The Danish Pesticide Leaching Assessment Programme

Monitoring results May 1999–June 2006

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Preface

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

The work was conducted by the Geological Survey of Denmark and Greenland (GEUS), the Faculty of Agricultural Sciences (DJF) and the National Environmental Research Institute (NERI) under the direction of a management group comprising Jeanne Kjær (GEUS), Walter Brüsch (GEUS), Ole Hørbye Jacobsen (DJF), Preben Olsen (DJF), Ruth Grant (NERI), Christian Ammitsøe (Danish Environmental Protection Agency) and Steen Marcher (Danish Environmental Protection Agency). From 2007 Ole Hørbye Jacobsen was replaced by Lis Wollesen de Jonge (DJF).

This report presents the results for the period May 1999–June 2006. Results covering part of the period (May 1999–June 2004) have been reported previously (Kjær *et al.*, 2002, Kjær *et al.*, 2003, Kjær *et al.*, 2004 and Kjær *et al.*, 2005). The present report should therefore be seen as a continuation of previous reports with the main focus being on the leaching risk of pesticides applied during 2003 and 2004.

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

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

Jeanne Kjær
July 2007

Summary

In 1998, the Danish Parliament initiated the Pesticide Leaching Assessment Programme (PLAP), an intensive monitoring programme aimed at evaluating the leaching risk of pesticides under field conditions. The objective of the PLAP is to improve the scientific foundation for decision making in the Danish registration procedures for pesticides. The specific aim is to analyse whether pesticides applied in accordance with current regulations leach to the groundwater in unacceptable concentrations. The programme presently evaluates the leaching risk of 31 pesticides applied at five agricultural sites ranging in size from 1.1 to 2.4 ha. The results so far show that:

- Of the 31 pesticides applied, six (clomazone, desmedipham, linuron, metsulfuron-methyl, triazinamin-methyl and triasulfuron) did not leach during the current monitoring period.

- The monitoring data indicate pronounced leaching of 11 of the applied pesticides and three of their degradation products. Thus ethofumesate, bentazone, pendimethalin, propyzamid, glyphosate and its degradation product AMPA, metamitron and its degradation product metamitron-desamino, azoxystrobin and its degradation product CyPM, as well as the degradation products of metribuzin, terbutylazine, pirimicarb and rimsulfuron, leached through the root zone (1 m b.g.s.) in average concentrations exceeding the maximum allowable concentration of 0.1 µg/L. Except for a degradation product of metribuzin and rimsulfuron leaching was mainly confined to a depth of 1 m, where pesticides were frequently detected in samples from suction cups and drainage systems. Only the metribuzin degradation product was detected beneath this depth at average concentration exceeding 0.1 µg/L.

- The monitoring data also indicate leaching of an additional 14 pesticides, but not in high concentrations. Thus, although the concentration exceeded 0.1 µg/L in several samples, the average leaching concentration (1 m b.g.s.) did not.

The PLAP initially evaluated the leaching risk at six agricultural sites representing a range of Danish soil and climate conditions. Monitoring at the Slaeggerup site was terminated on 1 July 2003, and results from that site are not included in the present report. For the monitoring results from this site see Kjær *et al.* (2004). The pesticides were all applied at the maximum permitted dose. In order to describe water transport a bromide tracer was applied to the fields. Bromide and pesticide concentrations are measured monthly in both the unsaturated and the saturated zones, and weekly in the drainage water. This report presents the monitoring results from the five agricultural sites at which monitoring presently is performed and covers the period May 1999–June 2006. The main focus is on evaluating the leaching risk of the pesticides applied during 2003 and 2004. The report should be viewed as an interim report because not all of the pesticides applied have been monitored for at least two consecutive years.

Dansk sammendrag

I 1998 vedtog Folketinget at iværksætte projektet ”Varslingssystem for udvaskning af pesticider til grundvandet” (VAP). VAP er et omfattende moniteringsprogram, der undersøger udvaskning af pesticider under reelle markforhold. Programmet har til formål at undersøge, om godkendte pesticider eller deres nedbrydningsprodukter – ved regelret brug – udvaskes til grundvandet i koncentrationer over grænseværdien, for herigennem at udvide det videnskabelige grundlag for danske myndigheders (Miljøstyrelsens) procedurer for registrering af sprøjtemidler. 31 stoffers udvaskningsrisiko undersøges således på fem marker af en størrelse på mellem 1,1 og 2,6 ha. De hidtidige resultater viser at:

- Af de 31 pesticider, der er blevet udbragt, blev de seks (clomazon, desmedipham, linuron, metsulfuron-methyl, triazinamin-methyl og triasulfuron) ikke fundet udvasket i løbet af perioden 1999–2006.

- 11 af de udbragte stoffer, eller nedbrydningsprodukter heraf, gav anledning til en markant udvaskning. Ethofumesat, bentazon, pendimethalin, propyzamid, glyphosat, dettes nedbrydningsprodukt AMPA, metamitron, dettes nedbrydningsprodukt metamitrnon-desamino, azoxystrobin, dettes nedbrydningsprodukt CyPM, samt nedbrydningsprodukter fra henholdsvis metribuzin, terbutylazin, pirimicarb og rimsulfuron blev udvasket fra rodzonen (1 m.u.t.) i gennemsnitskoncentrationer over grænseværdien på 0,1 µg/L. På nær gældende metribuzins og rimsulfurons nedbrydningsprodukter var udvaskningen primært begrænset til 1 m.u.t., hvor stofferne hyppigt blev fundet i prøver udtaget i sugeceller og dræn. Markant udvaskning under denne dybde blev kun observeret for metribuzins nedbrydningsprodukt, som i større dybder blev fundet i gennemsnitskoncentrationer over 0,1 µg/L.

- Andre 14 stoffer gav anledning til udvaskning. Selv om flere af disse stoffer ofte blev fundet i koncentrationer over 0,1 µg/L, var der ikke tale om, at udvaskningen som årsmiddel oversteg grænseværdien på 0,1 µg/L.

VAP-programmet omfattede oprindeligt seks marker placeret så de repræsenterer forskellige typer geologi og tillige tager hensyn til de klimatiske variationer i Danmark, specielt hvad angår nedbørforhold. Monitering på den ene forsøgsmark (Slæggerup) stoppede 1 juli 2003. Resultater fra denne mark er ikke inkluderet i denne rapport, men kan findes i Kjær *et al.* (2004). De anvendte pesticider bliver udbragt i maksimalt tilladte doser. Bromid anvendes som sporstof for at beskrive vandtransporten. Bromid- og pesticidkoncentrationer bliver analyseret månedligt i prøver udtaget i den umættede og mættede zone og ugentligt i prøver af drænvand. I denne rapport præsenteres moniteringsresultaterne for de fem områder for perioden maj 1999-juni 2006, primært med fokus på pesticider udbragt i 2003 og 2004. En del af stofferne har kun været inkluderet i moniteringsprogrammet i én udvaskningssæson, og for disse er det derfor for tidligt at konkludere noget endeligt.

