing 0.11 µg/l of flamprop-M-isopropyl, all concentrations were below 0.1 µg/l (Figure 27).
- On 25 October 2001 the field was sprayed with glyphosate (1.44 kg/ha) in the form of Roundup Bio (4.0 l/ha). Prior to application there had been 4 major storm events yielding up to 11 mm/day of drainage runoff (Figure 28). The day before the field was sprayed there was 9 mm of precipitation. The preceding 13 days were practically precipitation-free, however. Five days after spraying, 12 mm of precipitation caused approximately 2 mm of runoff in which the flow-proportional concentration of glyphosate

was 4.7 μ g/l, and the time-proportional concentration was 1.9 μ g/l. The corresponding AMPA concentrations were 0.06 and 0.14 μ g/l, respectively (Figure 28B). The glyphosate concentration constantly decreased during the remainder of the leaching period 2001/2002. The AMPA concentration was lower, but more stable during the leaching period (Figure 28C; Appendix 6). Glyphosate and AMPA were detected in all drainage water samples except one. The weighted average concentration of glyphosate in the drainage water was 0.13 μ g/l, while that of AMPA was 0.06 μ g/l. The concentrations might have been even higher had not November and December been so much dryer than usual (Appendix 4), resulting in considerably greater drainage runoff than in the preceding and following periods (Figure 28). It should be noted that drainage runoff commenced about one month prior to the application of glyphosate, and that the weighted average concentration refers to the period from the date of application until 1 July 2002. In addition glyphosate was detected in 3 groundwater samples and AMPA in 7, in each case at concentrations below 0.1 μ g/l (Appendix 6).

At Silstrup, pesticide leaching appears to be associated with pronounced macropore transport resulting in very rapid movement of pesticides through the unsaturated zone. According to the hydrological modelling, flow was dominated by macropore flow generated during major storm events (Section 4.2.1.). These findings are in concert with the observed pattern of pesticide flow, where the leaching of pesticides to the drains was completely governed by the individual storm/flow events. Thus sudden storm events accounted for 92% of all the metamitron leached, 89% of the metamitron-desamino, 97% of the ethofumesate, 88% of the glyphosate and 80% of the AMPA.

It should be noted that in Figure 27 and Figure 28, time-proportional sampling refers to continuous drainage runoff occurring throughout the whole drainage season, whereas the flow-proportional sampling refers to the drainage runoff induced by the sudden storm events occurring several times during the drainage season.



Figure 27. Precipitation (A) together with concentration of flamprop-M-isopropyl (B), flamprop (free acid) (C) and propiconazole (D) in the drainage runoff at Silstrup. The green vertical lines indicate the date of application.



Figure 28. Precipitation (A) together with concentration of glyphosate (B), AMPA (C) and bromide (D) in the drainage runoff at Silstrup. The green vertical lines indicate the date of application. Bromide was applied in May 2000.

4.3 Summary

At Silstrup, the leaching risk of pesticides applied in 2000 can be summarized as follows:

- With desmedipham, phenmedipham and fluazifop-P-butyl, the leaching risk was negligible.
- Metamitron, metamitron-desamino, ethofumesate and pirimicarb leached from the root zone during the current monitoring period, but not at unacceptable levels. Although the concentration exceeded 0.1 μ g/l in several samples, the average concentration did not. Metamitron-desamino continued to leach from the root zone more than one year after application, whereas leaching of pirimicarb and metamitron/ethofumesate was confined to a six-month and nine-month period, respectively.

The leaching risk of pesticides applied in 2001 and 2002 cannot be fully evaluated at present as the potential leaching period extends beyond the current monitoring period. The preliminary findings are that:

- No evidence was found to indicate leaching of fenpropimorph and triazinamin-methyl (degradation product of tribenuron methyl), which were only detected in one sample (fenpropimorphic acid, 0.019 µg/l).
- Minor leaching of flamprop-M-isopropyl, flamprop (free acid), propiconazole and dimethoate, but not in unacceptable levels. Apart from two samples, all concentrations were below $0.1 \ \mu g/l$.
- Glyphosate leached from the root zone at concentrations exceeding 0.1 μ g/l, the average concentration in the drainage water being 0.13 mg/l. AMPA was also detected in the drainage water, but the average concentration was only 0.06 μ g/l. In addition, glyphosate was detected in 3 groundwater samples and AMPA in 7, in each case at concentrations below 0.1 μ g/l.

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. 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 at the other loamy sites (Table 1). The geological structure is complex comprising a clay till core with deposits of different age and composition (Figure 30). 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

The field was ploughed on 11 April 2000 whereafter spring barley (cv. Barke) was sown. The barley emerged on 25 April 2000. On 15 May the herbicide metsulfuron-methyl and potassium bromide tracer were applied. The herbicide flamprop-M-isopropyl was applied on 31 May. Combined fungicide and insecticide spraying with propiconazole, fenpropi-morph and dimethoate was carried out on 15 June and 5 July. The barley was harvested on 28 August yielding 52.6 hkg/ha of grain (85% dry matter). The low yield is attributable to at least two factors. Firstly, due to the instrumentation work the field had to be ploughed in the spring rather than in the autumn, as would normally be the case on this soil. As a consequence a proper seedbed could not be established, and crop establishment was therefore poor. Secondly, the soil in minor parts of the field had been compacted in autumn and winter 1999 during installation of the monitoring equipment.



Figure 29. 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).



Figure 30. Geological description of the Estrup site (Lindhardt et al., 2001).

On 13 October 2000, glyphosate was sprayed to combat couch grass. The field was ploughed on 23 October and sown with field pea (cv. Julia) on 2 May. The peas emerged on 13 May. Weeds were sprayed only once using bentazone and pendimethalin on 22 May. The insecticide pirimicarb was sprayed on 26 June. The crop was harvested on 22 August yielding 43.2 hkg/ha of peas (86% dry matter).

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 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 had been solved by repairing a drainpipe inadvertently damaged, presumably during installation of the monitoring equipment in the buffer zone (Lindhardt *et al*, 2001). Management practice at the site is detailed in Appendix 3 (Table A3.4).

5.1.3 Model set-up and calibration

The MACRO model was 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 was used to simulate the water flow in the unsaturated zone during the monitoring period from July 2000–June 2002 and to establish an annual water balance.

The model was calibrated to the observed groundwater table measured in the piezometers located in the buffer zone as well as to measured drainage flow and measured time series of soil water content at one depth (25 cm b.g.s.) from a single soil profile S1 (see Figure 29D). 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. The data from the soil profile S2 have been excluded due to the above-mentioned problem of water ponding above the TDR probes installed at S2.

Despite the lack of measured time series, a simple calibration procedure was applied that only necessitated minor adjustment of the hydraulic properties of the C horizon and the empirical BGRAD parameter regulating the boundary flow and the drain depth, which was determined by the groundwater level during drainage periods. All remaining parameters were based on measured data or literature/default values. For a detailed description of data acquisition, model set-up and calibration procedures, see Kjær *et al.* (2002).

5.2 Results and discussion

5.2.1 Soil water dynamics and water balances

The model simulations were generally consistent with the observed data, thus indicating a good model description of the overall soil water dynamics in the unsaturated zone (Figure 31).

The model was able to provide a good simulation of the measured groundwater table, including the rapid rise of the groundwater table at the end of October 2000. The simulated groundwater table often fluctuated slightly above the drain depth during periods where drainage flow occurred. The peaks corresponded to larger storm events and resulted in an almost fully saturated soil profile. This is also reflected by the TDR probes located at 25 cm b.g.s., where the soil water saturation approaches 100%.

The simulated accumulated drainage flow matches well with the measured drainage flow for both monitoring years. Moreover, both the drainage flow pattern and the onset of the drainage flow were well captured by the model. The measured drainage flow amounted to as much as 95% of the percolation modelled immediately above the drains (0.85 m b.g.s.). The high drainage runoff was due to the significantly lower permeability of the C horizon than that of the overlying A and B horizons. The percolation rate presumably exceeded the infiltration capacity of the C horizon for long periods, leaving the groundwater table to rise above the drain depth into the B horizon. Following minor adjustment of the hydraulic properties of the C horizon this process now seems to be captured well by the model.

The drainage season varied significantly between the three monitoring periods. Continuous drainage runoff started as early as the beginning of September in 2002 or as late as the end of October in 2001, and continued until mid April in 2002 and mid June in 2000. During the first and the third monitoring periods, drainage runoff amounted to 500 mm during the drainage season ($7\frac{1}{2}$ months), whereas the shorter drainage season during the second year (5 months) only resulted in 300 mm of drainage runoff. It should be noted that for the first monitoring period, simulated drainage volume is used because measured drainage runoff is only available from April 2000 (Figure 31C).

Percolation at Estrup is shown at 0.6 m b.g.s. instead of at 1 m b.g.s. because the soil at 1 m b.g.s. was saturated for longer periods (Figure 31). Percolation occurred continuously in the first two years from September to May/June, whereas the third year was characterized by a shorter percolation period with higher percolation rates. Percolation ceased at the end of March followed by minor peaks caused by major storm events in the spring/summer. The percolation pattern the first two years was characterized by a large initial peak at the onset (~30 mm/d) followed by a more stable period with minor peaks, all below 7 mm/d. The third year was characterized by less intense storm events and the absence of an initial large percolation peak.



Figure 31. Soil water dynamics at Estrup: Locally 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 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 (see Figure 29).

	Normal precipitation ²⁾	Precipitation	Actual evapotrans- piration	Measured drainage	Simulated drainage	Groundwater recharge ³⁾
1.7.99–30.6.00 ¹⁾	968	1173	440	_	518	216 ⁴⁾
1.7.00-30.6.01	968	887	386	356	307	145
1.7.01-30.6.02	968	1290	504	505	512	281

Table 9. Annual water balance for Estrup (mm/year). Precipitation is corrected to the soil surface according to the method of Allerup and Madsen (1979).

¹⁾ The monitoring was 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

The first monitoring period at Estrup (2000/2001) was dry, whereas the following period was rather wet. The year preceding the monitoring period was also rather wet (Table 9). This pattern is reflected in the accumulated drainage runoff and the estimated groundwater recharge. The high evapotranspiration in 2001/2002 was due to the fact that the crop was winter wheat.

5.2.2 Bromide leaching

At Estrup, total recovery of bromide in the drainage water during the two-year monitoring period amounted to 4.8 kg/ha, indicating that 24% of the applied tracer had leached into the drains. Although concentration levels decreased through the monitoring period, slightly elevated bromide concentrations were detected in both suction cups and drainage water at the end of the monitoring period (Figure 32A and B). This indicates that part of the bromide was still retained in the upper part of the soil profile, probably in the matrix. Retained bromide can therefore be expected to continue to leach for a long period of time.

The majority of the leached bromide probably left the system through drainage runoff as the modelled water balance suggested that 65–70% of the percolating water left through the drainage system. However, the results did show subsequent transport of small amounts of bromide to a depth of 2 and 3.5 m b.g.s. (Figure 32B and D). Slightly elevated concentrations were detected 2 m b.g.s in suction cups as well as in the horizontal well 3.5 m b.g.s. Although the concentration and frequency of detection were very low, slightly elevated concentrations were also detected in the downstream monitoring wells, especially in wells M3 and M4 (Figure 33).



Figure 32. Bromide concentration at Estrup. 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 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 33. Bromide concentration at Estrup. The data derive from the vertical monitoring wells (M2–M12). 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 began at Estrup in April 2000 and presently encompasses 12 pesticides and 13 degradation products as indicated in Table 10 and Figure 34. It should be noted that precipitation in Table 10 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).

Table 10. Pesticides analysed at Estrup with the product used shown in parentheses. Degradation products are in italics. Precipitation and percolation are accumulated from date of first application (App. date) until 1 July 2002. 1st month percolation refers to accumulated percolation within the first month after application. C_{mean} refers to average leachate concentration in the drainage water. The number of pesticide-positive samples is indicated in parentheses.

Analysed pesticides	App.	Precipitation	Percolation	1 st month	C _{mean} ¹⁾
	uate	(mm)	(mm)	(mm)	(ug/l)
Spring barley 2000		(11111)	()	()	(#8/1)
Metsulfuron-methyl (Ally)	May 00	2312	1191	33	<0.01(1)
Flamprop-M-isopropyl (Barnon Plus) - flamprop (free acid)	May 00	2235	1168	5	0.02(19) 0.01(12)
Propiconazole (Tilt Top) Fenpropimorph (Tilt Top)	Jun 00	2211	1158 1158	-8 -8	0.01(12) <0.01(1)
- <i>fenpropimorphic acid</i> Dimethoate (Perfection 500 S)	Jun 00	2211	1158	-8	<0.01(0) <0.01(0)
Pea 2001					
Glyphosate (Roundup Bio) - AMPA	Oct 00	1960	1165	135	0.54(70) 0.17(87)
Bentazone (Basagran 480) - 2-amino-N-isopropyl-benzamid	May 01	1363	686	15	0.03(48) <0.01(0)
Pendimethalin (Stomp)	May 01	1363	686	15	< 0.01(4)
Pirimicarb (Pirimor) - pirimicarb-desmethyl	Jun 01	1296	671	9	0.01(16) < $0.010)$ < $0.01(4)$
Winter wheat 2002					<0.01(4)
Ioxymil (Oxitril CM)	Nov 01	736	398	56	0.03(20)
Bromoxynil (Oxitril CM)	Nov 01	736	398	56	0.03(20)
Amidosulfuron (Gratil 75 WG)	Apr 02	282	53	12	- (0)
MCPA (Metaxon)	May 02	225	39	-2	- (4)
- 4-chlor,2-methylphenol Propiconazole (Tilt 250 EC)	May 02	193	41	38	- (0)

Chemical Abstract nomenclature for the analysed pesticides is given in Appendix 1.

¹) Weighted average concentration within the first drainage season after application (See Appendix 2 for calculation methods)



Figure 34. Pesticide application and precipitation (primary axis) together with simulated percolation 0.6 m b.g.s. (secondary axis) at Estrup. Pesticides applied later than April 2002 is not included.

With metsulfuron, fenpropimorph and dimethoate the leaching risk was found to be negligible at the Estrup site. Apart from one sample containing less than 0.1 μ g/l of metsulfuron, triazinamin and fenpropimorph, none of these compounds or the degradation products listed in Table 10 have yet been detected during the two-year monitoring period. Slight leaching of flamprop-M-isopropyl, flamprop (free acid) and propiconazole was observed. All three substances were detected in several drainage water samples, although at concentrations below 0.1 μ g/l. Leaching was confined to the 2000/2001 leaching period, with the last sample containing pesticide being detected in March 2001. For further details, see Kjær *et al.* (2002).

Glyphosate and its degradation product AMPA leached from the root zone at 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 2000/2001 leaching period was 0.54 μ g/l, while that of AMPA was 0.17 μ g/l (Figure 35). The leaching appeared to be governed by a combination of pronounced macropore flow occurring shortly after application and a limited sorption and degradation capacity. Both compounds leached continuously throughout the whole six-month drainage runoff period in 2000/2001. Leaching continued during the drainage runoff in 2001/2002. Although the concentration level was much lower, continuous leaching of AMPA in particular was observed during the second monitoring period (Table 11 and Figure 36.). Leaching was greatest with glyphosate during the first monitoring period, but with AMPA during the second period. The primary data and a detailed description of the leaching pattern in 2000/2001 are provided in Kjær *et al.* (2002). Apart from three samples containing 0.01–0.04 µg/l glyphosate, AMPA and glyphosate have not been detected in the groundwater monitoring screens located below the depth of the drainage system. Finally, it should be noted that monitoring of glyphosate and AMPA has not yet been completed, but will continue throughout the next monitoring period.

Table 11. AMPA and glyphosate in drainage water at Estrup during the two monitoring years. C_{mean} refers to the weighted average concentration ($\mu g/l$), Detection to percent of detection (% of analysed samples) and C_{max} to the maximum concentration found ($\mu g/l$).

	Glyphosate			AMPA		
	$C_{mean}(\mu g/l)$	C_{max} (µg/l)	Detection (%)	C_{mean} (µg/l)	C_{max} (µg/l)	Detection (%)
1.7.00-30.6.01	0.54	2.1	100%	0.17	0.73	100%
1.7.01-30.6.02	0.01	0.03	52%	0.05	0.15	93%

The leaching risk of the pesticides applied in 2001 and 2002 will not be evaluated until the 2003 monitoring results become available, i.e. when two years of monitoring data have been collated. The preliminary findings are:

- Slight leaching of ioxynil, pirimicarb and bentazone was observed. All three compounds were detected in several drainage water samples. In some cases the concentration exceeded 0.1 μ g/l, but the average concentrations were relatively low, ranging from 0.01 to 0.03 μ g/l (Table 10). The most frequently detected compound was bentazone, which was present in 81% of the analysed drainage water samples (Figure 37). It should be noted that drainage runoff commenced about two and a half months prior to the application of ioxynil and bromoxynil. The weighted concentration of ioxynil and bromoxynil refers to the period from the date of application until 1 July 2002
- Pendimethalin and bromoxynil was both detected in the drainage water, but only in very few samples. The concentration range was 0.07–0.6 μg/l for pendimethalin and 0.01– 0.04 μg/l for bromoxynil.

Pesticide leaching at Estrup has hitherto been confined to the depth of the drainage system. Thus pesticides have only very rarely been detected in groundwater monitoring screens located below the depth of the drainage system. The bulk of all leached pesticide probably left the system through drainage runoff since the water balance suggests that 65–70% of the percolation ran off through the drainage system (Section 5.2.1). Due to decreased hydraulic conductivity, water and solute transport at Estrup were much slower beneath the drainage system than above it (Lindhardt *et al.*, 2001). The slower transport time may also allow for dispersion, dilution, sorption and degradation, thereby reducing further transport.



Figure 35. Precipitation (A) together with concentration of glyphosate (B), AMPA (C) and bromide (D) in the drainage runoff in 2000/2001 at Estrup. The green vertical lines indicate the date of application.



Figure 36. Precipitation (A) together with concentration of glyphosate (B), AMPA (C) and bromide (D) in the drainage runoff in 2001/2002 at Estrup. Bromide and glyphosate was applied in April 2000 and October 2000, respectively. Please note that scales used for glyphosate and AMPA differ from those used in Figure 35.


Figure 37. Precipitation (A) together with concentration of bentazone (B), pirimicarb (C) and ioxynil (D) in the drainage runoff at Estrup. The green vertical lines indicate the date of application.

5.3 Summary

At Estrup the leaching risk of pesticides applied during 2000 can be summarized as follows:

- With metsulfuron, fenpropimorph and dimethoate the leaching risk was found to be negligible.
- Flamprop-M-isopropyl, flamprop (free acid) and propiconazole were detected in several drain water samples, but only in concentrations below 0.1 µg/l.
- Glyphosate and its metabolite AMPA leached from the root zone at average concentrations considerably exceeding 0.1 μ g/l. Thus the average concentration of glyphosate in the drainage water was 0.54 μ g/l during the 2000/2001 leaching period, while that of AMPA was 0.17 μ g/l. Leaching has hitherto been confined to the depth of the drainage system, pesticides rarely having been detected in the groundwater monitoring screens located below the depth of the drainage system.

The leaching risk of pesticides applied in 2001 and 2002 cannot be fully evaluated at present as the potential leaching period extends beyond the current monitoring period. The preliminary findings are that:

- Pendimethalin and bromoxynil were detected, but only in very few samples
- Slight leaching of ioxynil, pirimicarb and bentazone took place, all three compounds having been detected in several drainage water samples. The concentrations sometimes exceeded 0.1 μ g/l, but the average concentrations were relatively low, ranging from 0.01 to 0.03 μ 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 $1-3^{\circ}$. 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 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 (Figure 38). 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 38). During the monitoring period the groundwater table ranged from 1 to 2 and 2 to 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).

6.1.2 Agricultural management

The field was sprayed with glyphosate on 11 August 1999 and sown with winter wheat (cv. Stakado) on 20 August. Potassium bromide tracer was applied on 5 October. Weeds were sprayed on 14 October using ioxynil and bromoxynil and again on 4 April using fluroxypyr. Fungicide spaying was carried out on 5 May and 31 May using propiconazole and fenpropimorph. The insecticide pirimicarb was applied on 19 June. The crop was harvested on 28 August yielding 92.7 hkg/ha of grain and 76.2 hkg/ha of straw (85% and 100% dry mater, respectively).



Figure 38. 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).



Figure 39. Geological description of the Faardrup site (Lindhardt et al. 2001).

On 4 October 2000 the field was sprayed with glyphosate and ploughed 12 days later. Sugar beet (cv. Havanna) was sown on 2 May 2001. The herbicides metamitron, phenmedipham, desmedipham and ethofumesate were sprayed on 21 May, 30 May and 15 June. Fluazifop-P-butyl was sprayed on 21 June to combat wild oats, and pirimicarb on 17 July to combat pests. The crop was harvested on October 24 yielding 147.9 hkg/ha of roots and 38.0 hkg/ha of tops (both 100% dry matter).

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 the 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 a fungicide and a pesticide, propiconazole and dimethoate, respectively, 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).

6.1.3 Model set-up and calibration

The MACRO model was 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 was used to simulate the water flow in the unsaturated zone during the full monitoring period September 1999–June 2002 and to establish an annual water balance.

The model was calibrated to the observed groundwater table measured in the piezometers located in the buffer zone and 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 38). A simple calibration procedure was applied that only necessitated adjustment of the empirical BGRAD parameter regulating the boundary flow and the drain depth, which was determined by the groundwater level during drainage periods. All remaining parameters were based on measured data or literature/default values. For a detailed description of data acquisition, model set-up and calibration procedures, see Kjær *et al.* (2002).

Extending the modelling period to include the third monitoring year revealed problems with the general water balance. A thorough analysis was therefore performed of the measured time series of precipitation and drainage flow at Faardrup. This revealed that the precipitation data logging at Faardrup was influenced by electronic noise, possibly resulting in overestimation of the precipitation input. This noise is not present at any of the other five VAP sites. Until this electronic noise problem is resolved, precipitation measured at Flakkebjerg 3 km east of Faardrup will be used instead. The analysis also resulted in minor adjustments of the measured drainage flow compared to the previous reported data (Kjær *et al.*, 2002).

6.2 Result and discussion

6.2.1 Soil water dynamics and water balances

The model simulations were generally consistent with the observed data, thus indicating a good model description of the overall soil water dynamics in the unsaturated zone. The dynamics and level of the measured groundwater table were well captured by the model, as was the dynamics of the soil water content in all three horizons (Figure 40D, E and F). The dynamics of the drainage pattern also seems to be reasonably well described by the model, although the duration of the drainage periods was not fully captured. This resulted in an underestimation of the drainage flow in all three years by 13 to 63 mm. The difference between measured and modelled drain flow was greatest for the first monitoring period (July 1999–June 2000).

The underestimation of drainage volume might be due to uncertainty in the measurements of precipitation. As described in Section 6.1.3, precipitation measurements from nearby Flakkebjerg were used instead of measured precipitation at Faardrup. The underestimation of drainage volume could thus be due to the use of precipitation input at Flakkebjerg, which might underestimate the precipitation occurring at the Faardrup site. Until the Faardrup data have been further analysed, the Flakkebjerg time series will be used in the model.

The model generally has problems in simulating periods with low drainage flow, probably because these periods are characterized by partial drainage of the Faardrup site due to the topographic slope of the field. During such periods it is likely that only the lowest part of the field contributes to the drainage flow. The one-dimensional model will not be able to match the drainage flow on a field-scale where the groundwater table is above the drain depth in only part of the field. An example is the initial drainage period in 1999 (September to November), when the groundwater table was 1.65 m b.g.s., but 17 mm drained from the field.

The three monitoring periods at Faardrup are characterized as normal to wet years, with precipitation being 2–29 % higher than normal (Table 12). During the first monitoring period there was a long period in spring/summer 2000 with very little precipitation. As a consequence, the soil was very dry during autumn 2000 and the groundwater table was below 3 m. During the second monitoring period the drainage period was short and late, starting as late as January 2001. The model simulation showed that percolation 1 m b.g.s. was very similar for the first and third period, with continuous percolation from September to May. Averaged over the year, no groundwater recharge occurred during the first monitoring period since recharge during the dry months of May/June 2000 (-110 mm) counterbalanced the recharge during the period October 1999—April 2000 (98 mm). Despite the high precipitation input, groundwater recharge decreased to a low level. This can be explained by a combination of a high actual evapotranspiration (due to a winter crop type having high transpiration during winter and spring), a dry period in the spring/early summer and high drainage flow (due to a high groundwater level). In the third monitoring period, estimated total groundwater recharge was 121 mm, mainly due to the wet autumn of 2001 (102 mm).



Figure 40. Soil water dynamics at Faardrup: Measured precipitation and simulated percolation 1 m b.g.s. at Faardrup (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 38).

During the second monitoring period (July 2000–June 2001) precipitation was close to normal at Faardrup, precipitation input being only 2% above the yearly normal precipitation. Despite a fairly wet autumn, percolation did not start until mid November. It continued until July 2001, however. From March to July 2001, drainage flow was low. Because of the initially low groundwater table in autumn 2000 and the dry spring in 2001, drainage flow only totalled 50 mm. Despite the normal precipitation input, the simulated groundwater recharge was significantly higher than for the first and third monitoring periods, reflecting the low evapotranspiration and drainage flow during the second monitoring period.

ing to the method of Affetup and Madsen (1979).									
	Normal precipitation ¹⁾	Precipitation ²⁾	Actual evapotrans- piration	Measured drainage	Simulated drainage	Groundwater recharge ³⁾			
1.7.99-30.6.00	626	715	533	192	129	-10			
1.7.00-30.6.01	626	639	318	50	37	271			
1.7.01-30.6.02	626	810	492	197	174	121			

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⁾ 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

6.2.2 Bromide leaching

The bromide tracer was not detected 1 m b.g.s. until late December 1999, about three months after application (Figure 41A and B). The bromide concentration in the suction cups (1 m b.g.s.) peaked during spring 2000, reaching a maximum of 7.8 mg/l. Evidence of bromide leaching was also found in the analysis of the drainage water samples derived from 1 m b.g.s. (Figure 41C). The bromide breakthrough was similar to that detected in the suction cups located 1 m b.g.s. Still, the concentration during the leaching period 1999/2000 was lower. When interpreting the bromide concentration profiles of the suction cups it should be kept in mind that they were beneath the groundwater table during the winter seasons (as indicated in Figure 40B).

Total recovery during the 3-year monitoring period amounted to 3.6 kg/ha, indicating that only 18% of the applied tracer had leached into the drains. Although concentration levels decreased during 2002, elevated bromide concentrations were detected in both suction cups and drainage water at the end of the monitoring period. The results are thus consistent with those for Silstrup and Estrup, and indicate that part of the bromide is retained in the upper part of the soil profile, probably in the matrix. Bromide can therefore be expected to continue to leach for a long time to come.

The results also showed subsequent minor transport of bromide to a depth of 2 and 3.5 m b.g.s. (Figure 41A, B and D). Slightly elevated bromide concentrations were detected 2 m b.g.s in the suction cups as well as in a horizontal well 3.5 m b.g.s. The bromide concentration in the suction cups located 2 m b.g.s. never exceeded 1 mg/l during 1999/2000, but increased to approx. 2 mg/l during winter 2001/2002 at the same time as the concentration decreased at 1 m b.g.s. A small part of the applied bromide also reached the downstream monitoring wells. Although the concentration and detection frequency were very low, slightly elevated concentrations were detected during autumn 2001 in M4 and M5 and to a minor extent in M6 (Figure 42).



Figure 41. 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 42. 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 began at Faardrup in September 2000 and presently encompasses 18 pesticides and 14 degradation products. Pesticide application is shown together with precipitation and simulated percolation in Figure 43 and Table 13. 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 13).

With bromoxynil, ioxynil, fluroxypyr, fenpropimorph and propiconazole, which were applied to winter wheat in 1999, the leaching risk was found to be negligible at the Faardrup site. Apart from one sample containing less than 0.1 μ g/l of fluroxypyr, fenpropimorph and propiconazole, none of these compounds or their degradation products listed in Table 13 have yet been detected during the two-year monitoring period. For further details, see Kjær *et al.* (2003).

The leaching risk of the pesticides used on sugar beet in 2001 and spring barley in 2002 will not be evaluated until the 2003 monitoring results become available, i.e. when 2 years of monitoring data have been collated. The preliminary findings are that:

- Phenmedipham (0.01–0.02 μg/l) and MHPC (0.03–0.19 μg/l) were each detected in two samples.
- Pirimicarb and its degradation products were detected in several drainage water samples as well as in one groundwater sample, in all cases at concentrations below 0.1 μ g/l. As Pirimor was applied on two separate occasions, it is not possible to relate the findings to any one specific application.
- Glyphosate was applied to the field both in August 1999 and in October 2000. Both ap-• plications were followed by moderate precipitation input, and percolation commenced more than 1.5 months after glyphosate application. The leaching risk of glyphosate is minor at Faardrup as it was only found on 2 occasions in 4 water samples from the drainage system (time-proportional and flow proportional) and in 3 samples from the groundwater monitoring wells. The concentration interval was 0.01-0.093 µg/l. The degradation product AMPA was found more frequently in the drainage water (10 samples), suction cups (4 samples) and in 2 groundwater samples. AMPA was first detected in a suction cup 1 m b.g.s. in April 2001, 5 months after it had last been applied. From May 2001 to January 2002, AMPA was frequently detected at low concentrations (0.02-0.11 µg/l) in both time-proportional and flow-proportional drainage water samples. It was last detected in February in samples from the vertical monitoring well. Since glyphosate was applied on two separate occasions, it is not possible to relate the findings to one specific application. The more frequent detection of AMPA a relatively long time after glyphosate application indicates desorption in the uppermost part of the soil system.

Table 13. Pesticides analysed at Faardrup with the product used shown in parentheses. Degradation products are in italics. Precipitation and percolation are accumulated from date of first application (App. date) until 1 July 2002. 1^{st} month percolation refers to accumulated percolation within the first month after application. C_{mean} refers to weighted average concentration in the drainage runoff. The number of pesticide-positive samples is indicated in parentheses.

Analysed pesticides	App.	Precipitation ¹⁾	Percolation ²⁾	1 st month	C _{mean}
	date	1		percolation ²⁾	
		(mm)	(mm)	(mm)	(µg/l)
Winter wheat 1999					
Glyphosate (Roundup 2000)	Aug 99	2275	979	12	See text
- AMPA	U				See text
Bromoxynil (Briotril)	Oct 00	1847 ²⁾	886 ²⁾	52	< 0.01(0)
Ioxynil (Briotril)	Oct 00	1847 ²⁾	886 ²⁾	52	< 0.01(0)
Fluroxypyr (Starane 180)	Apr 00	1448 ²⁾	568 ²⁾	21	< 0.01(1)
Propiconazole (Tilt Top)	May 00	1548	564	2	< 0.01(1)
Fenpropimorph (Tilt Top)	May 00	1548	564	2	< 0.01(1)
- fenpropimorphic acid					< 0.01(0)
Pirimicarb (Pirimor G)	Jun 00	1463	569	0	See text
- pirimicarb-desmethyl					See text
- pirimicarb-desmethyl-formamido					See text
Sugar beet 2001					
Glyphosate (Roundup 2000)	Oct 00	1312	574	0	< 0.01(7)
- AMPA					0.01(18)
Metamitron (Goltix WG)	May 01	859	316	5	0.01(43)
- metamitron-desamino					0.01(49)
Ethofumesate (Betanal Optima)	May 01	859	316	5	0.06(42)
Desmedipham (Betanal Optima)	May 01	859	316	5	< 0.01(0)
- EHPC					< 0.01(0)
Phenmedipham (Betanal Optima)	May 01	859	316	5	< 0.01(3)
- MHPC					< 0.01(3)
Fluazifop-P-butyl (Fusilade X-tra)	Jun 01	803	310	5	< 0.01(1)
- fluazifop (free acid)					0.02(19)
Pirimicarb (Pirimor G)	Jul 01	310	310	5	< 0.01(11)
- pirimicarb-desmethyl					<0.01(9)
- pirimicarb-desmethyl-formamido					< 0.01(3)
Spring barley 2002					
Flamprop-M-isopropyl (Barnon Plus)	May 02	95	0	0	- (0)
- Flamprop-M (free acid)					- (0)
MCPA (Metaxon)	May 02	116	0	0	- (0)
- 4-chlor,2-methylphenol					- (0)
- Triazinamin-methyl ³⁾ (Express)	May 02	119	6	6	- (0)
Dimethoate (Perfection 500 S)	Jun 02	84	-1	-1	- (0)
Propiconazole (Tilt 250 EC)	Jun 02	84	-1	-1	- (0)

Chemical Abstracts nomenclature for the analysed pesticides is given in Appendix 1

¹) Weighted average concentration within the first drainage season after application (See Appendix 2 for calculation methods)

²⁾ Accumulated from date of application until monitoring ceased on 1 April 2002

³⁾ Degradation product of tribenuron methyl. The parent compound degrades too rapidly to be detected by monitoring



Figure 43. Pesticide application, precipitation (primary axis) together with simulated percolation (secondary axis) at Faardrup. Etho.: ethofumesate; Desm.: desmedipham; Phenm.: phenmedipham. Pesticides applied later than April 2002 are not included.

Metamitron, metamitron-desamino, ethofumesate and fluazifop (free acid) were found • to leach from the root zone, reaching both the drainage system and one monitoring well. All four compounds were detected in high concentrations in the drainage system in June/August 2001 after an intense precipitation event, indicating rapid macropore transport (Figure 44). Drainage runoff was very low (<1 mm) during this period, however. Despite the high concentrations, the total mass of the four compounds that leached out was small. The concentrations decreased after a short time, and were 0.01-0.05 µg/l during autumn 2001. When runoff eventually started to increase in January 2002 the concentrations of all four compounds were below the detection limit. As a consequence the average concentrations were low, ranging from 0.01 to 0.06 µg/l (Table 13). These four compounds were also very frequently detected in one of the monitoring wells, M5 (Figure 45 and Appendix 7). Thus ethofumesate, metamitron and metamitron-desamino were found in all 3 screens starting in August 2001, when the groundwater table was about 2 m b.g.s. At the same time bromide was detected at M5 in slightly elevated bromide concentrations, thus providing additional evidence that percolating water from the treated area had reached M5. During autumn 2001, the compounds were detected in concentration exceeding 0.1 µg/l in several samples from M5, but were not detected in any of the other monitoring wells (Appendix 7).

Evidence of rapid movement of surface-near water to M5 was also provided by the inorganic data (Appendix 8). Following the dry summer of 2000 chloride and nitrate concentrations decreased in M5, but remained more stable in other monitoring wells (M6 and M4). The summer of 2000 was characterized by an extremely low soil water saturation (May– September) and a groundwater table that fell to 3 m b.g.s. (Figure 40). The extreme low soil water content entails the possibility that deep desiccation fractures could penetrate from the root zone down towards the underlying till and hence enable rapid transport of near-surface water to the monitoring screens.

When interpreting the detection of pesticides in M5, however, it should be kept in mind that the lower filters of M5 were hydraulically interconnected. Thus purging of the second-lowest filter (3.5–4.5 m b.g.s.) affected the overlying screen (2.5–3.5 m b.g.s.) in terms of a decreasing groundwater table. M5 is located downstream of the test site in till interbedded with thin sandy till lenses. The hydraulic connection between the filters is probably attributable to these lenses of sandy till (Lindhardt *et al.*, 2001).

In conclusion, pesticides and their degradation products were transported through the unsaturated zone and reached the uppermost screen of M5. The detection of pesticides in the deeper screens should be interpreted with caution, however, as this might possibly be caused by screen purging. To clarify this matter, additional purging tests are planned in 2003. Moreover, a tracer test will also be conducted near well M5 to determine whether the frequent detection of pesticides at this well is attributable to fracture transport.



Figure 44. Precipitation (A) together with concentration of metamitron (B), metamitron-desamino (C), ethofumesate (D) and fluazifop-P (free acid) in the drainage runoff at Faardrup. The green vertical lines indicate the date of application.



Figure 45. Measured concentration of bromide (A), metamitron (B), metamitron-desamino (C), ethofumesate (D) and fluazifop-P (free acid) (E) in the vertical monitoring well M5 at Faardrup. Well positions are indicated in Figure 38. The green vertical lines indicate the date of pesticide application. Bromide was applied in October 1999.

6.3 Summary

The risk of pesticide leaching at Faardrup can be summarized as follows:

• With bromoxynil, ioxynil, fluroxypyr, fenpropimorph and propiconazole applied to winter wheat in 2000 the leaching risk was found to be negligible.

The leaching risk of pesticides applied in 2001 and 2002 cannot be fully evaluated at present as the potential leaching period extends beyond the current monitoring period. The preliminary findings are that:

- Desmedipham was not detected, whereas two samples were found to contain phenmedipham $(0.01-0.02 \ \mu g/l)$ and MHPC $(0.03 0.19 \ \mu g/l)$.
- Pirimicarb and its degradation products were detected in several samples, although always at concentrations below $0.1 \mu g/l$.
- Glyphosate was detected at low concentrations in a very small number of samples. The degradation product AMPA was frequently detected for a relatively long period following application, thus indicating minor desorption in the uppermost metre of the soil. Apart from one sample containing 0.11 µg/l of AMPA, the concentration was always below 0.1 µg/l.
- Metamitron, metamitron-desamino, ethofumesate and fluazifop (free acid) were frequently detected in both drainage water and one monitoring well. Their average concentrations in the drainage water ranged from 0.02 to 0.06 μ g/l.

7 Pesticide leaching at Slaeggerup

7.1 Materials and methods

7.1.1 Site description and monitoring design

The Slaeggerup test site is located on Zealand near the village of Slaeggerup northeast of Roskilde (Figures 1 and 46). The test field area is 2.2 ha (130 x 165 m). The ground surface within the test field slopes gently (1-4°) towards the northeast, the difference in altitude between highest and lowest levels being around 4.5 m. Three soil profiles were excavated on the site, all of which are classified as Typic Argiudoll (Soil Survey Staff, 1999). The topsoil content of clay within the three profiles was 19-24%, whereas the organic matter content was 1.8–2.4%. The sediments penetrated when drilling the piezometers and monitoring wells could be subdivided into three lithological units (Figure 47). The upper unit was generally up to 2.5 m thick. Its uppermost part (0-0.65 m) consisted of meltwater clay with numerous desiccation cracks and biopores. Further down, the unit consisted of sandy meltwater gravel and then gravely meltwater sand. Within these two parts there were only small vertical and horizontal fractures. The middle unit consisted of up to 4 m of clay till with numerous horizontal and vertical fractures. The largest of these fractures traversed the entire unit and ended at the lowest unit consisting of sand till. The sand had no fractures. The content of clay decreased with depth from around 55% in the meltwater clay of the upper unit to 16.3% in the sand till of the lowest unit. 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).