1 Introduction

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

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

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

1.1 Objective

In 1998, the Danish Government initiated the Pesticide Leaching Assessment Programme (PLAP), an intensive monitoring programme aimed at evaluating the leaching risk of pesticides under field conditions. The PLAP is intended to serve as an early warning system providing decision makers with advance warning if approved pesticides leach in unacceptable concentrations. The programme focuses on pesticides used in arable farming and monitors leaching at five agricultural test sites representative of Danish conditions.

The objective of the PLAP is to improve the scientific foundation for decision making in the Danish registration and approval procedures for pesticides, enabling field studies to be included in risk assessment of selected pesticides. The specific aim is to analyse whether pesticides applied in accordance with current regulations leach at levels exceeding the maximum allowable concentration of 0.1 µg/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, 31 pesticides and several of their degradation products are included in the PLAP. All the compounds analysed are listed in Appendix 1.

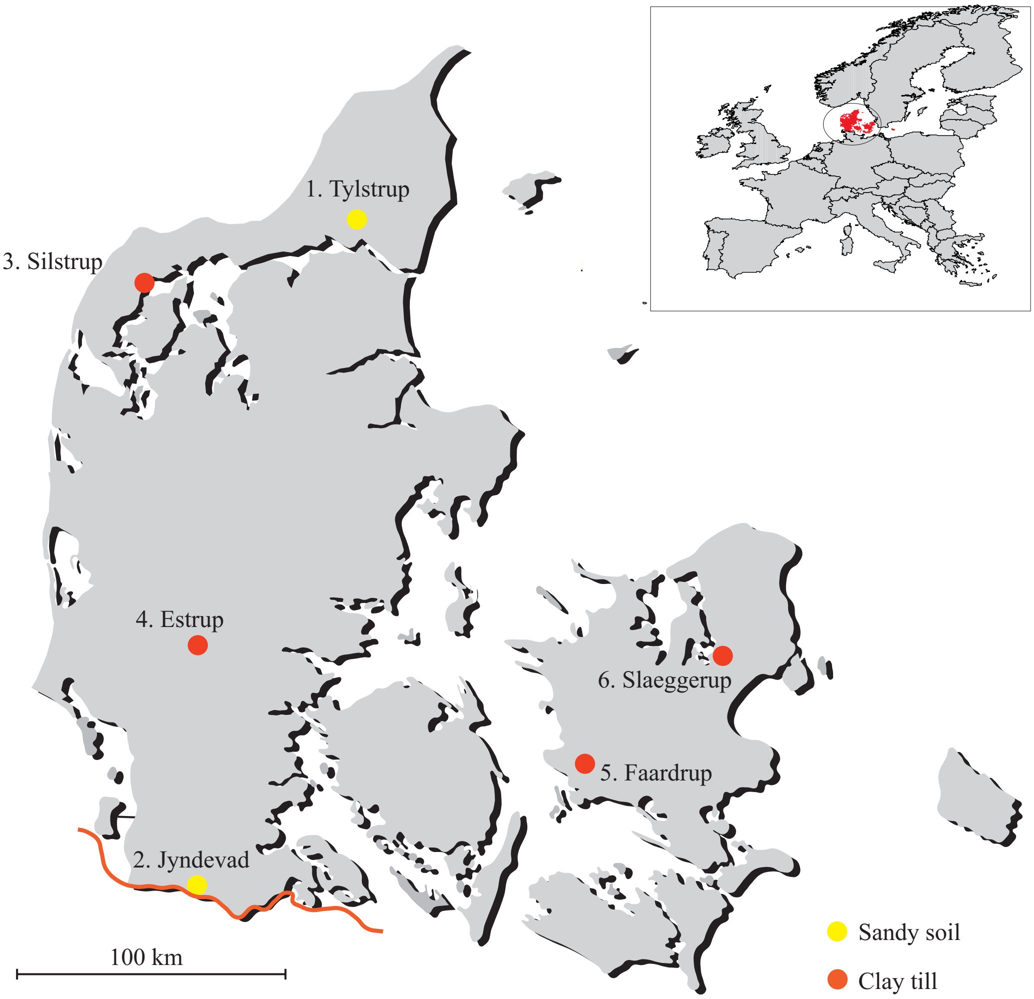


Figure 1. Location of the PLAP sites Tylstrup, Jyndevad, Silstrup, Estrup and Faardrup. Monitoring at Slaeggerup was terminated on 1 July 2003.

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

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

	Tylstrup	**Jyndevad**	**Silstrup**	**Estrup**	**Faardrup**
Location	Brønderslev	Tinglev	Thisted	Askov	Slagelse
Precipitation 1) (mm/y)	668	858	866	862	558
Pot. evapotransp.1) (mm/y)	552	555	564	543	585
W x L (m)	70 x 166	135 x 184	91 x 185	105 x 120	150 x 160
Area (ha)	1.1	2.4	1.7	1.3	2.3
Tile drain	No	No	Yes	Yes	Yes
Monitoring initiated	May 1999	Sep 1999	Apr 2000	Apr 2000	Sep 1999
Geological characteristics					
– Deposited by	Saltwater	Meltwater	Glacier	Glacier/meltwater	Glacier
– Sediment type	Fine sand	Coarse sand	Clayey till	Clayey till	Clayey till
– DGU symbol	YS	TS	ML	ML	ML
– Depth to the calcareous matrix (m b.g.s.)	6	5–9	1.3	1–4 2)	1.5
– Depth to the reduced matrix (m b.g.s.)	>12	10–12	5	>5 2)	4.2
– Max. fracture depth 3) (m)	–	–	4	>6.5	8
– Fracture intensity 3–4 m depth (fractures/m)	–	–	<1	11	4
– Ks in C horizon (m/s)	$2.0\cdot10^{-5}$	$1.3\cdot10^{-4}$	$3.4\cdot10^{-6}$	$8.0\cdot10^{-8}$	$7.2\cdot10^{-6}$
Topsoil characteristics					
– DK classification	JB2	JB1	JB7	JB5/6	JB5/6
– Classification	Loamy sand	Sand	Sandy clay loam/ sandy loam	Sandy loam	Sandy loam
– Clay content (%)	6	5	18–26	10–20	14–15
– Silt content (%)	13	4	27	20–27	25
– Sand content (%)	78	88	8	50–65	57
– pH	4–4.5	5.6–6.2	6.7–7	6.5–7.8	6.4–6.6
– TOC (%)	2.0	1.8	2.2	1.7–7.3	1.4