7.1.2 Agricultural management

Herbicide spraying was carried out on 9 May 2000 using metsulfuron-methyl, on 5 June using flamprop-M-isopropyl and on 14 June using tribenuron methyl. Fungicide spraying was carried out on 9 June and 26 June with propiconazole and fenpropimorph. The pesticide dimethoate was sprayed on 9 June. The crop was harvested on 8 August yielding just 39.8 hkg/ha of grain and 10.2 hkg/ha of straw (85% and 100% dry matter, respectively), which is about half of the normal yield for the location. The low yield is probably attributable to the fact that installation of monitoring equipment had prevented autumn ploughing, and the field was instead ploughed in the spring. As a consequence seedbed establishment was poor, as reflected in the very low final plant number (only 142 plants/m²). The harvested field was ploughed in November 2000.



Figure 46. Overview of the Slaeggerup 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).



Figure 47. Geological description of the Slaeggerup site (Lindhardt et al., 2001).

Field peas were sown on 11 April 2001. Weeds were spayed with bentazone and pendimethalin on 1 May and pests with pirimicarb. It was intended that fluazifop-P-butyl should be sprayed to combat wild oats, but this was erroneously omitted. Due to heavy infestation, the wild oats had to be weeded out by hand. From the beginning of June the field was heavily invaded by wood pigeons (L. *Columba palumbus*). According to an official from the Danish Forest and Nature Agency, problems with wood pigeons are widespread on Zealand. In this particular year, the late sowing caused by rainy conditions further aggravated the problem caused by the wood pigeons. At the time they need large amounts of food for their young, the height of the pea plants will normally keep them from landing in the field. This was not the case, however. In spite of considerable effort to control bird damage using advanced scarecrows, balloons painted as birds of prey, and culling, pea yield at harvest on 19 August was only 26.6 hkg/ha (86% dry matter), which is around half of the normal yield.

On 26 September 2001 the field was sprayed with glyphosate in the form of Roundup Bio (using 4.0 l/ha), at which time it still had not been possible to remove the pea residues. On 10 October it was decided to shred the residues and on 13 October the field was ploughed. Two days later the field was sown with winter wheat (cv. Bill). The wheat emerged on 1 November. One week later, ioxynil and bromoxynil were sprayed to combat weeds. Weeds were sprayed again on 22 April using amidosulfuron and on 15 May using flamprop-M-isopropyl. Fungicide spraying was carried out on 31 May and 14 June using propiconazole, and pests were sprayed using pirimicarb on 14 June. The winter wheat was harvested on 20 August 2002 yielding 72.3 hkg/ha of grain (85% dry matter). The yield was lower than normal for the location, probably due to the late sowing caused by the wet weather of autumn 2001. Management practice at the site is detailed in Appendix 3 (Table A3.6).

7.1.3 Model set-up and calibration

The MACRO model was applied to the Slaeggerup 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 the water flow in the unsaturated zone during the full monitoring period April 2000–June 2002 and to establish an annual water balance.

The model was calibrated to the observed groundwater table measured in the piezometers located in the buffer zone as well as to three time series of soil water content measured at 25, 60 and 110 cm b.g.s. in the two profiles S1 and S2 (see Figure 46). A simple calibration procedure was applied that only necessitated adjustment of the empirical BGRAD parameter regulating the boundary flow and the drain depth, which was determined by the groundwater level during drainage periods. All remaining parameters were based on measured data or literature/default values. For a detailed description of data acquisition, model set-up and calibration procedures, see Kjær *et al.* (2002).

7.2 Results and discussion

7.2.1 Soil water dynamics and water balances

The model simulations were generally consistent with the observed data during the whole monitoring period, thus indicating that the model describes the overall soil water dynamics in the unsaturated zone reasonably well. The model was able to match the measured groundwater table, and the dynamics of the soil water as determined from the TDR probes was well captured by the model.

Measured drainage flow during the first winter period was very low (11 mm). The next winter the flow was ten-fold greater (110 mm). The model simulation yielded similar figures (7 and 116 mm, respectively), but the modelled drainage flow was delayed compared to the measured drainage flow in the first monitoring year. The measured drainage flow started to accumulate in mid December 2000, at which time the groundwater table was located 2 m b.g.s. Thus it was not possible to match the dynamics of the measured drainage flow without an unreasonable increase in the groundwater level or an unreasonable low drain depth. A better description of the drainage dynamics was obtained the following year, when the two major flow events are well captured. The overall trends in soil water content as measured by the TDR probes were successfully modelled (Figure 48D, E and F).

	Normal precipitation ¹⁾	Precipitation	Actual evapotrans- piration	Measured drainage	Modelled drainage	Groundwater recharge ²⁾
1.7.99–30.6.00 ³⁾	660	511	392	_	0	119 ⁴⁾
1.7.00-30.6.01	660	683	343	11	7	328
1.7.01-30.6.02	660	823	472	110	116	241

Table 14. Annual water balance for Slaeggerup (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) Groundwater recharge is calculated as precipitation - actual evapotranspiration - measured drainage

3) The monitoring was started in April 2000

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

The first monitoring period (July 2000–June 2001) was close to normal at Slaeggerup, whereas the following year was wet (Table 14). The previous year was very dry with 17% less precipitation than normal. The modelled, accumulated drainage flow corresponded well to the measured drainage flow for both years. The simulated groundwater recharge differed significantly between the years, ranging from 119 mm in 1999/2000 to 328 mm in 2000–2001, probably because of the large precipitation deficit during 1999/2000 and the limited drainage flow in 2000/2001. The high evapotranspiration in 2001/2002 is due to the crop (winter wheat) and the wet soil conditions during the growing season in the spring and early summer 2002. As shown by the modelled percolation 1 m b.g.s., spring and summer 2002 were characterized by continued percolation until the end of the monitoring period at the end of June 2002 (Figure 48A). In the previous two years, in contrast, percolation ceased at the beginning of June.

Bromide tracer studies could not be carried out at Slaeggerup because the water supply authorities refused permission due to the presence of a large municipal drinking water supply in the vicinity. Hence, no bromide data are available to verify water transport patterns.



Figure 48. Soil water dynamics at Slaeggerup: Locally measured precipitation and simulated percolation at 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 46).

7.2.2 Pesticide leaching

Monitoring at Slaeggerup began in April 2000 and presently encompasses 12 pesticides and 8 degradation products (Figure 49 and Table 15). It should be noted that precipitation in Table 15 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) 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 15.

Table 15. Pesticides analysed at Slaeggerup with the product used shown in parentheses. Degradation products are in italics. Precipitation and percolation are accumulated from date of first application (App. date) until 1 July 2002. 1^{st} month percolation refers to accumulated percolation within the first month after application. C_{mean} refers to weighted average concentration in the drainage runoff. The number of pesticide-positive samples is indicated in parentheses.

Analysed pesticides	App. date	Precipitation	Percolation	1 st month percolation	C _{mean} ¹⁾
		(mm)	(mm)	(mm)	(µg/l)
Spring barley 2000			<u>·</u> ·		
Metsulfuron-methyl (Ally) - triazinamin	May 00	1554	667	10	<0.01(0) <0.01(0)
Flamprop-M-isopropyl (Barnon Plus) - <i>flamprop (free acid)</i>	Jun 00	1527	657	0	<0.01(5) <0.01 (1)
Propiconazole (Tilt Top)	Jun 00	1522	656	0	< 0.01 (0)
Fenpropimorph (Tilt Top) - fenpropimorphic acid	Jun 00	1522	656	0	<0.01 (0) <0.01 (1)
Dimethoate (Perfection 500 S)	Jun 00	1522	656	0	< 0.01 (0)
Triazinamin-methyl ²⁾ (Express)	Jun 00	1522	656	0	< 0.01 (0)
Peas 2001					
Pendimethalin (Stomp SC)	May 01	930	408	22	< 0.01 (1)
Bentazone (Basagran 480)	May 01	930	408	22	0.02(11)
- 2-amino-N-isopropyl-benzamid					< 0.01 (0)
Pirimicarb (Pirimor G)	Jul 01	826	373	0	< 0.01(1)
- pirimicarb-desmethyl					< 0.01(0)
- pirimicarb-desmethyl-formamido					< 0.01(0)
Winter wheat 2002					
Glyphosate (Roundup Bio) - AMPA	Sep 01	529	314	50	0.04(21) 0.06(24)
Ioxynil (Oxitril)	Nov 01	454	259	39	< 0.01(3)
Bromoxynil (Oxitril)	Nov 01	454	259	39	< 0.01(1)
Amidosulfuron (Gratil)	Apr 02	173	9	6	- (0)
Flamprop-M-isopropyl (Barnon Plus) - <i>flamprop-free acid</i>	May 02	127	5	5	- (0) - (0)
Propiconazole (Tilt 250 EC)	Jun 02	98	2	0	- (0)
Pirimicarb (Pirimor G) - pirimicarb-desmethyl	Jul 02	67	0	0	- (0) - (0)
- pirimicarb-desmethyl-formamido					- (0)

Chemical Abstracts nomenclature for the analysed pesticides is given in Appendix 1

¹⁾ Weighted average concentration in the first drainage season after application (See Appendix 2 for calculation methods)

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



Figure 49. Pesticide application and precipitation (primary axis) together with simulated percolation 1 m b.g.s. (secondary axis) at Slaeggerup. Pesticides applied later than April 2002 is not included.

With metsulfuron-methyl, propiconazole, triazinamin-methyl, dimethoate and fenpropimorph, the leaching risk was found to be negligible at the Slaeggerup site. Apart from one drainage sample containing 0.25 μ g/l fenpropimorphic acid, none of these compounds or their degradation products listed in Table 15 have yet been detected during the two-year monitoring period. All of these compounds were applied during summer 2000, when precipitation input was close to normal and almost counterbalanced by actual evapotranspiration such that there was little percolation during the first month after application. The detection of fenpropimorphic acid at a concentration of 0.25 μ g/l occurred in connection with a major storm event on 5 September 2000 (58 mm of precipitation) (Figure 49).

Flamprop-M-isopropyl and flamprop (free acid) were detected at Slaeggerup, but only in a few water samples. Following the major storm event on 5 September, they were detected at a concentration of 0.02 μ g/l and 0.35 μ g/l, respectively, in a single flow-proportional drain



Figure 50. Precipitation (A) together with the drainage water concentration of glyphosate (B) and AMPA (C) at Slaeggerup. The green vertical line indicates the date of application.

age water sample. In addition, flamprop-M-isopropyl was detected in five drainage water samples at concentrations of $0.014-0.035 \mu g/l$. For further details, see Kjær *et al.* (2002).

The leaching risk of pesticides used on both the pea crop in 2001 and the winter wheat crop in 2002 will not be evaluated until the 2003 monitoring results become available, i.e. when two years of monitoring data have been collated. The preliminary findings are that:

• On 16 May, just 16 days after application, bentazone was detected at a concentration of 0.01 µg/l in soil water sampled 1 m b.g.s. at S2 as well as in the two uppermost screens of the vertical well M6. The following autumn, minor leaching of bentazone was detected. Bentazone was thus found in one flow-proportional sample of drainage water collected on 24 October 2001 (0.024 µg/l) and in five time-proportional samples collected between 6 February and 12 March 2002 (0.01–0.03 µg/l). The average concentration in the drainage water during the 2002/2003 leaching period was 0.02 µg/l.

• On 27 November 2001, 13 days after application, ioxynil and bromoxynil were detected in a time-proportional drainage water sample at concentrations of 0.18 μ g/l and 0.14 μ g/l, respectively. Moreover, ioxynil was detected at a concentration of 0.02 μ g/l in a time-proportional sample collected on 4 December 2001 and at a concentration of 0.046 μ g/l in a flow-proportional sample collected on 1 March 2002.

•

August and in particular September 2001 were rainier than usual, causing drainage flow earlier than usual for the location (Figure 48; Appendix 4). When the field was sprayed with Roundup Bio (4.0 l/ha) on 26 September 2001, drainage flow had been occurring for a good week, although at very low levels (0.1 to 0.3 mm ha/day). When glyphosate and AMPA initially appeared in the drainage water just six days after application and after 34 mm of precipitation, the level of drainage flow was low. When the concentrations subsequently started to increase, the flow was still low due to a dry November and December (Figure 50; Appendix 4). Despite the very high concentrations detected (5.1 μ g/l glyphosate and 5.4 μ g/l AMPA), the amount leached during this period was thus very small. When runoff eventually started to increase due to the wetter than normal weather in January and February (Appendix 4), the concentration of both glyphosate and AMPA had decreased to low levels (Figure 50; Appendix 9). During the 2001/2002 leaching season, the average drainage water concentration of glyphosate was 0.04 µg/l, while that of AMPA was 0.06 µg/l. Apart from a single sample containing 0.017 µg/l AMPA, glyphosate and AMPA were not detected in samples from the groundwater monitoring wells.

No evidence was found to indicate leaching of the other pesticides applied in 2001 and 2002 since they were only detected in two samples, one containing 0.01 μ g/l pirimicarb and one containing 0.01 μ g/l pendimethalin (Table 15).

7.3 Summary

At Slaeggerup, the leaching risk of pesticides applied in 2000 can be summarized as follows:

- With metsulfuron-methyl, propiconazole, triazinamin-methyl fenpropimorph and dimethoate, the leaching risk was found to be negligible.
- Flamprop-M-isopropyl and flamprop (free acid) were detected, but only in very few samples and only in one case at a concentration exceeding $0.1 \mu g/l$.

The leaching risk of pesticides applied in 2001 and 2002 cannot be fully evaluated at present as the potential leaching period extends beyond the current monitoring period. The preliminary findings are that:

- There was no evidence to indicate leaching of pentimenthalin and pirimicarb, both compounds only being detected in a single sample in very low concentrations (0.01 μ g/l).
- Bromoxynil, ioxynil, flamprop-M-isopropyl and dimethoate were detected, but only in very few water samples.
- Bentazone, glyphosate and AMPA did leach from the root zone, but not at unacceptable levels. During the 2001/2002 leaching period the average concentration of bentazone in the drainage water was 0.02 μ g/l, while that of glyphosate and AMPA was 0.04 and 0.06 μ g/l, respectively. Bentazone was only detected in three samples from the ground-water monitoring wells (0.01 μ g/l), while AMPA was detected in one sample (0.017 μ g/l).

8 Degradation and sorption parameters

Information on degradation and sorption is of considerable importance for determining the fate of pesticides, including for the modelling of leaching. Site-specific information is usually sparse, however, and data from the literature often have to be used instead. To eliminate the uncertainty associated with the use of data from the literature and facilitate interpretation of the results of pesticide analyses, the present project incorporates studies on both half-life and K_d (K_{oc}) in Danish soils to demonstrate degradation and sorption, respectively. Microbial biomass and microbial activity of the soils at the sites were also determined to clarify the level of microbial activity in the soil. The degradation and sorption parameters have been determined for combinations of seven pesticides and six soil types (both plough layer and subsoil) (Table 16). With fenpropimorph and flamprop-M-isopropyl, important degradation products were also investigated.

Active ingredient	Trade name	Application rate	Investigated sites
		(g a.i./ha)	
Bromoxynil (H)	Briotril, Oxitril	200	Faardrup, Slaeggerup
Dimethoate (I)	Perfection 500 S	300	Estrup, Slaeggerup
Fenpropimorph (F)	Tilt Top	375	Tylstrup, Jyndevad, Faardrup, Slaeggerup
Flamprop-M-isopropyl (H)	Barnon Plus	630	Estrup, Slaeggerup
Ioxynil (H)	Briotril, Oxitril	200	Faardrup, Slaeggerup
Metamitron (H)	Goltix WG	2100	Silstrup, Faardrup
Propiconazole (F)	Tilt Top	125	Tylstrup, Jyndevad, Faardrup, Slaeggerup

 Table 16. Soil-pesticide combinations included in the degradation and sorption studies.

H: Herbicide, I: Insecticide, F: Fungicide

8.1 Materials and methods

8.1.1 Soil sampling

Degradation and sorption were determined in the laboratory using pooled soil samples. The samples were collected as short a time preceding pesticide application as possible from both the plough layer (0-20 cm) and the subsoil (80-100 cm). To avoid microbial and chemical contamination, the sampling equipment was cleaned with ethanol prior to use.

The plough layer samples were collected using a hand auger (2 cm inner diameter and 20 cm long). A sample based on 50 to 100 subsamples was collected from the plough layer within the test field at the Tylstrup, Silstrup, Estrup, and Slaeggerup sites. At the other two sites, Jyndevad and Faardrup, spraying had been carried out before soil sampling could be undertaken and the samples were therefore collected from the buffer zone surrounding the test field. Subsoil samples were collected from the walls of two 50 x 100 cm pits excavated in the buffer zone with the samples being collected horizontally. Each sample consisted of at least 2 kg of soil per substance per field per depth.

The samples were stored at 5°C until needed for the experiments. All results are expressed on a dry weight basis. Prior to the experiments, the soils were homogenized and sieved (2 mm) to remove any stones and plants.

8.1.2 Microbial biomass and activity

Microbial biomass was measured using the substrate-induced respiration (SIR) method (Anderson and Domsch, 1978), which is a physiological method based on the increase in the respiration rate when glucose is added to the soil. The concentration of glucose yielding the most CO_2 was determined prior to the experiment. CO_2 evolution was measured by gas chromatography. Microbial activity was measured by the degradation of ¹⁴C-labelled Na-acetate. ¹⁴C Na-acetate (5 µg/g) was added to the soil in an Erlenmeyer flask and the ¹⁴CO₂ evolved was collected and counted using a scintillation counter. All studies were performed in quadruplicate.

8.1.3 Incubation of soil

The degradation studies were performed on mixed, homogenized soil from each field site. After homogenization, the water content of the soil was determined. The soil was air-dried and sieved. During the drying process the soil was mixed frequently to avoid excessive drying of part of the soil. For each degradation experiment, 10 replicates of each soil were prepared in Erlenmeyer flasks. An aquatic solution of the test pesticide was added to each flask and the water content adjusted to 40–60% of the water holding capacity (WHC). The initial pesticide content was 0.5 mg/kg dry soil. The plough layer (0–20 cm) and subsoil (80–100 cm) samples were incubated at 20°C and 10°C, respectively. The Erlenmeyer flasks were closed with rubber stoppers and hydrophobic cotton, which allowed diffusion of air and minimized desiccation of the soil during incubation.

At certain time intervals the incubation was discontinued for one replicate at a time, and the soil sample stored at -18°C until analysis. The time intervals were set for each pesticide according to the half-life reported in the literature, ensuring that the incubation period encompassed at least three half-lives. Each degradation experiment was performed in duplicate.

8.1.4 Analysis

The extraction of pesticides was normally performed by ASE (Accelerated Solvent Extraction) at specific temperatures, pressures and duration. Exceptions were fenpropimorph and propiconazole, which were extracted and afterwards shaken on a Mastermixer (Spliid, 2000). Dimethoate was detected by means of GC/MS, whereas the other pesticides were detected by means of LC/MS (Tabel 17). Blanks and recovery were analysed in each run of the ASE apparatus and for each batch of shaking. If recovery differed significantly from 100%, the results were corrected to 100% recovery. Certificate standards were obtained from Dr. Ehrenstorfer in Germany. Stability tests were performed by adding the pesticides to soil samples and then storing them at -18°C for a period corresponding to the storage period of the test samples. If the recovery was low, the analytical results were corrected to 100% recovery. The detection limits for the pesticides and degradation products are shown in Table 17.

Pesticide	Site and soil depth	Detection limit (µg/kg)	Detection
Bromoxynil	Slaeggerup 0-20 cm	10.1	LC/MS
Dimethoate	Estrup 0–20 cm	18.5	GC/MS
Fenpropimorph	Faardrup 80–100 cm	5.5	LC/MS
Fenpropimorph acid	Faardrup 80–100 cm	4.7	LC/MS
Flamprop-M-isopropyl	Slaeggerup 0-20 cm	14.2	LC/MS
Flamprop-M-isopropyl acid	Slaeggerup 0-20 cm	4.8	LC/MS
Ioxynil	Faardrup 80–100 cm	3.7	LC/MS
Propiconazole	Jyndevad 0-20 cm	2.4	LC/MS

 Table 17. Detection limits for the pesticides and degradation products included in the degradation and sorption studies.

8.1.5 Degradation kinetics

The registration procedures for pesticides and many published degradation studies assume that the degradation of pesticides follows simple first-order degradation kinetics. The half-life is thus estimated and used for further evaluation. A number of recent publications have shown that a two-compartment $1^{st} + 1^{st}$ order model better describes the degradation processes (Fomsgaard, 1999). In a two-compartment model, one part of the added pesticide is rapidly degraded, while another part is adsorbed to the soil, and thus degraded much more slowly.

Once a sufficient number of data points had been obtained, a curve-fitting analysis was performed comparing the use of a simple 1^{st} order model and a two-compartment $1^{st} + 1^{st}$ order model. The modelling was performed using the software TableCurve 2D. The mathematical expressions are:

 I^{st} order model: $c(t) = a \cdot e^{-k_1 \cdot t}$

 $I^{st} + I^{st}$ order model: $c(t) = a \cdot e^{-k_1 \cdot t} + b \cdot e^{-k_2 \cdot t}$

Where:

c(t) = amount of pesticide remaining at time t

a = initial amount of pesticide degraded through one I^{st} order process

b = initial amount of pesticide degraded through the other 1^{st} order process

t = time in days

 k_1 = degradation rate constant 1

 k_2 = degradation rate constant 2

8.1.6 Determination of sorption

Sorption was determined in both plough layer and subsoil samples. The soil samples were sieved (2 mm) and homogenized. To reduce microbial activity the soils were irradiated with 10 Kgray. Sorption experiments were carried out in a manner similar to that described in OECD (1997). The ratio between soil and 0.01 M CaCl₂ was fixed on the basis of literature values for K_d as described in Table 18. The ratio was selected in order to obtain an acceptable concentration ratio after equilibration. All experiments were performed in triplicate using the same concentration of unlabelled pesticides. After shaking the soil with 0.01 M

 $CaCl_2$ for 24 hours the suspension was centrifuged, and the concentration of the pesticide in the aqueous phase determined by LC/MS. The pesticide concentration sorbed on soil was then calculated, and the constants K_d and K_{oc} calculated as follows:

 $K_{d} = \frac{\mu g \text{ pesticide / g soil}}{\mu g \text{ pesticide / ml solution}}$ $K_{oc} = \frac{K_{d} \cdot 100}{\text{total organic carbon}}$

Table 18. Pesticide concentrations and water:soil ratios used in the sorption experiments.

	Pesticide concentration (mg/l)	Water:soil ratio
Plough layer (0–20 cm)		
Bromoxynil, dimethoate, flamprop-M-isopropyl, ioxynil, metamitron	0.5	5
Fenpropimorph, propiconazole	0.5	12.5
Subsoil (80–100 cm)		
Bromoxynil, dimethoate, flamprop-M-isopropyl, ioxynil, metamitron,		
propiconazole	0.5	1

8.2 Results and discussion

8.2.1 Soil characteristics

As could be expected, the microbial biomass and the content of total organic carbon were significantly greater in the plough layer than in the subsoil at all test sites (Table 19). The biomass was highest in the soil from Silstrup (641 mg biomass C/kg) and lowest in the sandy soil from Tylstrup and Jyndevad (142 and 194 mg biomass C/kg, respectively). The high microbial biomass at Silstrup might be due to the frequent application of manure at the site in previous years (Lindhardt *et al.*, 2001). The microbial activity is expressed as the percentage ¹⁴C evolved in the form of ¹⁴CO₂ from ¹⁴C-labelled acetate during 2 and 96 hours of incubation (Table 19). The evolution from plough layer soil was fastest in soil from Estrup (20% evolved after 2 hours) and slowest in soil from Faardrup (9% evolved after 2 hours). After 96 hours, almost the same percentage had evolved from all soils. In the subsoil, ¹⁴CO₂ evolution after 2 hours amounted to less than 2% in all soils, thus confirming the low microbial biomass in these soils. On the other hand, more than 40% of the ¹⁴C from ¹⁴C-labelled acetate had evolved after 96 hours, thus indicating the potential for degradation of the very easily degradable acetate.

		Tylstrup	Jyndevad	Silstrup	Estrup	Faardrup	Slaeggerup
Total organic carbon (%)							
	0–20 cm	2.0	1.9	2.2	3.2	1.3	1.2
	80–100 cm	0.5	0.1	0.2	0.3	0.1	0.1
Microbial biomass ¹⁾ (mg C/kg soil)							
	0–20 cm	142	194	641	430	372	346
	80–100 cm	17	42	48	54	35	38
Microbial activity $^{2)}$ (% C ¹⁴ evolved)							
	0–20 cm						
	- 2 hours	16	18	14	20	9	15
	- 96 hours	35	34	29	38	34	37
	80–100 cm						
	- 2 hours	1.8	1.3	0.9	0.8	0.8	0.7
	- 96 hours	45	55	41	53	40	36

Table 19. Organic carbon, microbial biomass and microbial activity determined in the plough layer (0-20 cm) and the subsoil (80-100 cm) at the PLAP sites.

¹⁾ Determined using the SIR method

²⁾ Determined using the Na-acetate method

All the experiments were performed on homogenized soil samples. To confirm that the soils were properly mixed, ¹⁴CO₂ evolution from 8 individual samples was determined after addition of acetate (2 replicates). The evolution was almost identical during the whole experimental period. Even though the ¹⁴C-Na-acetate method is not very sensitive to minor

differences in soil microbial activity, the identical evolution of ${}^{14}CO_2$ from the individual soil samples indicates that homogenization of the soil samples was satisfactory.

8.2.2 Sorption

The results of the sorption studies are summarized in Table 20.

Table 20. Site-specific sorption coefficients for each of the pesticides analysed. K_d is the mean of triplicate measurements ±SD. The organic carbon content of the soils is also shown. Literature K_{oc} ranges are included for comparison.

Pesticide	Field and soil depth	K _d	Org. C	K _{oc}	Literature $K_{oc}^{(1)}$
		(ml/g)	(g/100g)	(ml/g)	(ml/g)
D (1 2)					100 (01
Bromoxynil ²	F 1 0 00		1.0	07	108–634
	Faardrup 0–20 cm	1.2 ± 0.02	1.3	8/	
D' d i	Slaeggerup 0–20 cm	1.3 ± 0.1	1.2	106	1 6 50
Dimethoate			2.2	0.6	16-52
	Estrup $0-20 \text{ cm}$	2.7 ± 0.5	3.2	86	
	Estrup 80–100 cm	0.8 ± 0.8	0.29	• • •	
	Slaeggerup 0–20 cm	2.5 ± 0.3	1.2	203	
	Slaeggerup 80–100 cm	0.4 ± 0.6	0.13		
Fenpropimorph ²	T 1		• •		2817-4319
	Tylstrup 0–20 cm	38 ± 0.7	2.0	1875	
	Jyndevad 0–20 cm	30 ± 3	1.9	1532	
	Faardrup 0–20 cm	61 ±12	1.3	4581	
	Slaeggerup 0–20 cm	93±15	1.2	7496	
Flamprop-M-isopropyl					197–235
	Estrup $0-20$ cm ²⁾	29 ±2	3.2	888	
	Slaeggerup 0–20 cm	6.8 ± 0.5	1.2	552	
	Slaeggerup 80–100 cm	2.0 ± 0.03	0.13		
Ioxynil					234-1420
	Faardrup 0–20 cm	2.9 ± 0.03	1.3	219	
	Faardrup 80–100 cm	0.1 ± 0.02	0.15		
	Slaeggerup 0–20 cm ²⁾	1.9 ± 0.2	1.2	155	
Metamitron					17-700
	Silstrup 0–20 cm	3.5 ± 0.1	2.2	160	
	Silstrup 80–100 cm	0.4 ± 0.05	0.22		
	Faardrup 0–20 cm	1.7 ± 0.2	1.3	128	
	Faardrup 80–100 cm	0.1 ± 0.01	0.15		
Propiconazole					386-1813
-	Tylstrup 0–20 cm	40 ± 9	2.0	1989	
	Tylstrup 80–100 cm	2.6 ± 0.4	0.46		
	Jyndevad 0–20 cm	21 ±4	1.9	1112	
	Jyndevad 80–100 cm	1.1 ± 0.4	0.13		
	Faardrup 0–20 cm	11 ±4	1.3	891	
	Faardrup 80–100 cm	1.8 ±0.2	0.15		
	Slaeggerup 0–20 cm	14 ± 7	1.2	1196	
	Slaeggerup 80–100 cm	2.4 ± 0.8	0.13		

¹⁾ Linders et al., 1994; Lindhardt et al., 1998; Lindhardt et al., 2001; Roberts, 1998 ²⁾ The sorption data only pertain to the topsoil (0–20 cm). Several sorption studies were performed in subsoil, but could not be calculated (see text for further explanation)
Comparison of K_d for the individual pesticides in different soils reveals that compounds such as flamprop-M-isopropyl, metamitron and propiconazole exhibit increasing adsorption with increasing soil organic matter content. This correlation was less obvious for dimethoate, fenpropimorph, ioxynil and bromoxynil.

Compared with the literature values, K_{oc} was relatively low for bromoxynil and ioxynil, whereas K_{oc} for dimethoate and flamprop-M-isopropyl was high. With fenpropimorph, K_{oc} was lower than the literature range on sandy soils, but higher on loamy soils. K_{oc} of metamitron was within the literature range, while that of propiconazole was at the higher end of the literature range.

The data confirmed that sorption is generally very low in the subsoil, probably due to the very low organic matter content (Table 19). Due to the very low carbon content, K_{oc} has not been calculated for the subsoil analyses. K_d in subsoil was negative for flamprop-M-isopropyl in Estrup soil, for ioxynil in Slaeggerup soil and for bromoxynil in both Faardrup and Slaeggerup soil (data not shown). K_d could not be calculated for fenpropimorph in the subsoils.

8.2.3 Degradation

The degradation parameters for 6 pesticides in plough layer and subsoil are shown in Table 21. In the plough layer, the half-lives for the very short-lived pesticides bromoxynil, ioxynil and dimethoate varied little between soils, being less than one day for bromoxynil and ioxynil and up to a few days for dimethoate. With fenpropimorph, flamprop-M-isopropyl and propiconazole the inter-pesticide variation was much greater, as was the inter-site variation for the individual pesticides.

With propiconazole the first order half-lives varied from 106 to 444 days in these laboratory experiments in the order Faardrup < Jyndevad < Tylstrup < Slaeggerup. The difference in rate of degradation between the Faardrup, Jyndevad and Tylstrup soils may be due to the decreasing biomass (372, 194 and 142 mg C/kg, respectively) and increasing adsorption (11.8, 21.3 and 40.0, respectively). The correlation between degradation and biomass/sorption is less clear for the Slaeggerup soil, however. With fenpropimorph the degradation rate was also highest in the Faardrup soil and decreased in the order Faardrup > Jyndevad > Tylstrup. As mentioned above, the biomass decreased in the same order. As K_d was 60.7 at Faardrup, 29.3 at Jyndevad and 37.7 at Tylstrup, sorption did not seem to be very important for the degradation rate of fenpropimorph.

With flamprop-M-isopropyl, the half-life was 16 days in Slaeggerup soil and 125 days in Estrup soil. The difference did not correlate with the biomass, which was higher in Estrup soil (430 mg C/kg) than in Slaeggerup soil 346 mg C/kg), but is probably attributable to the fact that K_d was higher in Estrup soil (28.3 ml/g) than in Slaeggerup soil (6.8 ml/g), thus delaying bioavailability and hence pesticide degradation at Estrup.

From Table 20 it can be seen that degradation is considerably lower in subsoil than in plough layer (DT_{50} is generally much longer in subsoil). The half-life of the short-lived pesticides bromoxynil, ioxynil and dimethoate ranged from less than one day for bromoxynil in Faardrup subsoil to 70 days for dimethoate in Estrup soil. These short DT_{50} values indicate that these three pesticides degrade in subsurface soils, thus making it unlikely that they will

cause groundwater pollution. With fenpropimorph and propiconazole, the degradation rates in subsoils are so slow that their half-lives could not be calculated during the 300-day incubation period. In most cases DT_{50} exceeded 300 days. This indicates that these pesticides will be rather stable in the subsoil. On the other hand, as Table 20 shows high adsorption of fenpropimorph and propiconazole in plough layer (11.8 and 60.7 ml/g), the risk that they will leach seems to be low.

Table 21. Degradation parameters for the analysed pesticides. Half-lives are either estimated from drawn curves ($DT_{50} - Read$), calculated using a simple 1st order model ($DT_{50} - 1^{st}$ order) or calculated using a two-compartment 1st + 1st model ($DT_{50} - 1^{st} + 1^{st}$ order). 1st, 2nd and 3rd refer to the first, second and third half-lives determined using the two-compartment 1st + 1st mode. Literature DT_{50} ranges are shown for comparison.

Field and soil depth	DT 50-Read	$DT_{50} - 1^{st}$ order	DT	$50 - 1^{st} + 3$	1 st order	Literature DT ₅₀ ¹⁾
_	(days)	(days)		(days)	(days)
			1 st	2^{nd}	3 rd	
Bromoxynil						1–14
Faardrup $0-20$ cm ²⁾	<1					
Faardrup 80–100 cm ²⁾	<5					
Slaeggerup 0–20 cm		<1	<1	<1	<1	
Slaeggerup 80–100 cm		12	12	12	13	
Dimethoate						10-21
Estrup $0-20$ cm $^{3)}$	<2	-	-	-	-	
Estrup 80–100 cm		74	70	80	84	
Slaeggerup $0-20$ cm $^{3)}$		4	-	-	-	
Slaeggerup 80–100 cm		17	17	18	20	
Fenpropimorph						16-145
Tylstrup 0–20 cm		379	483	623	624	
Tylstrup 80–100 cm	>300					
Jyndevad 0–20 cm ³⁾		123	66	-	-	
Jyndevad 80–100 cm	>300					
Faardrup 0–20 cm		15	4	22	36	
Faardrup 80–100 cm	>300					
Flamprop-M-isopropyl						12-70
Estrup $0-20$ cm ³⁾		125	47	-	-	
Slaeggerup 0–20 cm		16	11	22	47	
Ioxynil						1.5–23
Faardrup 0–20 cm		<1	<1	<1	2	
Faardrup 80–100 cm		12	12	12	13	
Slaeggerup 0–20 cm		1	<1	1	9	
Slaeggerup 80–100 cm ⁴⁾						
Propiconazole						14–430
Tylstrup 0–20 cm		310	336	411	410	
Tylstrup 80–100 cm	>300					
Jyndevad 0–20 cm		191	157	25,103	59,636	
Jyndevad 80–100 cm	>300					
Faardrup 0–20 cm		106	98	133	144	
Faardrup 80–100 cm	>300					
Slaeggerup 0–20 cm		444	570	755	756	
Slaeggerup 80–100 cm	>150					

¹⁾ Linders et al., 1994; Lindhardt et al., 1998; Lindhardt et al., 2001; Roberts, 1998

²⁾ Modelling was not possible due to insufficient data

³⁾ When the asymptotic correlation was too high, the parameters of the chosen models could not be determined.

⁴⁾ Degradation studies in the subsoil were performed but half-lives could neither be calculated nor estimated

The correlation between the rate of degradation and adsorption/biomass is thus unclear. In several cases, degradation was fastest at high biomass content and seemed to be influenced

by adsorption – decreasing at increasing K_d . In other cases the correlation was solely explicable by either biomass or by adsorption.

Fenpropimorphic acid, an important degradation product of fenpropimorph, was identified in the plough layer soil (Table 22), but not in the subsoil. After 240 days the metabolite accounted for less than 5% of the applied parental compound.

Table 22. Concentration of fenpropimorphic acid in plough layer from Tylstrup, Jyndevad and Faardrup incubated for up to 240 days following application of fenpropimorph (0.5 mg/kg). Values are in mg/kg.

Day	/s 1	20	30	40	60	80	100	120	180	240
Tylstrup	n.d.	n.d.	n.d.	n.d.	n.d.	0.008	0.010	0.036	0.037	0.015
Jyndevad	n.d.	0.010	0.013	0.016	0.02	0.019	0.018	0.028	0.023	0.023
Faardrup	n.d.	0.019	0.012	0.017	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

n.d.: not detected

The analyses for the degradation product of flamprop-M-isopropyl (flamprop-M-isopropyl acid) was only performed in the plough layer. At Slaeggerup, but not at Estrup, small amounts were detected and after 270 days the metabolite accounted for about 5% of the 0.5 mg/kg of the parent compound applied (Table 23).

Table 23. Concentration of flamprop-M-isopropyl acid in plough layer from Estrup and Slaeggerup incubation for up to 270 days following application of flamprop-M-isopropyl (0.5 mg/kg). Values are in mg/kg.

Estrup n.d. n.d. n.d. n.d. n.d. n.d. n.d. - Slaeggerup 0.025 0.039 0.044 0.039 0.054 0.027 0.039 0.026 0.025	D	Days	5	10	20	30	45	90	135	180	225	270
Slaeggerup 0.025 0.039 0.044 0.039 0.054 0.027 0.039 0.027 0.026 0.025	Estrup		n.d.	-								
	Slaeggerup		0.025	0.039	0.044	0.039	0.054	0.027	0.039	0.027	0.026	0.025

n.d.: not detected

8.2.4 Degradation kinetics

In mathematical descriptions of the degradation of pesticides, the single first-order model (SFO) has been dominant for decades. From a conceptual point of view, this model is a logical choice since the rate of degradation is assumed to depend solely on the number of molecules expressed in terms of concentration or absolute mass. It is thus a well-known kinetic model. The single first-order (SFO) model can be expressed in both an integrated and a differential form. In its differentiated form, the SFO model can be used in dynamic leaching models that include a change in pesticide concentration over time. The equation can be analytically solved, and end-points (DT_{50} , DT_{90}) can easily be calculated. These end-points are typically used to assess whether a specific substance can be approved, or whether further studies have to be performed.