1) *Yearly normal based on a time series for the period 1961–90. The data refer to precipitation measured 1.5 m above ground.*
2) *Large variation within the field.*
3) *Maximum fracture depth refers to the maximum fracture depth found in excavations and wells.*

Site characterization and monitoring design are described in detail in Lindhardt *et al.* (2001). This report presents the results of the monitoring period May 1999–June 2006. Results covering part of the monitoring period (May 1999–June 2004) have been published previously (Kjær *et al.*, 2002; Kjær *et al.*, 2003 and Kjær *et al.*, 2004). The present report should therefore be seen as a continuation of the former reports, with the main focus being on the leaching risk of pesticides applied during 2003 and 2004. For a detailed description of the first part of the monitoring period (May 1999–June 2003), see Kjær *et al*. (2003), Kjær *et al*. (2004) and Kjaer *et al.* (2005c).

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

Hydrological modelling of the unsaturated zone at each PLAP site supports the monitoring data. The MACRO model (version 5.1) is used to describe the soil water dynamics at each site during the full monitoring period May 1999–June 2006. In previous PLAP modelling studies (Kjær *et al.*, 2004 and 2005c), older versions of MACRO (version 4.2 and 5.0) were used. Due to the changes in model version, the five site models have been recalibrated for the monitoring period May 1999-June 2004 and validated for the monitoring period July 2004-June 2006. The model set-up for the sites is very similar to that reported in Barlebo *et al. (*in press.).

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

2 Pesticide leaching at Tylstrup

2.1 Materials and methods

2.1.1 Site description and monitoring design

Tylstrup is located in northern Jutland (Figure 1). The test field covers a cultivated area of 1.1 ha (70 x 166 m) and is practically flat, with a windbreak bordering the eastern and western sides. Based on two soil profiles dug in the buffer zone around the test field the soil was classified as a Humic Psammentic Dystrudept (Soil Survey Staff, 1999). The topsoil is characterized as loamy sand with 6% clay and 2.0% total organic carbon (Table 1). The aquifer material consists of about 20 meters 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).

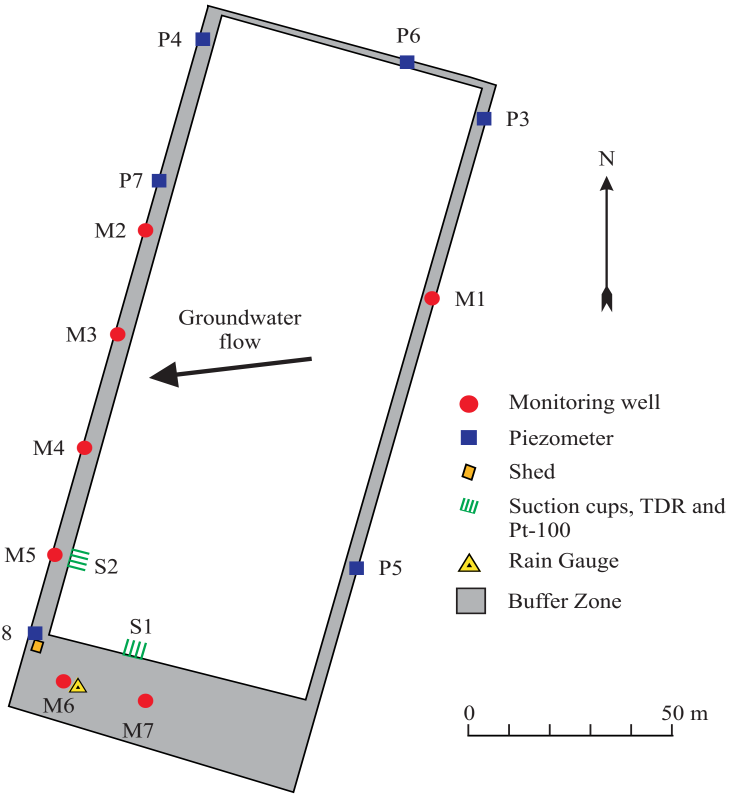


Figure 2.Overview of the Tylstrup test site. The innermost white area indicates the cultivated land, while the grey area indicates the surrounding buffer zone. The positions of the various installations are indicated, as is the direction of groundwater flow (by an arrow).

2.1.2 Agricultural management

Management practice during the 2003-2005 growing seasons is briefly summarized below and detailed in Appendix 3 (Table A3.1). For information about management practice during the first two monitoring periods see Kjær *et al*. (2003).

On 19 September 2002 the field was sown with winter wheat (cv. Solist). On 9 October, when the crop had 2 unfolded leaves, weeds were sprayed with a mixture of prosulfocarb, ioxynil and bromoxynil. Prosulfocarb was not included in the monitoring programme, however. Potassium bromide tracer was applied on 27 May, the second application since the start of the monitoring program. On 8 May, when the first joint of the wheat was detectable, the herbicide fluroxypyr was applied. Seven days later, when the second joint was detectable, an additional herbicide, flamprop-M-isopropyl, was applied. The fungicide propiconazole was applied on 28 May and 17 June (not included in the monitoring, however) and the pesticide dimethoate was applied on 8 July. Irrigation was performed once on 24 June using 23 mm/ha. The yield of grain was disappointingly low – 54.5 hkg/ha (85% dry matter). In field trials conducted this year on sandy soils by the Danish Farmers Association the average yield was 74.5 hkg/ha. The low yield at Tylstrup may be attributable to the local conditions. Considering the time of sowing, a plant density of 270 plants/m^2 was too low. Furthermore, due to heavy sand drift in the spring the plants suffered mechanical damage.

Cultivation of the stubble as well as ploughing was done in September and October, respectively. On 29 April 2004 potatoes for starch were planted (cv. Kuras). Spraying of weeds was done on 4 occasions. Aclonifen was sprayed on the 13 May, fluazifop-P-butyl both on 27 May and 17 June whereas rimsulfuron was applied on 3 June. Against pests were sprayed with cypermethrin on 7 July whereas fluazinam was applied against potato late blight (Phytophthora infestans) on 12 occasions between 22 June and 16 September. Fluazinam and cypermethrin were not included in the monitoring programme. The potatoes were irrigated twice in August using 28 mm/ha on 9th and 29 mm/ha on the 16th. The yield measured on 5 October was 512.0 hkg/ha of tubers, equalling 12.0 tons/ha of 100% dry matter, some 40 hkg/ha lower than in experiments conducted by the Farmers Association this year (Pedersen, 2004)

A crop of maize (cv. Vernal) was established on 28 April 2005. The crop emerged on 14 May and on 18 May when two leaves had unfolded, a first spraying of weeds using terbutylazine was done. On 6 June, when the maize had 5 leaves unfolded, the herbicides terbutylazine and bentazone were applied. Irrigation was carried out on 13 July using 38 mm/ha. On 10 October a total of 13.75 tons/ha of 100% dry matter was harvested. This was similar to that obtained in experiments by the Farmers Association (Pedersen, 2005).

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 water and bromide transport in the unsaturated zone during the full monitoring period May 1999–June 2006 and to establish an annual water balance.

Due to application of a newer version of MACRO than used in the previous reports (Kjær *et al.,* 2005c, and Barlebo *et al,* in press.), the model for the Tylstrup site was recalibrated for the monitoring period May 1999-June 2004 and validated for the monitoring period July

2004-June 2006. The model was recalibrated and validated against daily time series of groundwater table measured in the piezometers located in the buffer zone, soil water content measured at three different depths (25, 60 and 110 cm b.g.s.) from the two profiles S1 and S2 (Figure 2), and the bromide concentration measured in the suction cups located 1 and 2 m b.g.s. Data acquisition, model set-up and results related to simulated bromide transport are described in Barlebo *et al. (*in press.) and Rosenbom *et al.* (in prep.).

2.2 Results and discussion

2.2.1 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 results for the recent years, obtained with MACRO 5.1, were very similar to those obtained with MACRO 4.2 and 5.0 (Kjær *et al.,* 2004). Generally, the model provided a good simulation of the measured fluctuations in the groundwater table (Figure 3B). The dynamics were captured with some exceptions, but as with previous simulations the amplitude of the fluctuations were less well described. The overall trends in soil water content were modelled successfully, with the model capturing soil water dynamics at all depths (Figure 3C-E). The initial decrease in water saturation observed during the summer periods at 60 and 110 cm b.g.s. was however less well captured.

The resulting annual water balance is shown for each monitoring period (July–June) in Table 2. It is very similar to the previous balance calculated with MACRO 5.0 (Kjær *et al.,* 2005c). Precipitation in the latest monitoring year, July 2005–June 2006, was the lowest since the monitoring began at the site and was characterized by August, September, October and January being very dry (Appendix 4). This resulted in almost no percolation 1 m b.g.s. during the summer months and less percolation in the beginning of 2006 compared to previous monitoring years (Figure 3).

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).

	Normal precipitation [2)	Precipitation	Irrigation	Actual evapotranspiration	Groundwater recharge [3)
1.5.99–30.6.99 [1)	120	269	0	112	156
1.7.99–30.6.00	773	1073	33	498	608
1.7.00–30.6.01	773	914	75	487	502
1.7.01–30.6.02	773	906	80	570	416
1.7.02–30.6.03	773	918	23	502	439
1.7.03–30.6.04	773	758	0	472	287
1.7.03–30.6.05	773	854	57	477	434
1.7.03–30.6.06	773	725	67	488	304