Practical experience shows, however, that the best mathematical description of the kinetics of chemical decomposition frequently differs from single first-order kinetics. This applies both to the degradation of pharmaceuticals in living organisms and – as in the present case – to the degradation of chemicals in soil (Beulke and Brown, 2001; Reid *et al.*, 2000).

There may be many reasons why a single first-order model does not provide the best description of the degradation of a chemical. Both soil and water/sediment are complex environments where populations of degrading microorganisms vary considerably. Many chemicals can be degraded by different degradation pathways that may involve both chemical and microbiological steps. Furthermore, chemicals are distributed between soil and water by complex adsorption/desorption mechanisms that influence the availability of the chemical to microbial degradation.

A frequently used alternative model for describing degradation kinetics is the twocompartment $1^{st} + 1^{st}$ order model, Double First Order in Parallel (DFOP). Unfortunately, this model cannot be described in a differential form, and DT₅₀ and DT₉₀ can only be calculated by an iterative procedure. In cases where the DFOP model undoubtedly provides the best mathematical expression of a set of data, consideration must be given to whether an SFO model with a poor fit is preferable for the purpose of obtaining a result that can be used directly in a dynamic leaching model, or whether a DFOP or other alternative model with a better fit shall be used, even if the results from such a model cannot be used directly in the dynamic leaching models. To address this question, the EU has established a work group on degradation kinetics (FOCUS work group on degradation kinetics) to provide regulatory guidance for kinetic analyses in pesticide degradation studies.

In the two-compartment model, the first compartment – rapid degradation – is expected to occur within the soil water phase, where microorganisms have easy access to the pesticide. In the second compartment, degradation is slow. Here, the pesticide is expected to be adsorbed to soil particles or to be located in micropores in the soil matrix, with the degradation rate being governed by the slow desorption-diffusion processes. The distribution of pesticide between compartments is governed by the structure of the pesticide as well as by the amount and type of organic matter present in the soil. The speed at which the pesticide is transformed in the two compartments is expressed by the rate constants k_1 and k_2 .

The results from the curve fitting analysis are shown in Figure 51–Figure 56. In each figure, the measured data are shown together with the curves simulated by the SFO model and the DFOP model (provided fits were obtained). The parameters *a*, *b*, k_1 and k_2 for each model are shown in Appendix 10 together with the correlation coefficient for each curve. A more comprehensive evaluation of the goodness of fit including an evaluation of standard errors for each parameter and further testing will be presented in future publications. With bromoxynil in Slaeggerup subsoil (Figure 51), dimethoate in Estrup and Slaeggerup subsoil (Figure 52) and ioxynil in Faardrup subsoil (Figure 55), the DFOP model was not notably better than the SFO model. With dimethoate in Estrup plough layer, no fit could be obtained due to the low concentration detected on day 0. With dimethoate in Slaeggerup plough layer, only the SFO model (Figure 52) could be used. With the remainder of the plough layer samples the degradation processes were best described by the DFOP model, while the SFO model provided a less satisfactory description of the degradation processes.



Figure 51. Degradation of bromoxynil in the plough layer (0-20 cm) and the subsoil (80-100 cm) from Slaeggerup. No corresponding figure is shown for Faardrup soil as insufficient data are available. Closed circles indicate the experimental data, while solid lines indicate the fitted curve for a 1st order model (black) and a two-compartment 1st + 1st order model (red).



Figure 52. Degradation of dimethoate in the plough layer (0-20 cm) and the subsoil (80-100 cm) from Estrup and Slaeggerup. Closed circles indicate the experimental data, while solid lines indicate the fitted curve for a 1^{st} order model (black) and a two-compartment $1^{\text{st}} + 1^{\text{st}}$ order model (red).



Figure 53. Degradation of fenpropimorph in the plough layer (0-20 cm) and the subsoil (80-100 cm) from Tylstrup, Jyndevad and Faardrup. Closed circles indicate the experimental data, while solid lines indicate the fitted curve for a 1st order model (black) and a two-compartment 1st + 1st order model (red).



Figure 54. Degradation of flamprop-M-isopropyl in the plough layer (0-20 cm) from Estrup and Slaeggerup. Closed circles indicate the experimental data, while solid lines indicate the fitted curve for a 1st order model (black) and a two-compartment 1st + 1st order model (red).



Figure 55. Degradation of ioxynil in the plough layer (0–20 cm) and the subsoil (80–100 cm) from Faardrup and in the plough layer (0–20 cm) from Slaeggerup. Closed circles indicate the experimental data, while solid lines indicate the fitted curve for a 1st order model (black) and a two-compartment $1^{st} + 1^{st}$ order model (red).



Figure 56. Degradation of propiconazole in the plough layer (0-20 cm) and the subsoil (80-100 cm) from Tylstrup, Jyndevad, Faardrup and Slaeggerup. Closed circles indicate the experimental data, while solid lines indicate the fitted curve for a 1st order model (black) and a two-compartment 1st + 1st order model (red).

With the DFOP model, half-lives can only be obtained if they lie on the curve or can be calculated through an iterative process. The SFO equation can be solved analytically such that $DT_{50} = \ln 2/k$, which means that the half-life will be the same irrespective of the stage in the process. In contrast, half-life determined with the DFOP model increases with time because the rate constant for the second compartment becomes increasingly dominant with time. The error that is introduced by using a simple 1st order model for the calculation of half-life varies among the soils and compounds. Guidelines for the evaluation of these errors will be established in the above-mentioned FOCUS group. In similar, long-term degradation studies, the biological activity after 200 days of incubation of selected samples was controlled to assure that the decline in degradation was not due to a substantial decrease in biological activity.

If the pesticides in the second compartment were only mobilized due to the use of a strong extraction technique, they would never have been available for use by the microorganisms or to leach to the groundwater. As a consequence, the use of a simple 1^{st} order model would overestimate pesticide persistence. If, on the other hand, the pesticides were truly available to the soil microorganisms or to leach to the groundwater, then the use of a simple 1^{st} order process would underestimate pesticide persistence. For example, 3 half-lives for fenpropimorph in Faardrup soil is only 45 days calculated using the 1^{st} order model, while the two-compartment $1^{st} + 1^{st}$ order model more correctly yields 62 days (4+22+36), as indicated in Table 21.

The distribution of pesticides between compartments is expected to be chiefly governed by the sorptive capacity of the soil for each compound. At the same time, microbial activity is expected to govern the rate of degradation in the soil water compartment. However, it can be expected that the degradation rate in the soil water compartment will also influence the distribution. Thus complex patterns are expected to govern the overall process. With a view to elucidating all the relationships between compartments and degradation rates, modelling studies are currently being performed. The results will be presented in subsequent reports. Further modelling will take into consideration the guidelines being elaborated by the EU FOCUS work group on degradation kinetics.

8.3 Summary

Sorption and degradation parameters were determined on various combinations of pesticides and soil types representative of the PLAP. The results confirmed the low microbial activity, sorption, and degradation rates generally found in subsoil. Both degradation rates and sorption differed markedly between soils, thus stressing the importance of having sitespecific parameters when modelling the leaching of pesticides.

Compared with published values, sorption determined in the present study was higher for dimethoate and flamprop-M-isopropyl, lower for bromoxynil and ioxynil and within the published range for fenpropimorph, metamitron and propiconazole. The DT_{50} of ioxynil and bromoxynil were remarkably low, ranging from <1 day in the plough layer and from <5 to 12 days in the subsoil.

In some cases the degradation rate was better described by a two-compartment $1^{st} + 1^{st}$ order model than by the usual 1^{st} order model. As degradation often involves one initial fast degradation rate with a short half-life followed by slower degradation rates with longer halflives, an error is introduced if the simple 1^{st} order half-life is used in the evaluation of pesticide persistence. Further analysis of the significance of the introduced error for risk assessment of pesticide leaching is thus required.

9 Pesticide analysis quality assurance

Scientifically valid methods of analysis are essential for the integrity of the present monitoring programme. The field monitoring work has therefore been supported by intensive quality assurance entailing continuous evaluation of the analyses employed. Pesticide analysis quality assurance (QA) data for the period July 2001–June 2002 are presented below, whereas the QA data for the preceding monitoring periods are given in Kjær *et al.* (2001) and Kjær *et al.* (2002).

9.1 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 laboratory's 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 Danish Aquatic Monitoring and Assessment Programme (NOVA-2003).

9.1.1 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.

9.1.2 External QA

Every third month, two control samples were analysed at the laboratories along with the various water samples from the 6 test sites. Two stock solutions of different concentrations were prepared from 2 standard mixtures in ampoules prepared by Promochem, Germany (Table 24). 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-l 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 2 days before a sampling day. The pesticide concentration in the solution is indicated in Table 24. 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	High-level control	Low-level control
		(mg/l)	(ng/l)	(ng/l)
Mixture 1	Dimethoate	1	117	50
	Ethofumesate	1	117	50
	Fenpropimorph	1	117	50
	Metamitron	1	117	50
	Metribuzin	1	117	50
	Propiconazole	1	117	50
	Pirimicarb	1	117	50
	Terbuthylazine	1	117	50
	Triazinamin-methyl	1	117	50
	Triazinamin	1	117	50
Mixture 2				
	Bentazone	1	117	50
	Bromoxynil	1	117	50
	Desmedipham	1	117	50
	Flamprop (free acid)	1	117	50
	Fluazifop (free acid)	1	117	50
	Fluroxypyr (free acid)	1	117	50
	Glyphosate	1	117	50
	Ioxynil	1	117	50
	Phenmedipham	1	117	50

Table 24. Pesticide concentrations in the spike solution and in the high-level and low-level control samples.

9.2 Results and discussion

9.2.1 Internal QA

The internal QA data have been analysed to obtain an impression of the day-to-day variation and within-day variation. The statistical analysis encompasses all duplicate pesticide analyses, single analyses being excluded. One-way analysis of variance was used to separate day-to-day variation from within-day variation. The results are presented in Table 25.

With 38 out of 47 of the pesticides, day-to-day variation accounted for most of the uncertainty. Thus when s_t exceeded 10, this was due to a high day-to-day variation. F>F_{critical} indicates that the day-to-day variation is significantly higher than the within-day variation (95% confidence interval). F<F_{critical} indicates that the random errors dominate the overall uncertainty.

The overall standard deviation (s_t) of the various pesticide analyses lie within the range 0.003–0.029 µg/l. Reproducibility of the degradation products was generally found to be poorer than that of the mother compounds, although within the same range. Standard deviation for mother compounds and degradation products was in the range 0.003–0.025 µg/l and 0.004–0.029 µg/l, respectively. With seven of the compounds, reproducibility was relatively poor (s_t ≥0.02).

Laboratory 1 2-amino-N-isopropylbenzamid (D) 0.008 0.018 0.020 5.59 3.23 9 3-aminophenol (D) 0.007 0.022 0.023 8.70 4.39 6 Bentazone 0.001 0.003 0.003 5.73 2.72 12 Bromoxynil 0.003 0.003 0.005 1.30 3.87 7 Clomazone 0.006 0.006 0.009 1.28 3.87 7 Desmedipham 0.003 0.005 0.006 3.66 2.72 12 Dimethoate 0.002 0.011 0.011 48.02 3.87 7 EHPC (D) 0.004 0.005 0.006 3.66 2.72 12 Dimethoate 0.002 0.003 0.004 4.19 1.99 24 EHPC (D) 0.004 0.004 0.005 0.99 3.02 10 Ethofumesate 0.002 0.003 0.004 3.87 2.72 12 Fenpropimorph 0.004 0.008 0.009 3.87 2.29 17		Pesticide	$s_w (\mu g/l)^{1}$	$s_{b} (\mu g/l)^{1}$	$s_t (\mu g/l)^{2}$	F	F _{critical}	N
2-amino-N-isopropylbenzamid (D)0.0080.0180.0205.593.2393-aminophenol (D)0.0070.0220.0238.704.396Bentazone0.0010.0030.0035.732.7212Bromoxynil0.0030.0030.0051.303.877Clomazone0.0060.0060.0091.283.877Clopyralid0.0020.0110.01148.023.877Desmedipham0.0020.0030.0050.0063.662.7212Dimethoate0.0020.0030.0044.191.9924EHPC (D)0.0040.0040.0050.993.0210Ethofumesate0.0020.0030.0043.872.7212Fenpropimorph0.0040.0080.0093.872.2917Flamprop free acid0.0020.0030.0042.681.9924Flamprop-M-isopropyl0.0010.0030.0033.471.9924	Laboratory 1							
3-aminophenol (D) 0.007 0.022 0.023 8.70 4.39 6 Bentazone 0.001 0.003 0.003 5.73 2.72 12 Bromoxynil 0.003 0.003 0.005 1.30 3.87 7 Clomazone 0.006 0.006 0.009 1.28 3.87 7 Clopyralid 0.002 0.011 0.011 48.02 3.87 7 Desmedipham 0.002 0.011 0.011 48.02 3.87 7 Dimethoate 0.002 0.003 0.006 3.66 2.72 12 EHPC (D) 0.004 0.004 0.005 0.99 3.02 10 Ethofumesate 0.002 0.003 0.004 3.87 2.72 12 Fenpropimorph 0.004 0.004 0.005 0.99 3.02 10 Ethofumesate 0.002 0.003 0.004 3.87 2.72 12 Fenpropimorph acid (D) 0.003 0.012 0.013 19.80 2.29 17 Fl	-	2-amino-N-isopropylbenzamid (D)	0.008	0.018	0.020	5.59	3.23	9
Bentazone0.0010.0030.0035.732.7212Bromoxynil0.0030.0030.0051.303.877Clomazone0.0060.0060.0091.283.877Clopyralid0.0020.0110.01148.023.877Desmedipham0.0030.0050.0063.662.7212Dimethoate0.0020.0030.0044.191.9924EHPC (D)0.0040.0040.0050.993.0210Ethofumesate0.0020.0030.0043.872.7212Fenpropimorph0.0040.0080.0093.872.2917Flamprop free acid0.0020.0030.0042.681.9924Flamprop-M-isopropyl0.0010.0030.0033.471.9924		3-aminophenol (D)	0.007	0.022	0.023	8.70	4.39	6
Bromoxynil0.0030.0030.0051.303.877Clomazone0.0060.0060.0091.283.877Clopyralid0.0020.0110.01148.023.877Desmedipham0.0030.0050.0063.662.7212Dimethoate0.0020.0030.0044.191.9924EHPC (D)0.0040.0040.0050.993.0210Ethofumesate0.0020.0030.0043.872.7212Fenpropimorph0.0040.0080.0093.872.2917Fenpropimorph acid (D)0.0030.0120.01319.802.2917Flamprop free acid0.0020.0030.0042.681.9924Flamprop-M-isopropyl0.0010.0030.0033.471.9924		Bentazone	0.001	0.003	0.003	5.73	2.72	12
Clomazone0.0060.0060.0091.283.877Clopyralid0.0020.0110.01148.023.877Desmedipham0.0030.0050.0063.662.7212Dimethoate0.0020.0030.0044.191.9924EHPC (D)0.0040.0040.0050.993.0210Ethofumesate0.0020.0030.0043.872.7212Fenpropimorph0.0040.0080.0093.872.2917Fenpropimorph acid (D)0.0030.0120.01319.802.2917Flamprop free acid0.0020.0030.0042.681.9924Flamprop-M-isopropyl0.0010.0030.0033.471.9924		Bromoxynil	0.003	0.003	0.005	1.30	3.87	7
Clopyralid0.0020.0110.01148.023.877Desmedipham0.0030.0050.0063.662.7212Dimethoate0.0020.0030.0044.191.9924EHPC (D)0.0040.0040.0050.993.0210Ethofumesate0.0020.0030.0043.872.7212Fenpropimorph0.0040.0080.0093.872.2917Fenpropimorph acid (D)0.0030.0120.01319.802.2917Flamprop free acid0.0020.0030.0042.681.9924Flamprop-M-isopropyl0.0010.0030.0033.471.9924		Clomazone	0.006	0.006	0.009	1.28	3.87	7
Desmedipham0.0030.0050.0063.662.7212Dimethoate0.0020.0030.0044.191.9924EHPC (D)0.0040.0040.0050.993.0210Ethofumesate0.0020.0030.0043.872.7212Fenpropimorph0.0040.0080.0093.872.2917Fenpropimorph acid (D)0.0030.0120.01319.802.2917Flamprop free acid0.0020.0030.0042.681.9924Flamprop-M-isopropyl0.0010.0030.0033.471.9924		Clopyralid	0.002	0.011	0.011	48.02	3.87	7
Dimethoate0.0020.0030.0044.191.9924EHPC (D)0.0040.0040.0050.993.0210Ethofumesate0.0020.0030.0043.872.7212Fenpropimorph0.0040.0080.0093.872.2917Fenpropimorph acid (D)0.0030.0120.01319.802.2917Flamprop free acid0.0020.0030.0042.681.9924Flamprop-M-isopropyl0.0010.0030.0033.471.9924		Desmedipham	0.003	0.005	0.006	3.66	2.72	12
EHPC (D)0.0040.0040.0050.993.02100Ethofumesate0.0020.0030.0043.872.72120Fenpropimorph0.0040.0080.0093.872.29170Fenpropimorph acid (D)0.0030.0120.01319.802.29170Flamprop free acid0.0020.0030.0042.681.99240Flamprop-M-isopropyl0.0010.0030.0033.471.99240		Dimethoate	0.002	0.003	0.004	4.19	1.99	24
Ethofumesate0.0020.0030.0043.872.7212Fenpropimorph0.0040.0080.0093.872.2917Fenpropimorph acid (D)0.0030.0120.01319.802.2917Flamprop free acid0.0020.0030.0042.681.9924Flamprop-M-isopropyl0.0010.0030.0033.471.9924		EHPC (D)	0.004	0.004	0.005	0.99	3.02	10
Fenpropimorph0.0040.0080.0093.872.2917Fenpropimorph acid (D)0.0030.0120.01319.802.2917Flamprop free acid0.0020.0030.0042.681.9924Flamprop-M-isopropyl0.0010.0030.0033.471.9924Flamprop-M-isopropyl0.0010.0030.0033.471.9924		Ethofumesate	0.002	0.003	0.004	3.87	2.72	12
Fenpropimorph acid (D)0.0030.0120.01319.802.2917Flamprop free acid0.0020.0030.0042.681.9924Flamprop-M-isopropyl0.0010.0030.0033.471.9924Flamprop-M-isopropyl0.0010.0030.0033.471.9924		Fenpropimorph	0.004	0.008	0.009	3.87	2.29	17
Flamprop free acid0.0020.0030.0042.681.9924Flamprop-M-isopropyl0.0010.0030.0033.471.9924LDDDDDDD		Fenpropimorph acid (D)	0.003	0.012	0.013	19.80	2.29	17
Flamprop-M-isopropyl 0.001 0.003 0.003 3.47 1.99 24 Flamprop-M-isopropyl 0.002 0.003 0.003 3.47 1.99 24		Flamprop free acid	0.002	0.003	0.004	2.68	1.99	24
		Flamprop-M-isopropyl	0.001	0.003	0.003	3.47	1.99	24
Fluazifop-P (free acid) $0.002 \ 0.006 \ 0.006 \ 8.61 \ 2.72 \ 12$		Fluazifop-P (free acid)	0.002	0.006	0.006	8.61	2.72	12
FMC65317 (D) 0.006 0.006 0.008 1.08 3.87 7		FMC65317 (D)	0.006	0.006	0.008	1.08	3.87	7
Ioxynil 0.016 0.019 0.025 1.38 3.87 7		Ioxynil	0.016	0.019	0.025	1.38	3.87	7
Metamitron 0.002 0.016 0.016 57.62 2.72 12		Metamitron	0.002	0.016	0.016	57.62	2.72	12
Metamitron desamino (D) 0.002 0.003 0.004 3.24 2.85 11		Metamitron desamino (D)	0.002	0.003	0.004	3.24	2.85	11
Metribuzin 0.002 0.003 0.003 2.92 2.72 12		Metribuzin	0.002	0.003	0.003	2.92	2.72	12
Metribuzin-desamino (D) 0.002 0.003 0.004 1.54 3.02 10		Metribuzin-desamino (D)	0.002	0.003	0.004	1.54	3.02	10
Metribuzin-desamino-diketo (D) 0.008 0.010 0.013 1.70 2.72 12		Metribuzin-desamino-diketo (D)	0.008	0.010	0.013	1.70	2.72	12
Metribuzin-diketo (D) 0.022 0.020 0.029 0.82 2.72 12		Metribuzin-diketo (D)	0.022	0.020	0.029	0.82	2.72	12
Metsulfuron-methyl 0.002 0.005 0.006 5.77 2.85 11		Metsulfuron-methyl	0.002	0.005	0.006	5.77	2.85	11
MHPC (D) 0.002 0.006 0.007 7.19 2.85 11		MHPC (D)	0.002	0.006	0.007	7.19	2.85	11
Pendimethalin 0.002 0.003 0.003 2.79 1.99 24		Pendimethalin	0.002	0.003	0.003	2.79	1.99	24
Phenmedipham 0.001 0.004 0.004 21.38 2.72 12		Phenmedipham	0.001	0.004	0.004	21.38	2.72	12
Pirimicarb 0.003 0.003 0.005 1.21 2.18 19		Pirimicarb	0.003	0.003	0.005	1 21	2.18	19
Pirimicarb desmethyl (D) 0 011 0 021 0 023 3 65 2 14 20		Pirimicarb desmethyl (D)	0.011	0.021	0.023	3 65	2.14	20
Pirimicarb-desmethyl-formamido (D) 0 002 0 007 0 007 9 86 2 02 23		Pirimicarb-desmethyl-formamido (D)	0.002	0.007	0.007	9.86	2.02	23
Propiconazole 0.002 0.003 0.003 1.97 1.99 24		Propiconazole	0.002	0.003	0.003	1 97	1 99	24
Triasulfuron 0.003 0.005 0.005 3.74 2.72 12		Triasulfuron	0.003	0.005	0.005	3 74	2.72	12
Triazinamin (D) 0.002 0.004 0.005 4.04 2.06 22		Triazinamin (D)	0.002	0.004	0.005	4 04	2.06	22
Triazinamin (D) $0.002 0.004 0.005 4.04 2.06 22$		Triazinamin methyl (D)	0.002	0.004	0.005	4 04	2.06	22
Laboratory 2	Laboratory 2	· · · · · · · · · · · · · · · · · · ·	0.002	0.001	0.000		2.00	
AMPA (D) 0 004 0 009 0 010 4 17 1 50 68	Eucoratory 2	AMPA (D)	0.004	0.009	0.010	4 17	1.50	68
Bromoxynil 0.004 0.012 0.013 9.72 1.81 32		Bromoxynil	0.004	0.012	0.013	9 72	1.81	32
Dimethoate 0.002 0.006 0.007 8.88 3.87 7		Dimethoate	0.002	0.006	0.007	8 88	3 87	7
Ethofumesate 0.003 0.009 0.009 6.55 1.62 48		Ethofumesate	0.002	0.009	0.009	6 55	1.62	, 48
Euroraniesace 0.005		Fenpronimorph	0.005	0.003	0.009	12 51	1.62	43
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		Fluroxypyr	0.007	0.019	0.021	8 20	1.00	25
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		Glyphosate	0.007	0.028	0.021	5.96	1.20	71
Ioxymil 0.003 0.014 0.014 17.02 1.81 32		Ioxynil	0.003	0.000	0.000	17.02	1.10	32
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		Metamitron	0.003	0.014	0.014	24 54	1.61	48
Phenmedinham 0.004 0.022 0.023 25.51 1.70 AC		Phenmedinham	0.003	0.013	0.013	27.54 25.51	1.02	40
Pirimicaphan 0.004 0.022 0.025 25.51 1.70 40 Pirimicarb 0.002 0.007 0.008 10.10 1.62 48		Pirimicarh	0.004	0.022	0.023	10 10	1.70	48 48
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		Proniconazole	0.002	0.007	0.000	10.10	1.02	32
Terbuthylazine 0.007 0.006 0.006 5.73 2.85 11		Terbuthylazine	0.007	0.010	0.011	5 73	2.85	11