[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*

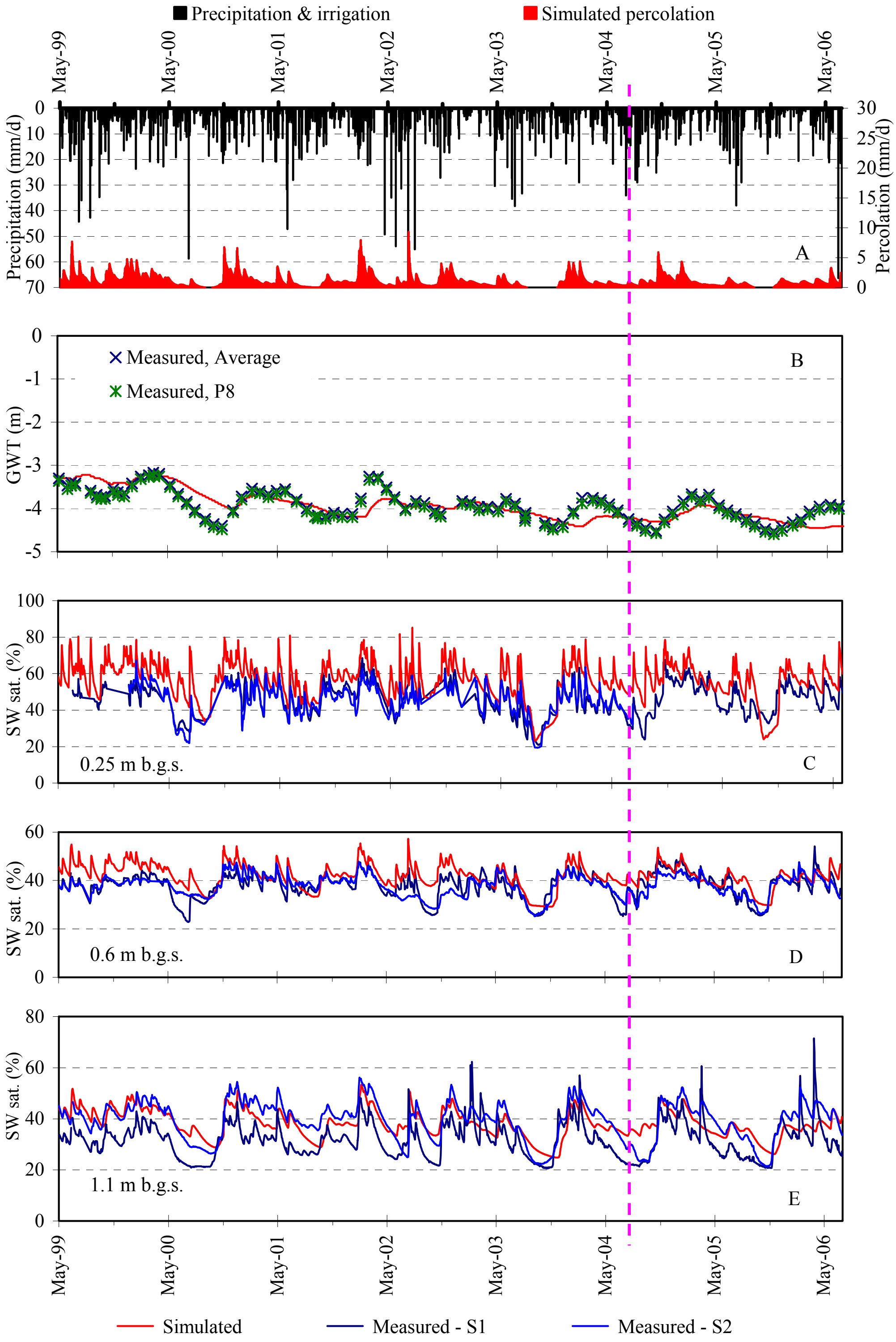


Figure 3. Soil water dynamics at Tylstrup: Measured precipitation, irrigation and simulated percolation 1 m b.g.s. (A), simulated and measured groundwater level GWT (B), and simulated and measured soil water saturation (SW sat.) at three different soil depths (C, D and E). The measured data in B derive from piezometers located in the buffer zone. The measured data in C, D and E derive from TDR probes installed at S1 and S2 (Figure 2). The broken vertical line indicates the beginning of the validation period (July 2004-June 2006).

2.2.2 Bromide leaching

Bromide has now been applied twice at Tylstrup. The bromide concentrations measured up to April 2003 (Figure 4 and Figure 5) relate to the bromide applied in May 1999, as described further in Kjær *et al.* (2003). Unsaturated transport of the bromide applied in March 2003 is evaluated in Barlebo *et al.* (in press.) and Rosenbom *et al.* (in prep.)

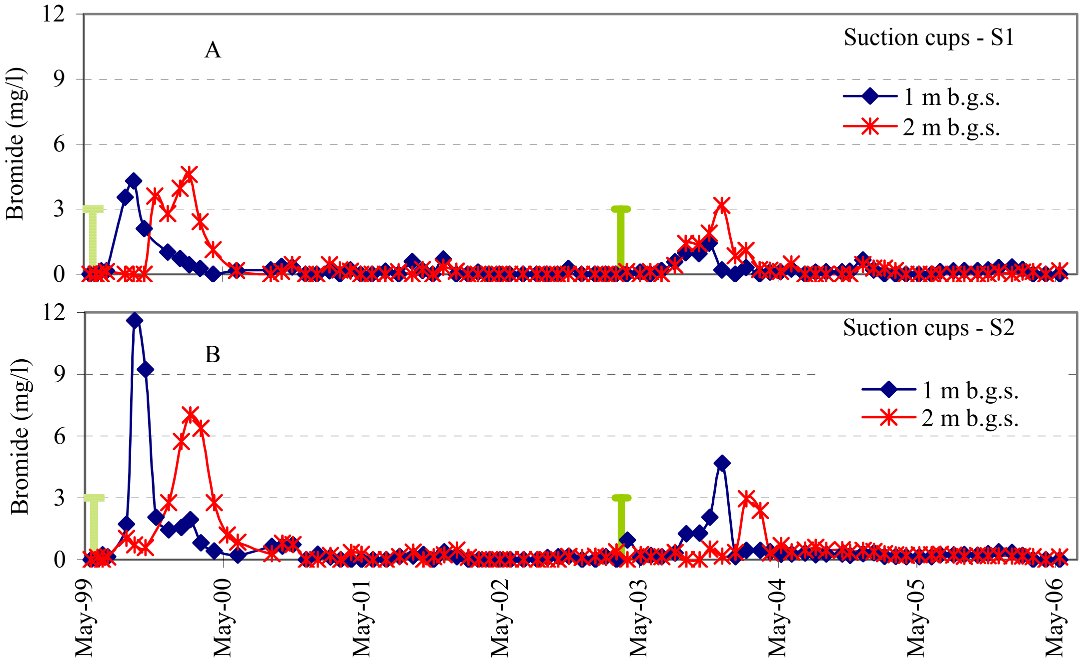


Figure 4. Measured bromide concentration in the unsaturated zone at Tylstrup. The measured data derive from suction cups installed (A) 1 m b.g.s. and (B) 2 m b.g.s. at locations S1 and S2 indicated in Figure 2. The green vertical lines indicate the dates of bromide applications.

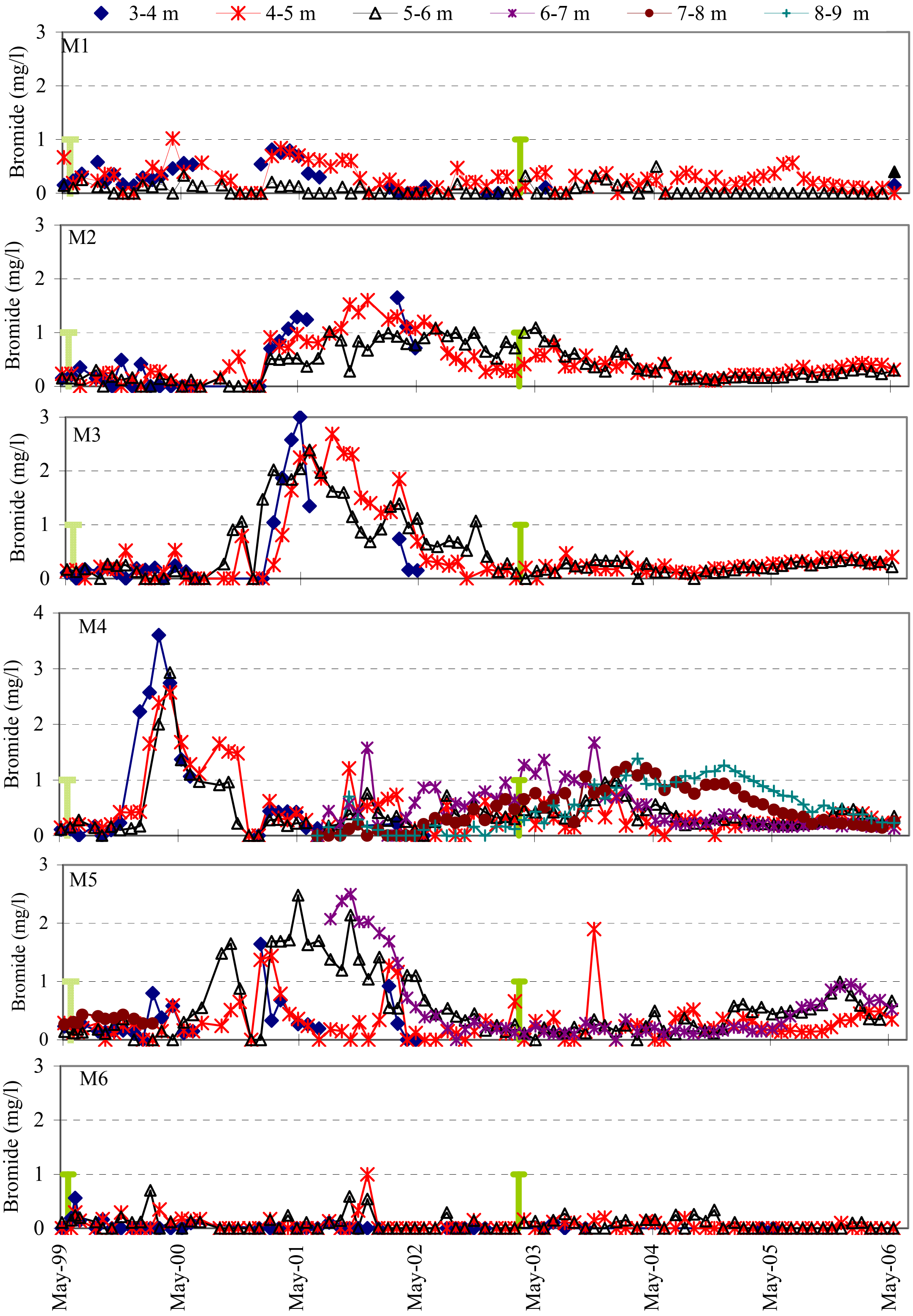


Figure 5. Bromide concentration in the groundwater at Tylstrup. The data derive from monitoring wells M1–M7. Screen depth is indicated in m b.g.s. The green vertical lines indicate the dates of bromide application.

2.2.3 Pesticide leaching

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

It should be noted that precipitation in Table 3 is corrected to the soil surface according to Allerup and Madsen (1979), whereas percolation (1 m b.g.s.) refers to accumulated percolation as simulated with the MACRO model. It should also be noted that as mancozeb (applied here as Dithane DG), tribenuron methyl (applied here as Express) and rimsulfuron (applied here as Titus) degrade rapidly, the leaching risk is more associated with their respective degradation products, ETU, triazinamin-methyl, PPU and PPU-desamino. For the same reasons it is the degradation products and not the parent compounds that are monitored in the PLAP (Table 3). Pesticides applied later than April 2006 are not evaluated in this report and hence are not included in Table 3 and Figure 6.

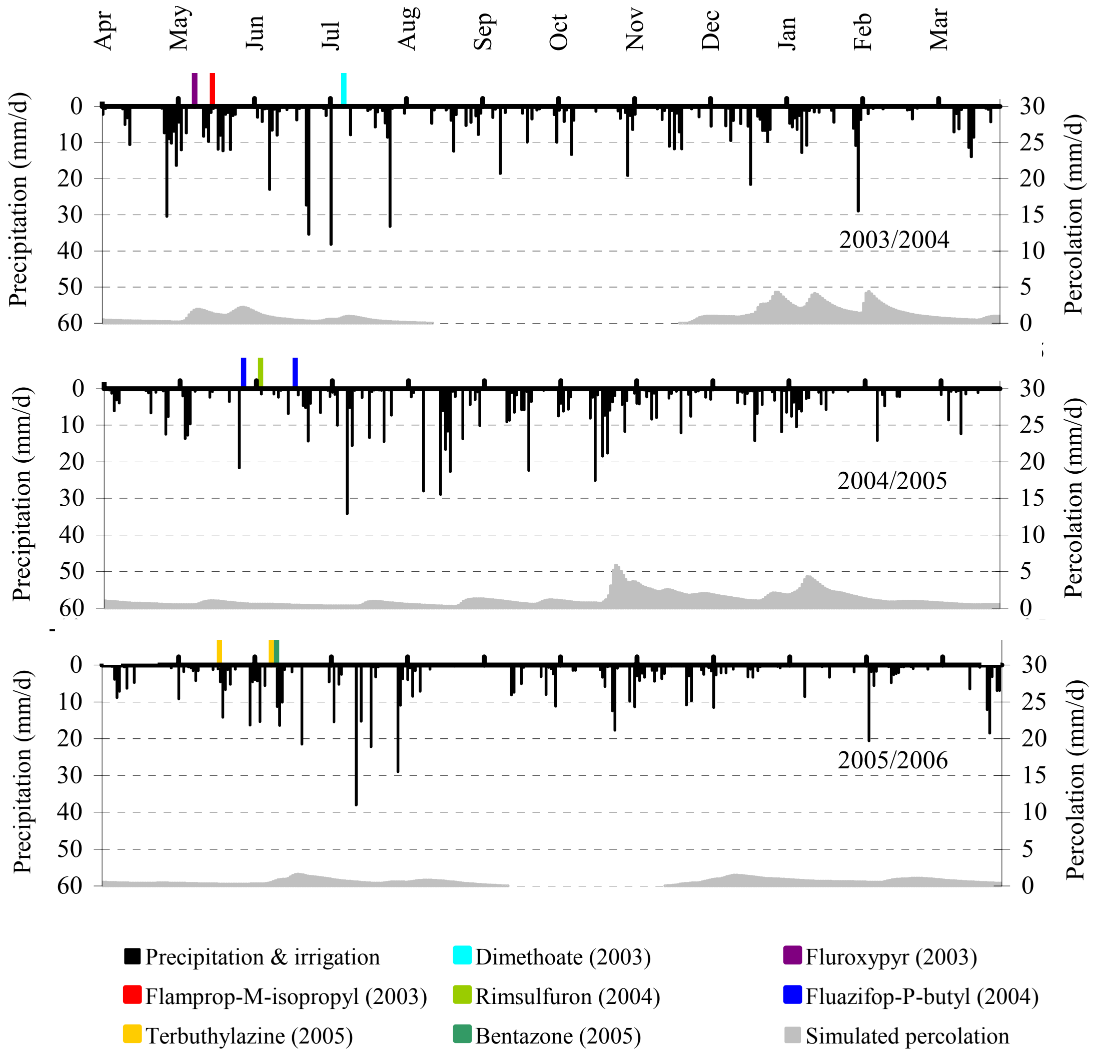


Figure 6. Pesticide application, precipitation and irrigation (primary axis) together with simulated percolation 1 m b.g.s. (secondary axis) at Tylstrup in 2003/2004 (upper), 2004/2005(middle) and 2005/2006 (lower).