Table 25. One-way analysis of variance of pesticide analyses. $\alpha = 0.05$.

¹⁾ s_w and s_b are the within-day and day-to-day standard deviation, respectively ²⁾ s_t is the total standard deviation calculated as $s_t = \sqrt{s_w^2 + s_b^2}$ (Lund et al., 1994) n = number of duplicate analyses, D = degradation product

9.2.2 External QA

Table 26 provides an overview of the recovery of all spiked samples based on 1–3 observations. Recovery of the spiked samples is generally good (>70%). Exceptions are desmedipham and phenmedipham, glyphosate, flamprop free acid, fenpropimorph and pirimicarb, for which recovery was low at some of the field sites.

Pesticide	Tylstrup	Jyndevad	Silstrup	Estrup	Faardrup	Slaeggerup
Bentazone				93/88		77/79
Bromoxynil				95/82	92/94	84/85
Desmedipham*			64/66		92/97	
Dimethoate			91/89	84/90	106/111	81/87
Ethofumesate			95/90		103/101	
Fenpropimorph	77/72	85/78	72/67	35/32	85/85	72/79
Flamprop (free acid)			67/86	93/90	82/94	91/91
Fluazifop-P (free acid)			91/90		89/94	
Fluroxypyr					123/103	
Glyphosate		93/98	97/100	66/74	101/97	62/63
Ioxynil				107/112	90/83	96/103
Metamitron*			89/87		103/88	
Metribuzin	106/109					
Phenmedipham*			54/54		95/103	
Pirimicarb	76/81		69/74	53/59	99/97	84/82
Propiconazole	100/105	111/105	93/96	95/95	85/80	98/99
Triazinamin	110/162			70/76		76/80
Triazinamin-methyl	82/73	92/82	94/77		88/94	109/102

Table 26. Average recovery (%) at low/high concentration level indicated for each site. Recovery refers to the ratio of the observed and nominal concentrations.

* indicates that the compound was partly transformed into a degradation product as shown in Appendix 11 Values in bold indicate that recovery is based on a single observation

The low recovery reported for desmedipham and phenmedipham is most likely due to stability problems. Degradation products were thus detected in the spiked samples – see Appendix 11, where the concentration of mother compounds and degradation products in the spiked samples is indicated on the control cards. Stability problems were also observed with these particular compounds by Kjær *et al.* (2002) in an analysis of the stability of a large number of compounds. Total recovery, including also the degradation products, thus provides a more realistic picture of the recovery. As acidity and other water quality parameters differ between sites, matrix effects may explain some of the differences in recovery between sites.

Table 27 provides an overview of the number of times each compound was detected at each site during the 2001/–2002 monitoring period together with the maximum concentration. Nineteen pesticides and twelve degradation products were detected in samples from the experimental fields, and QA data connected to these findings are of special interest.

Pesticide	Tylstrup	Jyndevad	Silstrup	Estrup	Faardrup	Slaeggerup
4-chlor-2-methylphenol (D)		-	-	1(0.05)		
AMPA (D)			40 (0.35)	50 (0.18)	15 (0.11)	24 (5.40)
Bentazone				48 (0.73)		8 (0.03)
Bromoxynil				3 (0.60)		1 (0.14)
Clopyralid	2 (0.72)		1 (4.09)			
Desethylterbuthylazine (D)		10 (0.06)	1 (1.08)			
Desmedipham			1 (0.03)			
Dimethoate			2 (1.42)			
Ethofumesate			1 (0.02)		41 (12.0)	
Fenpropimorphic-acid (D)			1 (0.02)			
Flamprop (free acid)			7 (0.10)	1 (0.01)	1 (0.33)	
Flamprop-M-isopropyl			13 (0.11)		1 (0.15)	
Fluazifop-P (free acid)			1 (0.07)		20 (3.80)	
Fluazifop-P-butyl					1 (0.21)	
Glyphosate			36 (4.70)	31 (0.04)	5 (0.09)	21 (5.10)
Ioxynil				20 (0.25)	2 (0.01)	3 (0.18)
MCPA				4 (3.89)		
Metamitron			1 (0.06)		41 (1.70)	
Metamitron-desamino (D)			8 (0.18)		47 (2.50)	
Metribuzin-desamino-diketo (D)	105 (0.52)					
Metribuzin-diketo (D)	177 (0.51)	3 (0.09)				
MHPC (D)					1 (0.03)	
Pendimethalin				4 (0.04)		1 (0.01)
PHCP (D)			1 (2.69)			
Phenmedipham					3 (0.03)	
Pirimicarb				16 (0.08)	12 (0.13)	1 (0.01)
Pirimicarb-desmethyl (D)					9 (0.05)	
Pirimicarb-desmethyl-formamido				4 (0.02)	4 (0.14)	
(D)						
Propiconazole			6 (0.03)	3 (0.86)	1 (0.13)	
Terbuthylazine			1 (1.55)			
Triazinamin (D)				1 (0.04)		

Table 27. Number of times each compound was detected at each site during the 2001/2002 monitoring period together with the maximum concentration (μ g/l) in parentheses.

Recovery of pesticides in external QA samples was found to be acceptable for the great majority of pesticides detected in field samples (recovery \geq 70%) Exceptions are desmedipham and pirimicarb at Silstrup, fenpropimorph, glyphosate (low concentration) and pirimicarb at Estrup and glyphosate at Slaeggerup. The internal QA data generally showed good recovery. With some compounds, however, a few of the results are either high (>130%) or low (<70%). This is also reflected in the table of standard deviations (Table 25), typically resulting in s_t values above 0.02 µg/l. For all compounds that have been detected in more than one sample, the external and internal QA results are shown in Appendix 11.

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. All the pesticides in the spiked samples were detected in all samples.

9.3 Summary

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

- Reproducibility of the pesticide analyses was good, standard deviation being in the range $0.003-0.025 \ \mu g/l$.
- Reproducibility of the degradation products was a little poorer than that of the mother compounds, being in the range 0.004–0.029µg/l.
- Recovery was generally good (>70%) in external QA samples, exceptions being fenpropimorph, desmedipham, glyphosate, phenmedipham and pirimicarb at single sites.
- Variations in recovery of the same compound in spiked samples from all field sites indicate uncertainties in analysis caused by differences in matrix composition.
- No contamination of samples occurred during collection, storage and analysis.

10 Summary of monitoring results

The monitoring data identified three different leaching patterns for the applied pesticides – no leaching, slight leaching and unacceptable leaching (see Table 28). It should be noted, though, that the present evaluation of the leaching risk of many of these pesticides is still preliminary as their potential leaching period extends beyond the current monitoring period. This does not apply to those pesticides marked with a single asterisk in Table 28. The monitoring results indicate an unacceptable degree of leaching by two of the applied pesticides or their degradation products.

- 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. Both degradation products appear to be relatively stable and leached throughout the entire monitoring period. Average concentrations reaching 0.1 µg/l were thus seen as much as three years after application. There was also evidence that their degradation products may 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.
- The findings indicate that glyphosate, when applied in late autumn, can leach through the root zone at unacceptable concentrations in loamy soils. At the loamy sites Estrup and Silstrup, glyphosate leached from the root zone into the drainage water at average concentrations exceeding $0.1 \mu g/l$. At Estrup its degradation product AMPA leached at an average concentration exceeding $0.1 \mu g/l$. This appeared to be attributable to a combination of pronounced macropore flow occurring shortly after application and limited sorption and degradation capacity. Long-term leaching was especially pronounced with AMPA, which was frequently detected more than one and a half years after application. So far the leaching of AMPA and glyphosate has 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. 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.

The monitoring data also indicate leaching of a further fourteen pesticides, but not in unacceptable levels, however. Although the concentration exceeded 0.1 μ g/l in several samples, the average concentration did not. This is summarized in Table 29, 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 Jyndevad, where incipient leaching of desethylterbuthylazine (degradation product of terbuthylazine) was observed, leaching within this group of pesticides was only observed at the loamy soil sites, where leaching was associated with pronounced macropore transport that resulted in very rapid movement of pesticides through the unsaturated zone.

Table 28. Pesticide leaching at the 6 PLAP sites. The number of asterisks indicates the number of monitoring periods the pesticide was included in the PLAP. The colours indicate the degree of leaching. Pesticides applied in spring 2002 are not included in the table.

	Tylstrup	Jyndevad	Silstrup	Estrup	Faardrup	Slaeggerup
Metribuzin	***	**1)				
Glyphosate		**	*	**		*
Metamitron			**		*	
Ethofumesate			**		*	
Bentazone				*		*
Ioxynil				*	**	*
Flamprop-M-isopropyl			*			*
Fluazifop-P			**		*	
Pirimicarb	*		**			*
Terbuthylazine		*				
Propiconazole	**	**	*	**	**	**
Bromoxynil				*	**	*
Pendimethalin	**			*		*
Phenmedipham			**		*	
Fenpropimorph	**	**	*	**	**	**
Dimethoate			*	**		**
Clomazone	*					
Clopyralid	*			_		
Desmedipham			**		*	
Fluroxypyr					**	
Metsulfuron-methyl				**		**
Triazinamin-methyl	*	**	*			**
(Tribenuron methyl)						
Pendimethalin	**			*		
ETU (Mancozeb)	**					
Linuron	**					
Triasulfuron	**					
Pyridate		*				

Deriving from previous application

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

Pesticide (or its degradation product) was detected in either several 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 $0.1 \, \mu g/l$

On several occasions single precipitation events caused leaching to the drainage water in high concentrations. In most cases the concentration decreased to a low level after a short period of time, and leached mass and average concentration in the drainage water were generally low. The observed leaching was typically confined to a 6–9 month period following pesticide application, exceptions being metamitron-desamino and bentazone. With these two compounds there was evidence of slight leaching one year after application.

Eleven of the 27 pesticides applied – about 40% – did not leach during the 3-year monitoring period. This group includes the three different sulfonylureas – metsulfuronmethyl, triasulfuron and tribenuronmethyl – which were tested on several field applications.

Table 29. Number of samples in which the various pesticides were detected at each site with the maximum concentration $(\mu g/l)$ in parentheses. The table only encompasses those pesticides/degradation products detected in either several consecutive samples or in a single sample in concentrations exceeding 0.1 $\mu g/l$. Pesticides applied in spring 2002 are not included.

	Tylstrup	Jyndevad	Silstrup	Estrup	Faardrup	Slaeggerup
Metribuzin	3(0.02)					
- metribuzin-desamino-diketo	238(2.1)	20(1.83)				
- metribuzin-diketo	353(0.69)	29(1.40)				
Glyphosate			36(4.7)	70(2.1)	7(0.09)	21(5.1)
- AMPA		3(0.02)	40(0.35)	87(0.73)	16(0.11)	24(5.4)
Metamitron			69(0.55)		32(1.7)	
- metamitron-desamino			60(0.67)		38(2.5)	
Ethofumesate			24(0.23)		37(12)	
Bentazone				48(0.73)		11(0.03)
Ioxynil				20(0.25)	2(0.01)	3(0.18)
Flamprop-M-isopropyl			13(0.11)	19(0.07)		5(0.04)
- flamprop (free acid)			7(0.096)	12(0.03)		1(0.35)
Fluazifop-P (free acid) ¹⁾			1(0.07)		17(3.8)	
Pirimicarb	0		17(0.05)	16(0.08)	9(0.13)	1(0.01)
- pirimicarb-desmethyl			1(0.05)		9(0.05)	
- pirimicarb-desmethyl-formamido				4(0.02)	3(0.01)	
Terbuthylazine		0				
- desethylterbuthylazine		13(0.06)				
Propiconazole	0	0	6(0.03)	12(0.86)	0	0
Bromoxynil		0		3(0.6)	0	1(0.14)
Pendimethalin	0			4(0.04)		1(0.01)
Phenmedipham			0		2(0.03)	
- MHPC			0		2(0.19)	
Fenpropimorph	0	2(0.04)	0	1(0.01)	1(0.02)	0
- fenpropimorphic-acid	0	0	1(0.02)	0	0	1(0.25)
Dimethoate			2(1.42)	0		0

Degradation products are indicated in italics, ¹⁾ degradation product of fluazifop-P-butyl

Tribenuronmethyl was hence applied on 4 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 sulfonylureas or their degradation products, including triazinamin and triazinamin-methyl.

Fenpropimorph and propiconazole were tested at all 6 sites. They were always applied during spring, and percolation during the first month after application ranged from 0 to 13 mm. With fenpropimorph the leaching risk was found to be negligible at all sites. With propiconazole, slight leaching was seen at just one of the 6 sites. These findings complement those of the sorption/degradation studies, which indicate that the leaching risk is low due to strong sorption to the topsoil. Why leaching of propiconazole was particularly prevalent at the Estrup site is unclear and no degradation/sorption data are available to help clarify the matter. The hydrological conditions could play a role since percolation started much earlier in the autumn and was much more intense at Estrup than at any of the other sites.

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Parameter	Chemical Abstracts nomenclature
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
Clopyralid	3,6-dichloro-2-pyridinecarboxylic acid
Desmedipham	Ethyl 3-(phenylcarbamoyloxy)phenylcarbamate
Dimethoate	O,O-dimethyl S-methylcarbamoylmethyl-phosphorodithioate
EHPC*	Ethyl 3-hydroxy-phenylcarbamate
Ethofumesate	(\pm) -2-ethoxy-2,3-dihydro-3,3-dimethylbenzofuran-5-yl-methanesulfonate
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 (free acid)*	(R)-2-[4-(5-trifluoromethyl-2-puyridyloxy)phenoxy]propanoic acid
Fluroxypyr	(4-amino-3,5-dichloro-6-fluro-2-pyridinyl)oxy]acetic acid
Glyphosate	N-(phosphonomethyl)glycine
DPEPU-desamido*	N-((3-(ethylsulfonyl)-2-pyridyl)-4,6 dimethoxy-2 pyrimidinamine
DPEPU [*]	N-(4,6-dimethoxy-2-pyrimidinyl-N-((3-ethylsulfonyl)-2-pyridinyl)urea
Ioxynil	4-hydroxy-3,5-diiodobenzonitrile
МСРА	(4-cloro-2-methylphenoxy)acetic acid
Metamitron	4-amino-4,5-dihydro-3-methyl-6-phenyl-1,2,4-triazin-5-one
Metamitron-desamino*	4,5-dihydro-3-methyl-6-phenyl-1,2,4-triazin-5-one
Metribuzin-desamino- diketo [*]	6-tert-butyl-4,5-dihydro-3-methylthio-1,2,4-triazin-3,5-dione
Metribuzin-diketo*	4-amino-6-tert-butyl-4,5-dihydro-1,2,4-triazin-3,5-dione
Metsulfuron-methyl	Methyl 2-[[[[(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
PHPC*	3-phenyl-4-hydroxy-6-chloropyridazine

Table A1.1 Chemical Abstracts nomenclature for the pesticides and degradation products encompassed by the PLAP.