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

Crop and analysed pesticides	Application date	End of Monitoring	Prec. (mm)	Perc. (mm)	1st month perc. (mm)	C_{mean} (µg/L)
Potatoes 1999						
Linuron (Afalon)	May 99	Jul 01	2550	1253	87	<0.01 (0)
- *ETU*[1] (Dithane DG)	Jun 99	Oct 01	2381	1169	73	<0.01(9)
Metribuzin (Sencor WG)	Jun 99	Jul 03	4223	2097	85	<0.01 (3)
- *metribuzin-diketo*		Jul 06†	6685	3079	85	0.05–0.36 (598)
- *metribuzin-desamino*		Jul 03	4223	2097	85	<0.02 (0)
- *metribuzin-desamino-diketo*		Jul 06†	6685	3079	85	0.14–0.97 (314)
Spring barley 2000						
Triasulfuron (Logran 20 WG)	May 00	Apr 03	2740	1283	13	<0.02 (0)
- *triazinamin*						<0.02 (0)
Propiconazole (Tilt Top)	Jun 00	Jul 03	2948	1341	11	<0.01 (0)
Fenpropimorph (Tilt Top)	Jun 00	Jul 03	2948	1341	11	<0.01 (0)
- *fenpropimorphic acid*						<0.02 (0)
Pirimicarb (Pirimor G)	Jun 00	Apr 03	2622	1263	17	<0.01 (0)
- *pirimicarb-desmethyl*						<0.02 (0)
- *pirimicarb-desmethyl-formamido*						<0.02 (0)
Winter rye 2001						
Pendimethalin (Stomp SC)	Nov 00	Apr 03	2271	1219	109	<0.01 (0)
Triazinamin-methyl[2] (Express)	Nov 00	Apr 03	2271	1219	109	<0.02 (0)
Propiconazole (Tilt Top)	May 01	Jul 03	2948	1341	11	<0.01 (0)
Fenpropimorph (Tilt Top)	May 01	Jul 03	2948	1341	11	<0.01 (0)
- *fenpropimorphic acid*						<0.01 (0)
Winter rape 2002						
Clomazone (Command CS)	Sep 01	Jul 04	2534	1194	9	<0.01 (0)
- *propanamide-clomazone*						<0.02 (0)

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

[1] Degradation product of mancozeb. The parent compound degrades too rapidly to be detected by monitoring

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

† Monitoring will continue during the following year. The values for prec. and perc. are accumulated up to July 2006

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

As seen from Table 3, there have been no detections of the herbicides *bromoxynil, ioxynil, fluroxypyr, flamprop-M-isopropyl* and its metabolite *flamprop-M* (free acid) or *fluazifop-P (free acid)* since the application of the substances (Table 3). The same is the case regarding the insecticide *dimethoate*.

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

Crop and analysed pesticides	Application date	End of Monitoring	Prec. (mm)	Perc. (mm)	1st month perc. (mm)	C_{mean} (µg/L)
Winter wheat 2003						
Bromoxynil (Oxitril CM)	Oct 02	Apr 05	2082	995	53	<0.01 (0)
Ioxynil (Oxitril CM)	Oct 02	Apr 05	2082	995	53	<0.01 (0)
Fluroxypyr (Starane 180)	May 03	Jul 05	1867	787	50	<0.02 (0)
Flamprop-M-isopropyl (Barnon Plus)	May 03	Jul 05	2635	1031	42	<0.01 (0)
- Flamprop-M (free acid)						
Dimethoate (Perfekthion 500 S)	Jul 03	Jul 05	1629	722	14	<0.01 (0)
Potatoes 2004						
-Fluazifop-P (free acid)[1] (Fusilade X-tra)	May 04	Jul 06	1754	704	16	<0.01 (0)
- PPU[2]	June 04	Jul 06†	1754	700	13	<0.02 (15)
- PPU- desamino[2]	June 04	Jul 06†	1754	700	13	<0.02 (1)
Maize 2005						
Terbutylazine (Inter-Terbutylazine)	May 05	Jul 06†	940	290	16	<0.01 (0)
-desethyl-terbutylazine						<0.01 (2)
-2-hydroxy-terbutylazine						<0.01 (0)
-desisopropyl-atrazine						<0.01 (1)
-2-hydroxy-desethyl-terbutylazine						<0.01 (1)
Bentazone (Laddok TE)	Jun 05	Jul 06†	855	283	33	<0.01 (1)
-AIBA						<0.01 (0)

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

[1] *Degradation product of fluazifop-P-butyl. The parent compound degrades too rapidly to be detected by monitoring*

[2] *Degradation product of rimsulfuron. The parent compound degrades too rapidly to be detected by monitoring*

† Monitoring will continue during the following year. The values for prec. and perc. are accumulated up to July 2006

Rimsulfuron, degrades rapidly in the soil, and the leaching risk is therefore more associated with the degradation products PPU and PPU-desamino. PPU has been found several times in suction cups situated 1 m b.g.s. at S1, with concentrations ranging between 0.021 and 0.058 µg/L (Figure 7). Further, at S1 PPU has been found in 2 m b.g.s. five times, maximum concentration being 0.11 µg/L (Figure 7B) and once in the groundwater, 0.045µg/L in M4 (4.4-5.4 m b.g.s.). The other metabolite, PPU-desamino, has been found once at S2 2 m b.g.s. in a concentration of 0.022 µg/L (data not shown). When evaluating these results it should be noted that precipitation following the application of rimsulfuron (applied on 3 June 2004) amounted to 68 mm in May 2002 (20% higher than normal) and 51 mm in June 2002 (21% lower than normal). Precipitation and percolation following the application at Tylstrup was thus much lower than that observed at Jyndevad in 2003 where rimsulfuron have also been applied (Appendix 4, Figure 7 and Figure 12). Finally, it should be noted that the concentration of PPU is likely to be underestimated by 14 - 47% due to stability problems (Section 7.2.2). Results from the field-spiked samples thus indicated that PPU is unstable and tends to degrade further to PPU-desamido during storage and transport. Thus the observed PPU-desamido probably derives from degradation in the sample during subsequent storage and transport rather than from degradation occurring in the soil. As a consequence the concentration of PPU is likely to be underestimated, while that of PPU-desamido is likely to be overestimated.