*Degradation product

Parameter	Chemical Abstracts nomenclature
Pirimicarb	2-(dimethylamino)-5,6-dimethyl-4-pyrimidinyldimethylcarbamate
Pirimicarb-desmethyl*	2-(dimethylamino)-5,6-dimethyl-4-pyrimidinylmethylcarbamate
Pirimicarb-desmethyl- formamido [*]	2-methylformamido-5,6-dimethylpyrimidine-4-yl dimethylcarbamate
Propiconazole Rimsulfuron	1-[[2-(2,4-dichlorophenyl)-4-propyl-1,3-dioxolan-2-yl]methyl]-1H-1,2,4-triazole N-[[(4,6-dimethoxy-2-pyrimidinyl)amino]carbonyl]-3-(ethylsulfonyl)-2- pyridinesulfonamide
Terbuthylazine	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
*) Degradation product	

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

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. 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 completely the day before sampling. With the horizontal monitoring wells sampling was performed using a peristaltic pump, allowing a purge volume of 200 1 equivalent to 1.6 times the volume of the screen.

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, 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 $(\mu g/l)$
- Ct_i = Pesticide concentration in the weekly samples collected by means of the time-proportional sampler $(\mu g/l)$

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 and Ca, pH and conductivity are measured monthly, whereas HCO₃, Fe, Mg, Mn, DOC, Na, NO₃, NO₂, PO₄, total-P, dissolved total-P, suspended matter and SO₄ are 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 screen was extended to six months except for the suction cups 2 m b.g.s. at Tylstrup, where the 4month interval was retained (Table A2.1).

Site	Monthly monitoring	Half-yearly monitoring	Not
	(Extensive)	(Intensive)	Measured
Tylstrup	M5, M4, S1a, S1b	M1, M3, M4, M5, M6, S1 (1 m b.g.s.)a, S2a*,	M7, M2
		S1b, S2b*	
Jyndevad	M1, M4, S1a, S1b	M1, M2, M4, M5, M7, S1a, S2a,	M6, M3, S2b, S1b
Silstrup	M5, H2.2, H1.2	M4, M5, M6, M12, M13, M9, H1.1, H1.2, H1.3,	M10, M11
		H2.1, H2.2, H2.3	
Estrup	M5, H1.2	M1, M3, M4, M5, M6, H1.1, H1.2, H1.3	M2, M7
Faardrup	M5, H1.3, H2.3	M1, M2, M3, M4, M5, M6, H1.1, H1.2, H1.3,	M7
		H2.1, H2.2, H2.3	
Slaeggerup	M6, H2.2, H1.2	M1, M3, M5, M6, M7, H1.1, H1.2, H1.3, H2.1,	M2, M4
		H2.2, H2.3	

Table A2.1 Pesticide monitoring programme in the suction cups (S), horizontal monitoring wells (H) and vertical monitoring (M) wells as of March 2002.

*) Measured every fourth month

S1a and S1b refer to suction cups installed 1 and 2 m b.g.s., respectively, at location S1, whereas S2a and S2b refer to suction cups installed 1 and 2 m b.g.s., respectively, at location S2.

Date	Management practice
19.11.98	Ploughing – 20 cm depth
23 04 99	Fertilization – 121 kg N/ha and 8 kg P/ha
27 04 99	Fertilization – 63 kg K/ha
04 05 99	Potatoes planted – cultivar Dianella
25 05 99	Herbicide – 1.0 l/ha Afalon (linuron)
25.05.99	Herbicide $= 0.2 \text{ kg/ha}$ Sencor WG (metribuzin)
27.05.99	Tracer application -30 kg/ha potassium bromide
07.06.99	Herbicide $= 0.15$ kg/ha Sencor WG (metribuzin)
11.06.99	Insecticide – 0.3 l/ha Karate (lambda-cyhalothrin)
22.06.99–14.09.99	Ten fungicide applications – each comprising 2.0 kg/ha Dithane DG (man-
22.00.99 11.09.99	cozeb)
12.09.99	Irrigation – 33 mm/ha
20.10.99	Potatoes harvested (tuber vield 475 hkg/ha, 24% drv matter)
22.10.99	Disc harrowed -6 cm depth
01.11.99	Harrowed – 3 cm depth
11.11.99	Harrowed – 5 cm depth
25.11.99	Harrowed – 7 cm depth
17.03.00	Ploughed -20 cm depth
24.03.00	Rolled with a concrete roller
28.03.00	Fertilization – 124 kg N/ha, 18 kg P/ha and 59 kg K/ha
29.03.00	Spring barley sown – cultivar Bartok
13.05.00	Herbicide – 20 g/ha Logran 20 WG (triasulfuron)
19.06.00	Fungicide – 1.0 l/ha Tilt Top (propiconazole + fenpropimorph)
19.06.00	Insecticide – 0.25 l/ha Pirimor G (pirimicarb)
07.07.00	Irrigation – 31 mm/ha
21.08.00	Spring barley harvested (grain yield 73.3 hkg/ha; 85% dry matter. Straw yield
	28.6 hkg/ha; 100% dry matter)
14.09.00	Ploughing – 25 cm depth
01.10.00	Winter rye sown – cultivar Dominator
02.11.00	Herbicide – 20 g/ha Express (tribenuron methyl)
02.11.00	Herbicide – 2.0 l/ha Stomp SC (pendimethalin)
14.05.01	Fungicide – 0.5 l/ha Tilt Top (propiconazole + fenpropimorph)
31.05.01	Irrigation – 23 mm/ha
13.06.01	Fungicide – 0.5 l/ha Tilt Top (propiconazole + fenpropimorph)
21.06.01	Irrigation – 21 mm/ha
28.08.01	Winter rye harvested (grain yield 63.6 hkg/ha; 85% dry matter. Straw yield 36.0
	hkg/ha; 100% dry matter)
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)

Table A3.1 Management practice at Tylstrup. The active ingredients of the various pesticides are indicated in parentheses.

-_

Date	Management practice
10.03.99	Rotary cultivated – 5 cm depth
10.03.99	Ploughed – 20 cm depth
15.03.99	Rolled with a concrete roller
25.03.99	Spring barley sown – cultivar Alexis
20.04.99	Fertilization – 49 kg N/ha ammonium nitrate limestone
22.04.99	Fertilization – 17 kg P/ha and 87 kg K/ha
07.05.99	Fertilization – 85 kg N/ha as ammonium nitrate limestone
10.05.99	Herbicide – 15 g/ha Logran 20 WG (triasulfuron)
29.05.99	Irrigation – 31 mm/ha
09.08.99	Spring barley harvested (grain yield 47.7 hkg/ha; 85% dry matter. Straw yield 40.3 hkg/ha: 100% dry matter)
22.09.99	Herbicide – 2.0 1/ha Roundup 2000 (glyphosate)
05.10.99	Rotary cultivated – 5 cm depth
11.10.99	Ploughed -20 cm depth
11.10.99	Rolled with a concrete roller
13.10.99	Winter rye sown – cultivar Dominator
12.11.99	Tracer application – 30.0 kg/ha potassium bromide
12.11.99	Herbicide – 7.5 g/ha Express (tribenuron methyl)
04.04.00	Fertilization – 115 kg N/ha, 16 kg P/ha and 55 kg K/ha
05.04.00	Fungicide – 0.5 l/ha Tilt Top (propiconazole + fenpropimorph)
05.05.00	Irrigation – 29 mm/ha
07.06.00	Fungicide – 0.5 l/ha Tilt Top (propiconazole + fenpropimorph)
09.08.00	Spring barley harvested (grain yield 56.2 hkg/ha; 85% dry matter. Straw yield 38.1 hkg/ha; 100% dry matter)
24.04.01	Fertilization – cattle slurry 49 tonnes/ha, 68 kg total-N/ha, 34 kg P/ha and 196 kg K/ha
26.04.01	Ploughing – 20 cm depth
30.04.01	Maize sown – cultivar Loft
30.04.01	Fertilization – 59 kg/ha ammonia nitrate
30.04.01	Fertilization – 21 kg N/ha and 40 kg P/ha
14.05.01	Fungicide – 1.5 l/ha Lido (terbuthylazine + pyridate)
30.05.01	Fungicide – 1.5 l/ha Lido (terbuthylazine + pyridate)
04.07.01	Irrigation – 31 mm/ha
23.07.01	Irrigation – 30 mm/ha
01.10.01	Maize harvested (cob yield 84.4 hkg/ha; 100% dry matter. Stalk yield 67.0 hkg/ha;
	100% dry matter)
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)

Table A3.2 Management practice at Jyndevad. The active ingredients in the various pesticides are indicated in parentheses.

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Date	Management practice
19.04.00	Fertilization – cattle slurry 36.5 tonnes/ha, 150 kg total-N/ha, 36 kg P/ha and 162 kg K/ha
19.04.00	Ploughing – 22 cm depth
04.05.00	Fodder beat sown – cultivar Kyros
15.05.00	Fertilization – 103 kg N/ha, 26 kg P/ha and 78 kg K/ha
22.05.00	Herbicide – 1.0 l/ha Goltix WG and 1 l/ha Betanal Optima
	(metamitron, phenmedipham, desmedipham and ethofumesate)
22.05.00	Tracer application – 30 kg/ha potassium bromide
15.06.00	Herbicide – 1.0 l/ha Goltix WG and 1 l/ha Betanal Optima
	(metamitron, phenmedipham, desmedipham and ethofumesate)
28.06.00	Herbicide – 1.5 l/ha Fusilade X-tra (fluazifop-P-butyl)
05.07.00	Insecticide – 0.3 kg/ha Pirimor G (pirimicarb)
12.07.00	Herbicide – 1.0 l/ha Goltix WG and 1 l/ha Betanal Optima
	(metamitron, phenmedipham, desmedipham and ethofumesate)
15.11.00	Fodder beet harvested (beet yield 134.5 hkg/ha; 100% dry matter)
01.04.01	Ploughing – depth 18 cm
08.05.01	Fertilization – 91 kg N/ha, 13 kg P/ha and 34 K kg/ha
09.05.01	Spring barley sown – cultivar Otira
22.05.01	Fertilization – 27 kg N/ha, 4 kg P/ha and 10 kg K/ha
09.06.01	Herbicide – 20 g/ha Express (tribenuron methyl)
21.06.01	Herbicide – 3.0 l/ha Barnon Plus 3 (flamprop-M-isopropyl)
21.06.01	Fungicide – 0.5 l/ha Tilt Top (propiconazole + fenpropimorph)
04.07.01	Fungicide – 0.5 l/ha Tilt Top (propiconazole + fenpropimorph)
16.07.01	Herbicide – 0.6 l/ha Perfection 500 (dimethoate)
05.09.01	Spring barley harvested (grain yield 74.8 hkg/ha; 85% dry matter. Straw yield 28.6 hkg/ha
	100% dry matter)
25.10.01	Herbicide – 4.0 l/ha Roundup Bio (glyphosate)
18.12.01	Ploughed – 22 cm depth
23.04.02	Fertilization – 46.5 kg N/ha
25.04.02	Seedbed preparation – 8 cm depth
25.04.02	Maize sown – cultivar Loft
19.05.02	Herbicide – 1.5 l/ha Lido (terbuthylazine + pyridate)
03.06.02	Herbicide – 1.5 l/ha Lido (terbuthylazine + 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)

Table A3.3 Management practice at Silstrup. The active ingredients in the various pesticides are indicated in parentheses.

Date	Management practice
11.04.00	Ploughing – depth 22 cm
12.04.00	Spring barley sown – cultivar Barke
27.04.00	Fertilization – 131 kg N/ha, 19 kg P/ha and 63 kg K/ha
15.05.00	Herbicide – 20 g/ha Ally (metsulfuron-methyl)
15.05.00	Soil treatment – 2.0 l/ha manganese sulphate
15.05.00	Tracer application – 30 kg/ha potassium bromide
31.05.00	Herbicide – 3.0 l/ha Barnon Plus 3 (flamprop-M-isopropyl)
07.06.00	Soil treatment – 2.0 l/ha manganese sulphate
15.06.00	Fungicide – 0.5 l/ha Tilt Top (propiconazole + fenpropimorph)
15.06.00	Insecticide – 0.4 l/ha Perfection 500 S (dimethoate)
05.07.00	Fungicide – 0.5 l/ha Tilt Top (propiconazole + fenpropimorph)
05.07.00	Insecticide – 0.4 l/ha Perfection 500 S (dimethoate)
28.08.00	Spring barley harvested (grain yield 52.6 hkg/ha; 85% dry matter. Straw yield 13.1
	hkg/ha; 100% dry matter)
13.10.00	Herbicide – 4.0 l Roundup Bio (glyphosate)
23.10.00	Ploughing – depth 20 cm
01.05.01	Fertilization – 20 kg P/ha and 105 kg K/ha
02.05.01	Peas sown – cultivar Julia
22.05.01	Herbicide – 1.0 I/ha Basagran 480 (bentazone)
22.05.01	Herbicide – 1.5 I/ha Stomp (pendimethalin)
27.06.01	Insecticide – 0.25 kg/ha Pirimor G (pirimicarb)
22.08.01	Peas harvested (seed yield 51.8 hkg/ha; 86% dry matter)
30.08.01	Spreading of pea residues
18.10.01	Ploughed – 20 cm depth
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)

Table A3.4 Management practice at Estrup. The active ingredients in the various pesticides are indicated in parentheses.

Date	Management practice
11.08.99	Herbicide – 2.0 l/ha Roundup 2000 (glyphosate)
10.09.99	Stubble harrowed – 10 cm depth
19.09.99	Ploughed – 20 cm depth
19.09.99	1 st seed bed preparation – with power harrow, 5 cm depth
20.09.99	2^{nd} seed bed preparation – with power harrow, 5 cm depth
20.09.99	Winter wheat sown – cultivar Stakado
05.10.99	Tracer application – 30 kg/ha potassium bromide
14.10.99	Herbicide – 1.0 l/ha Briotril (ioxynil and bromoxynil)
21.03.00	Fertilization – 70 kg N/ha, 10 kg P/ha and 25 kg K/ha
08.04.00	Herbicide – 0.8 l/ha Starane 180 (fluroxypyr)
19.04.00	Fertilization – 99 kg N/ha, 14 kg P/ha and 36 kg K/ha
05.05.00	Fungicide – 0.5 l/ha Tilt Top (propiconazole + fenpropimorph)
31.05.00	Fungicide – 0.5 l/ha Tilt Top (propiconazole + fenpropimorph)
19.06.00	Insecticide – 0.25 l/ha Pirimor G (pirimicarb)
28.08.00	Winter wheat harvested (grain yield 92.7 hkg/ha; 85% dry matter. Straw yield 76.2
	hkg/ha; 100% dry matter)
04.10.00	Herbicide – 2.0 l/ha Roundup 2000 (glyphosate)
16.10.00	Ploughing – depth 20 cm
02.05.01	Fertilization – 110 kg N/ha, 21 kg P/ha and 63 kg K/ha
02.05.01	Sugar beet sown – cultivar Havana
21.05.01, 30.05.01	Herbicide - 1.0 l/ha Goltix WG and 1.5 l/ha Betanal Optima (metamitron, phenmedi-
& 15.06.01	pham, desmedipham and ethofumesate)
21.06.01	Herbicide – 1.5 l/ha Fusilade X-tra (fluazifop-P-butyl)
17.07.01	Insecticide – 0.3 l/ha Pirimor G (pirimicarb)
24.10.01	Sugar beet harvested (beet yield 147.9 hkg/ha; 100% dry matter)
30.10.01	Ploughed – 25 cm depth
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 Perfection 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)

Table A3.5 Management practice at Faardrup. The active ingredients in the various pesticides are indicated in parentheses.

Date	Management Practice
05.04.00	Ploughing – depth 22 cm
07.04.00	Fertilization – 81.8 kg N/ha, 20.5 kg P/ha and 61.4 kg K/ha
08.04.00	Spring barley sown – cultivar Optic
09.05.00	Herbicide – 20 g/ha Ally (metsulfuron-methyl)
05.06.00	Herbicide – 3.0 l/ha Barnon Plus 3 (flamprop-M-isopropyl)
09.06.00	Fungicide – 0.5 l/ha Tilt Top (propiconazole + fenpropimorph)
09.06.00	Insecticide – 0.6 l/ha Perfection 500 S (dimethoate)
14.06.00	Herbicide – 15 g/ha Express (tribenuron methyl)
26.06.00	Fungicide – 0.5 l/ha Tilt Top (propiconazole + fenpropimorph)
22.08.00	Spring barley harvested (grain yield 39.8 hkg/ha; 85% dry matter. Straw yield 10.2
	hkg/ha; 100% dry matter)
20.11.00	Ploughing – depth 22 cm
11.04.01	Peas sown – cultivar Pinocchio
01.05.01	Fertilization – 7.5 kg P/ha and 39.3 kg K/ha
01.05.01	Herbicide – 1.0 l/ha Basagran 480 (bentazone)
01.05.01	Herbicide – 1.5 l/ha Stomp SC (pendimethalin)
01.07.01	Insecticide – 0.25 kg/ha Pirimor G (pirimicarb)
19.08.01	Peas harvested (seed yield 26.6 hkg/ha; 86% dry matter)
26.09.01	Herbicide – 4.0 l/ha Roundup Bio (glyphosate)
13.10.01	Ploughed – 22 cm depth
15.10.01	Winter wheat sown – cultivar Bill
08.11.01	Herbicide – 1.0 l/ha Oxitril CM (ioxynil + bromoxynil)
05.04.02	Fertilization – 64 kg N/ha, 19 kg P/ha and 53 kg K/ha
22.04.02	Herbicide – 20 g/ha Gratil 75 WG (amidosulfuron)
02.05.02	Fertilization – 69 kg N/ha, 16 kg P/ha and 58 kg K/ha
15.05.02	Herbicide – 3.0 l/ha Barnon Plus 3 (flamprop-M-isopropyl)
31.05.02	Fungicide – 0.25 1/ha Tilt 250 EC (propiconazole)
14.06.02	Insecticide – 0.25 kg/ha Pirimor G (pirimicarb)
14.06.02	Fungicide – 0.25 l/ha Tilt 250 EC (propiconazole)
20.08.02	Winter wheat harvested (seed yield 72.3 hkg/ha; 85% dry matter)

Table A3.6 Management practice at Slaeggerup. The active ingredients in the various pesticides are indicated in parentheses.



Figure A4.1. Monthly precipitation (A) and potential evapotranspiration (B) at Tylstrup for the monitoring period May 1999–June 2002. Normal values (1961–1990) compared to locally measured (precipitation) or calculated (evapotranspiration).



Figure A4.2. Monthly precipitation (A) and potential evapotranspiration (B) at Jyndevad for the monitoring period May 1999–June 2002. Normal values (1961–1990) compared to locally measured (precipitation) or calculated (evapotranspiration).



Figure A4.3. Monthly precipitation (A) and potential evapotranspiration (B) at Silstrup for the monitoring period April 2000–June 2002. Normal values (1961–1990) compared to locally measured (precipitation) or calculated (evapotranspiration).



Figure A4.4. Monthly precipitation (A) and potential evapotranspiration (B) at Estrup for the monitoring period June 2000– June 2002. Normal values (1961–1990) compared to locally measured (precipitation) or calculated (evapotranspiration).


Figure A4.5. Monthly precipitation (A) and potential evapotranspiration (B) at Faardrup for the monitoring period May 1999–June 2002. Normal values (1961–1990) compared to locally measured (precipitation) or calculated (evapotranspiration).



Figure A4.6. Monthly precipitation measured (A) and potential evapotranspiration (B) at Slaeggerup for the monitoring period April 2000–June 2002. Normal values (1961–1990) compared to locally measured (precipitation) or calculated (evapotranspiration).

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:

$$P_i = \sum_{t_1}^{t_2} P_t$$

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.

Sı	action cup S	1 – 1 m b.g.s.		Su	ction cup S2	cup S2 – 1 m b.g.s.			
Date	Perc. (mm)	MDD (µg/l)	MD (µg/l)	Date	Perc. (mm)	MDD (µg/l)	MD (µg/l)		
ti	P_i	C_i	C_i	ti	P_i	C_i	C_i		
23.08.99	93	n.a.	n.a.	23.08.99	93	n.a.	n.a.		
09.09.99	47	*	*	09.09.99	47	*	< 0.2		
04.11.99	98	*	< 0.2	04.11.99	127	*	< 0.2		
08.12.99	87	0.25	0.22	10.01.00	154	0.25	0.08		
10.01.00	98	0.72	0.62	03.02.00	57	0.23	0.11		
03.02.00	54	2.05	0.39	02.03.00	67	0.23	0.07		
02.03.00	67	2.10	0.17	06.04.00	56	0.20	0.14		
06.04.00	56	1.96	0.50	10.05.00	26	0.21	0.09		
10.05.00	26	1.39	n.a.	07.06.00	38	0.21	< 0.02		
07.06.00	38	1.06	0.48	03.10.00	39	0.11	0.09		
03.10.00	10	0.28	0.15	05.12.00	165	0.30	0.12		
31.10.00	91	0.10	0.17	04.01.01	71	0.24	0.08		
05.12.00	212	0.11	0.01	07.02.01	42	0.37	0.10		
30.04.01	93	0.74	0.20	06.03.01	19	0.30	0.11		
30.05.01	20	0.56	0.18	03.04.01	19	0.42	0.12		
04.07.01	12	0.21	0.09	30.04.01	56	0.66	0.23		
08.08.01	1	0.07	0.21	04.07.01	26	0.52	0.13		
13.09.01	5	0.03	0.09	08.08.01	1	0.37	0.18		
10.10.01	40	0.03	0.15	13.09.01	5	0.18	0.08		
06.11.01	27	< 0.02	0.15	10.10.01	40	0.14	0.05		
04.12.01	31	0.04	0.09	06.11.01	27	0.14	< 0.02		
07.01.02	26	0.06	0.10	04.12.01	31	0.12	0.06		
06.02.02	138	0.05	0.16	07.01.02	26	0.12	0.11		
05.03.02	75	0.07	< 0.02	06.02.02	138	0.19	0.13		
03.04.02	24	0.20	0.08	05.03.02	75	0.23	0.08		
30.04.02	17	0.06	0.14	03.04.02	24	0.16	0.04		
28.05.02	30	< 0.02	0.11	30.04.02	17	0.12	0.11		
02.07.02	13	0.05	0.12	28.05.02	30	0.12	0.12		
				02.07.02	13	0.06	0.07		
1.7.99-30.6.00		0.87-0.97	0.26-0.36	1.7.99-30.6.00		0.14-0.27	0.05-0.10		
1.7.00-30.6.01		0.33	0.13	1.7.00-30.6.01		0.33	0.12		
1.7.01-30.6.02		0.06	0.11	1.7.01-30.6.02		0.19	0.09		

Table A5.1 Estimated percolation rate (Perc.) and measured concentration of metribuzin-diketo (MD) and metribuzin-desamino-diketo (MDD). The estimated average concentrations for each monitoring period are also shown.

*Degradation product detected in the range 0.05–0.5 µg/l; n.a.: Not analysed

As the analysis methods for these degradation products were developed during the present project, results are only available from September 1999 onwards. The bromide transport studies indicate that the degradation products are unlikely to have reached the suction cups before late August 1999. The percolate concentration was therefore assumed to be zero during the period 1.6.99–23.8.99. The first analyses (October and November) were also subject to some uncertainty due to the high detection limit of $0.2 \mu g/l$. The average concentration for 1999/2000 is therefore given as a range representing the maximum and minimum concentrations estimated by applying a concentration equal to either zero or the detection limit.

	Time-pr	oportional sa	imples	Flow-proportional samples					
Date	AMPA	Glyphosate	Drainage runoff	Date	AMPA	Glyphosate	Drainage runoff		
	(µg/l)	(µg/l)	(mm)		(µg/l)	(µg/l)	(mm)		
18.09.01			5						
25.09.01			12						
02.10.01			5						
09.10.01	< 0.01	< 0.01	14	08.10.01	< 0.01	< 0.01	10		
16.10.01	< 0.01	< 0.01	22						
23.10.01	< 0.01	< 0.01	0						
30.10.01	0.14	1.90	2						
06.11.01	0.19	1.10	2	31.10.01	0.06	4.70	2		
13.11.01	0.16	0.65	3	12.11.01	0.35	1.20	3		
27.11.01	0.18	0.41	3	27.11.01	0.14	0.18	2		
04.12.01	0.07	0.17	9	30.11.01	0.07	0.42	2		
				04.12.01	0.11	0.24	5		
11.12.01	0.17	0.13	5	06.12.01	0.05	0.23	2		
27.12.01	0.08	0.06	5	27.12.01	0.10	0.07	4		
02.01.02	0.21	0.06	5	03.01.02	0.10	0.05	4		
08.01.02	0.06	0.05	1	17.01.02	0.06	0.05	1		
22.01.02	0.03	0.03	10	22.01.02	0.04	0.03	8		
29.01.02	0.04	0.04	38	28.01.02	0.05	0.05	34		
05.02.02	0.03	0.03	11						
13.02.02	< 0.01	< 0.01	24	13.02.02	n.a.	n.a.	11		
19.02.02	0.05	0.03	1						
26.02.02	0.05	0.03	14	26.02.02	0.10	0.07	14		
05.03.02	0.06	0.05	25	01.03.02	0.11	0.08	16		
12.03.02	0.05	0.02	10	08.03.02	0.05	0.03	6		
				12.03.02	0.04	0.03	2		
19.03.02	0.05	0.02	<1						
25.06.02	0.22	0.05	<1						

Table A6.1 Measured concentration of AMPA and glyphosate in drainage water at Silstrup. Drainage runoff refers to the accumulated runoff for each of the analysed samples. Glyphosate was applied to the field on 25.10.01.

n.a:. Not analysed

Monitoring well	H1.2	H1.3		M5	5	
Screen depth (m b.g.s)	3.5	3.5	1.5-2.5	2.5-3.5	3.5-4.5	4.5-5.5
AMPA						
09.10.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	
06.11.01	< 0.01		0.01	0.08	< 0.01	
04.12.01	< 0.01		< 0.01	0.01	< 0.01	
08.01.02	0.014		0.01	< 0.01	< 0.01	
05.02.02	< 0.01		< 0.01	< 0.01	< 0.01	
05.03.02	0.01		0.01	< 0.01	< 0.01	
02.04.02	< 0.01		< 0.01	< 0.01	< 0.01	
30.04.02	< 0.01			< 0.01	< 0.01	< 0.01
28.05.02	< 0.01		< 0.01	< 0.01	< 0.01	
Glyphosate						
09.10.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	
06.11.01	< 0.01		0.01	0.03	< 0.01	
04.12.01	< 0.01	< 0.01	< 0.01	0.01	< 0.01	
08.01.02	< 0.01		< 0.01	< 0.01	< 0.01	
05.02.02	< 0.01		< 0.01	< 0.01	< 0.01	
05.03.02	< 0.01		< 0.01	< 0.01	< 0.01	
02.04.02	< 0.01		< 0.01	< 0.01	< 0.01	
30.04.02	< 0.01			< 0.01	< 0.01	< 0.01
28.05.02	< 0.01		< 0.01	< 0.01	< 0.01	

Table A6.2. Measured concentration (μ g/l) of glyphosate and AMPA in vertical monitoring well M5 and horizontal monitoring well H1 at Silstrup. The location of the monitoring installations is indicated in Figure 20.

Monitoring well	M2		M4		M5			M6							
Screen number	1	2	3	4	1	2	3	4	1	2	3	1	2	3	4
Ethofumesate															
03.05.01	<	<	<		<	<	<		<	<	<	<	<	<	
30.05.01									<	<	<	<	<	<	
04.07.01									<	<	<	<	<	<	
08.08.01		<	<	<	<	<		<	1.40	0.29	0.44	<	<		<
12.09.01									0.03	0.07	0.10			<	<
10.10.01									0.33	0.15	0.14	<	<	<	
05.12.01									0.07	0.04	0.06	<	<	<	
07.02.02			<	<	<	<	<		0.01	0.02	0.02				
06.03.02									0.01	0.01	0.02				
04.04.02									0.01	0.01	0.01				
28.05.02									0.00	0.01	0.02	<	<	<	
03.07.02									0.01	0.01	0.01	<	<	<	
Metamitron															
03.05.01	<	<	<		<	<	<		<	<	<	<	<	<	
30.05.01									<	<	<	<	<	<	
04.07.01									<	<	<	<	<	<	
08.08.01		<	<	<	<	<		<	0.63	0.15	0.21	<	<		<
12.09.01									0.27	0.08	0.10			<	<
10.10.01									0.08	0.05	0.05	<	<	<	
05.12.01									0.03	0.04	0.03	<	<	<	
07.02.02			<	<	<	<	<		0.02	0.01	0.01				
06.03.02									<	<	0.01				
04.04.02									0.01	0.01	0.01				
28.05.02									<	0.01	0.01	<	<	<	
03.07.02									0.01	<	<	<	<	<	
Metamitron-															
desamino															
03.05.01	<	<	<		<	<	<		<	<	<	<	<	<	
30.05.01									<	<	<	<	<	<	
04.07.01									<	<	<	<	<	<	
08.08.01		<	<	<	<	<		<	1.30	0.33	0.62	<	<		<
12.09.01									0.50	0.18	0.21			<	<
10.10.01									0.23	0.16	0.15	<	<	<	
05.12.01				<					0.16	0.27	0.15	<	<	<	
07.02.02			<		<	<	<		0.04	0.05	0.05				
06.03.02									0.03	0.04	0.04				
04.04.02									0.02	0.02	0.02				
28.05.02									0.00	0.02	0.02	<	<	<	
03.07.02									0.01	0.02	0.02	<	<	<	
04.04.01									<	<	<	<	<	<	
03.05.01	<	<	<		<	<	<		<	<	<	<	<	<	

Table A7.1 Concentration (μ g/l) of ethofumesate, metamitron and metamitron-desamino in the vertical monitoring wells at Faardrup. The location of the monitoring installations is indicated in Figure 38.

*) Screens 1,2,3 and 4 are located 1.5–2.5, 2.5–3.5, 3.5–4.5, and 4.5–5.5 m b.g.s., respectively

<) Below the detection limit of 0.01 μ g/l

None of the compounds listed in Table A7.1 were found in any of the water samples from the horizontal monitoring wells.



Figure A8.1 Chloride and nitrogen concentrations at Faardrup. Data derive from the vertical monitoring wells M4, M5 and M6. The concentrations in water sampled from the drainage water and horizontal monitoring well are included for comparison. The location of the monitoring installations is indicated in Figure 38.

	Time-pro	portional samp	oles		Flow-pr	oportional sam	ples
Date	AMPA	Glyphosate	Drainage runoff	Date	AMPA	Glyphosate	Drainage runoff
	(µg/l)	(µg/l)	(mm)		(µg/l)	(µg/l)	(mm)
25.09.01	< 0.01	< 0.01	1				
02.10.01	0.01	0.16	1				
09.10.01	0.01	0.09	1				
15.10.01	0.01	0.34	<1				
23.10.01	n.a.	n.a.	<1				
13.11.01	5.4	5.1	<1				
27.11.01	3.5	1.8	<1				
04.12.01	1.1	0.46	1				
11.12.01	0.1	0.05	1				
27.12.01	0.17	0.14	<1				
02.01.02	0.04	0.05	<1				
08.01.02	0.02	0.04	<1				
15.01.02	0.03	0.03	<1				
22.01.02	0.01	0.01	<1				
29.01.02	0.03	0.02	15	29.01.02	0.05	0.03	14
06.02.02	0.02	0.01	17	06.02.02	0.03	0.02	13
13.02.02	0.02	0.01	7				
20.02.02	0.01	0.01	4				
26.02.02	0.02	0.02	19				
05.03.02	0.03	0.02	35	01.03.02	0.12	0.05	22
12.03.02	0.01	< 0.01	5				
19.03.02	< 0.01	< 0.01	<1				
26.03.02	0.01	< 0.01	<1				
03.04.02	< 0.01	< 0.01	<1				

Table A9.1. Measured concentrations of AMPA and glyphosate in drainage water at Slaeggerup. Drainage runoff refers to the accumulated runoff for each of the analysed samples. Glyphosate was applied to the field on 26.09.01.

n.a.: Not analysed

1 st order model:	$c(t) = a \cdot e^{-k_1 \cdot t}$
$I^{st} + I^{st}$ order model:	$c(t) = a \cdot e^{-k_1 \cdot t} + b \cdot e^{-k_2 \cdot t}$

Table A10.1 Parameters obtained in the curve fitting analyses of degradation data with the 1 st order and 1 st +
1 st order model.

		Depth					
Pesticide	Field	(cm b.g.s.)	а	\mathbf{k}_1	b	k ₂	<u>r²</u>
	set a set						
Bromoxynil	1 st order Slaeggerup	0-20	99.56	2.328	(a) -		0.98
	1 st +1 st order Slaeggerup	0-20	42.28	8.03	63.85	1.37	1.00
	l st order Slaeggerup	80–100	105.26	0.056			0.93
	1 st +1 st order Slaeggerup	80–100	52.59	0.056	52.67	5.58E-02	0.93
Dimethoate	1 st order Estrup	80–100	121.57	0.0093			0.95
	1 st +1 st order Estrup	80-100	20.78	0.025	103.48	8.12E-03	0.95
	1 st order Slaeggerup	0–20	117.73	0.375			0.99
	1 st +1 st order Slaeggerup	0–20					
	1 st order Slaeggerup	80-100	117.26	0.040			0.97
	1 st +1 st order Slaeggerup	80–100	113.43	0.043	4.37	0.0020	0.97
Fenpropimorph	1 st order Tylstrup	0–20	90.45	0.0018			0.86
	$1^{st} + 1^{st}$ order Tylstrup	0–20	13.83	0.032	81.19	0.0011	0.94
	1 st order Jyndevad	0–20	92.46	0.0056			0.72
	$1^{\text{st}} + 1^{\text{st}}$ order Jyndevad	0-20	62.88	0.029	44.09	1.0E-12	0.97
	1 st order Faardrup	0–20	84.14	0.046			0.96
	1 st +1 st order Faardrup	0–20	54.51	0.38	38.48	1.9E-02	1.00
Flamprop-M-isopropyl	1 st order Estrup	0–20	91.43	0.0055			0.88
	$1^{st} + 1^{st}$ order Estrup	0–20	69.02	0.0109	25.85	1E-12	0.90
	1 st order Slaeggerup	0–20	91.33	0.0444			0.96
	1 st +1 st order Slaeggerup	0–20	61.78	0.1084	35.58	0.0134	1.00
Ioxynil	1 st order Faardrup	0–20	81.74	0.96			0.96
5	$1^{\text{st}} + 1^{\text{st}}$ order Faardrup	0-20	70.50	1.29	11.52	6.1E-02	0.99
	1 st order Faardrup	80–100	82.51	0.056			1.00
	$1^{\text{st}} + 1^{\text{st}}$ order Faardrup	80-100	79.96	0.062	2.80	3.9E-03	1.00
	1 st order Slaeggerup	0–20	92.89	0.61			0.94
	1 st +1 st order Slaeggerup	0–20	77.41	1.37	23.14	0.05758	1.00
Propiconazole	1 st order Tylstrup	0–20	94.80	0.0022			0.97
1	$1^{\text{st}} + 1^{\text{st}}$ order Tylstrup	0-20	11.80	0.013	84.60	1.7E-03	0.98
	1 st order Jyndevad	0-20	95.75	0.0036			0.95
	$1^{st} + 1^{st}$ order Jvndevad	0–20	67.31	0.0088	33.83	1.2E-05	1.00
	1 st order Faardrup	0–20	96.52	0.0063			0.99
	$1^{st} + 1^{st}$ order Faardrup	0–20	22.99	0.031	82.36	4.9E-03	1.00
	1 st order Slaeggerup	0–20	86.14	0.0016			0.61
	1 st +1 st order Slaeggerup	0–20	18.75	0.26	79.85	0.00092	0.91



Figure A11.1 Pesticide concentrations in QA samples. The solid line and the closed circles indicate the nominal and observed concentrations, respectively, in internal laboratory controls. The closed red/blue squares indicate the nominal concentrations of the high-level/low-level external control samples. The red/blue diamonds indicate the observed concentrations of the high-level/low-level external control samples.



Figure A11.2 Pesticide concentrations in QA samples. The solid line and the closed circles indicate the nominal and observed concentrations, respectively, in internal laboratory controls. The closed red/blue squares indicate the nominal concentrations of the high-level/low-level external control samples. The red/blue diamonds indicate the observed concentrations of the high-level/low-level external control samples. Open diamonds indicate degradation products that are not present in the spike mixture.



Figure A11.3 Pesticide concentrations in QA samples. The solid line and the closed circles indicate the nominal and observed concentrations, respectively, in internal laboratory controls. The closed red/blue squares indicate the nominal concentrations of the high-level/low-level external control samples. The red/blue diamonds indicate the observed concentrations of the high-level/low-level external control samples.



Figure A11.4 Pesticide concentrations in QA samples. The solid line and the closed circles indicate the nominal and observed concentrations, respectively, in internal laboratory controls. The closed red/blue squares indicate the nominal concentrations of the high-level/low-level external control samples. The red/blue diamonds indicate the observed concentrations of the high-level/low-level external control samples.



Figure A11.5 Pesticide concentrations in QA samples. The solid line and the closed circles indicate the nominal and observed concentrations, respectively, in internal laboratory controls. The closed red/blue squares indicate the nominal concentrations of the high-level/low-level external control samples. The red/blue diamonds indicate the observed concentrations of the high-level/low-level external control samples. Open diamonds indicate degradation products that are not present in the spike mixture.