Terbutylazine was applied 18 May and 8 June 2005, at the later application in combination with bentazone. Terbutylazine as well as several of its metabolites were monitored. Neither terbutylazine itself nor the degradate 2-*hydroxy-terbutylazine* were detected. Occasionally, there were low detections of some of the other metabolites. *Desisopropylatrazine* was detected once on 14 June 2006 in suction cups located 1 m b.g.s. at location S2, concentration being 0.024 µg/L. 2-*hydroxy-desethyl-terbutylazine* was found 1 m b.g.s at S1 once on 14 June 2006 in a concentration of 0.016 µg/L whereas *desethylterbutylazine* was found twice, concentrations being 0.01 and 0.012 µg/L on 17 May and 14 June 2006, respectively (Table A6.1 in Appendix 6). The final evaluation awaits an additional year of monitoring.

Bentazone, applied concomitantly with terbutylazine on 8 June 2005, has hitherto turned up once in a concentration of 0.012 µg/ on 10 April 2006, also 1 m b.g.s. at S1. The final evaluation awaits an additional year of monitoring.

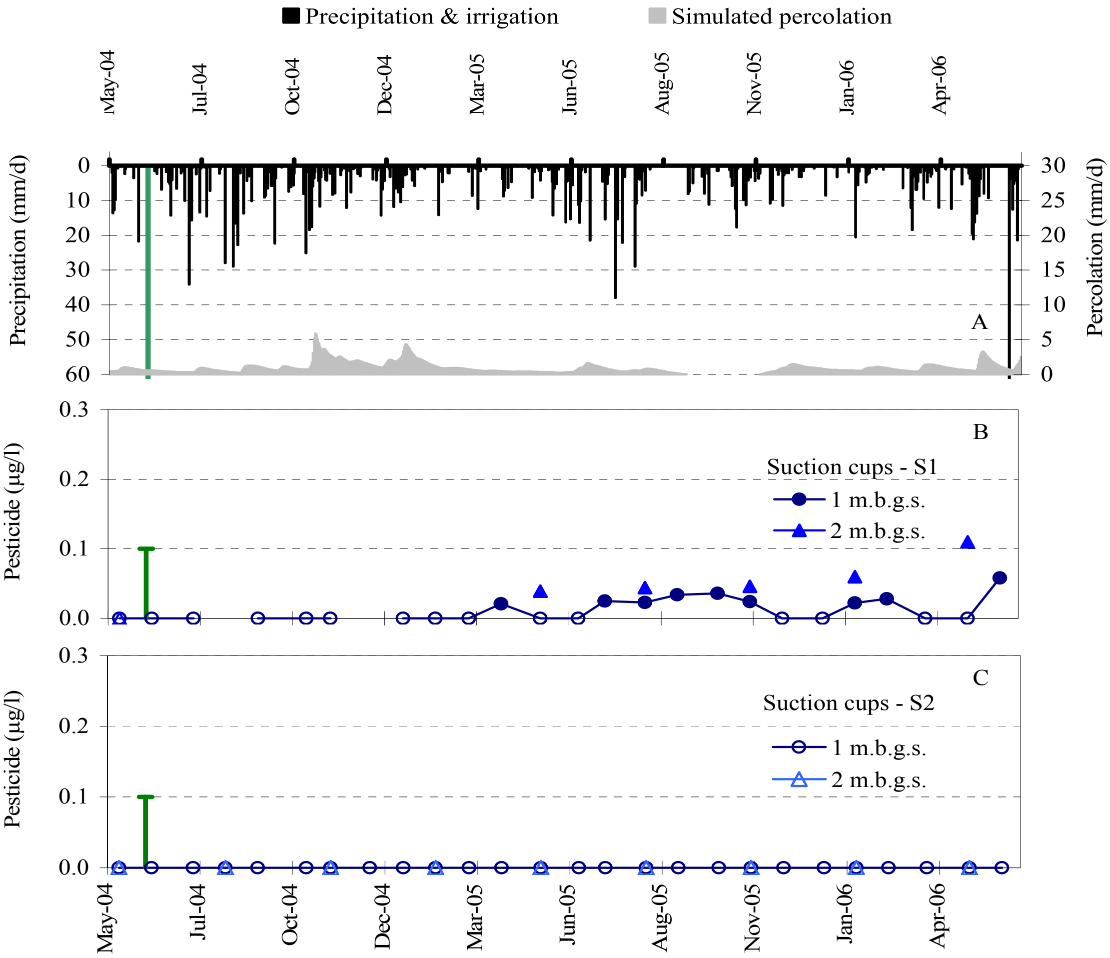


Figure 7. Precipitation, irrigation and simulated percolation 1 m b.g.s. (A) together with measured concentration of *PPU* in suction cups installed 1 and 2 m b.g.s.at location S1 (B) and S2 (C) at Tylstrup. The green vertical line indicates the date of pesticide application. µg/L. Open circles and triangles indicate concentrations below the detection limit of 0.02 µg/L.

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 8). 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 8). The soil can be classified as Arenic Eutrudept and Humic Psammentic Dystrudept (Soil Survey Staff, 1999) with coarse sand as the dominant texture class and topsoil containing 5% clay and 1.8% total organic carbon (Table 1). The geological description points to a rather homogeneous aquifer of meltwater sand, with local occurrence of thin clay and silt beds. A brief description of the sampling procedure is provided in Appendix 2. The monitoring design and test site are described in detail in Lindhardt *et al.* (2001) and the analysis methods in Kjær *et al.* (2002).

3.1.2 Agricultural management

Management practice during the 2003 - 2005 growing seasons is briefly summarized below and detailed in Appendix 3 (Table A3.2). For information about management practice during the first two monitoring periods see Kjær *et al.* (2003).

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

A crop of peas (cv. Algarve) was sown on 29 March 2004. On 5 May, when the peas had 5 visibly, extended internodes, weeds were sprayed with bentazone and pendimethalin. Irrigation was done once; using 27 mm/ha on 1 June, when the peas had 9 visibly extended internodes. Spraying of weeds as well as insects took place on 3 June using fluazifop-P-butyl and pirimicarb, respectively, at which time the first flower buds were visible. The yield of peas amounted to 4.29 ton/ha (86% dry matter) on 9 August and 2.40 t/ha of straw.

After ploughing, the field was sown with winter wheat (cv. Biscay) using a combined rotavator and drilling machine. Eight days later the wheat emerged. On 19 October 2005, when the plants had two leaves unfolded, weeds were sprayed with a mixture of ioxynil and bromoxynil. Additional spraying of weeds was done in the spring using amidosulfuron on 15 April and fluroxypyr on 3 May. Spraying of fungi was carried out on 18 May using

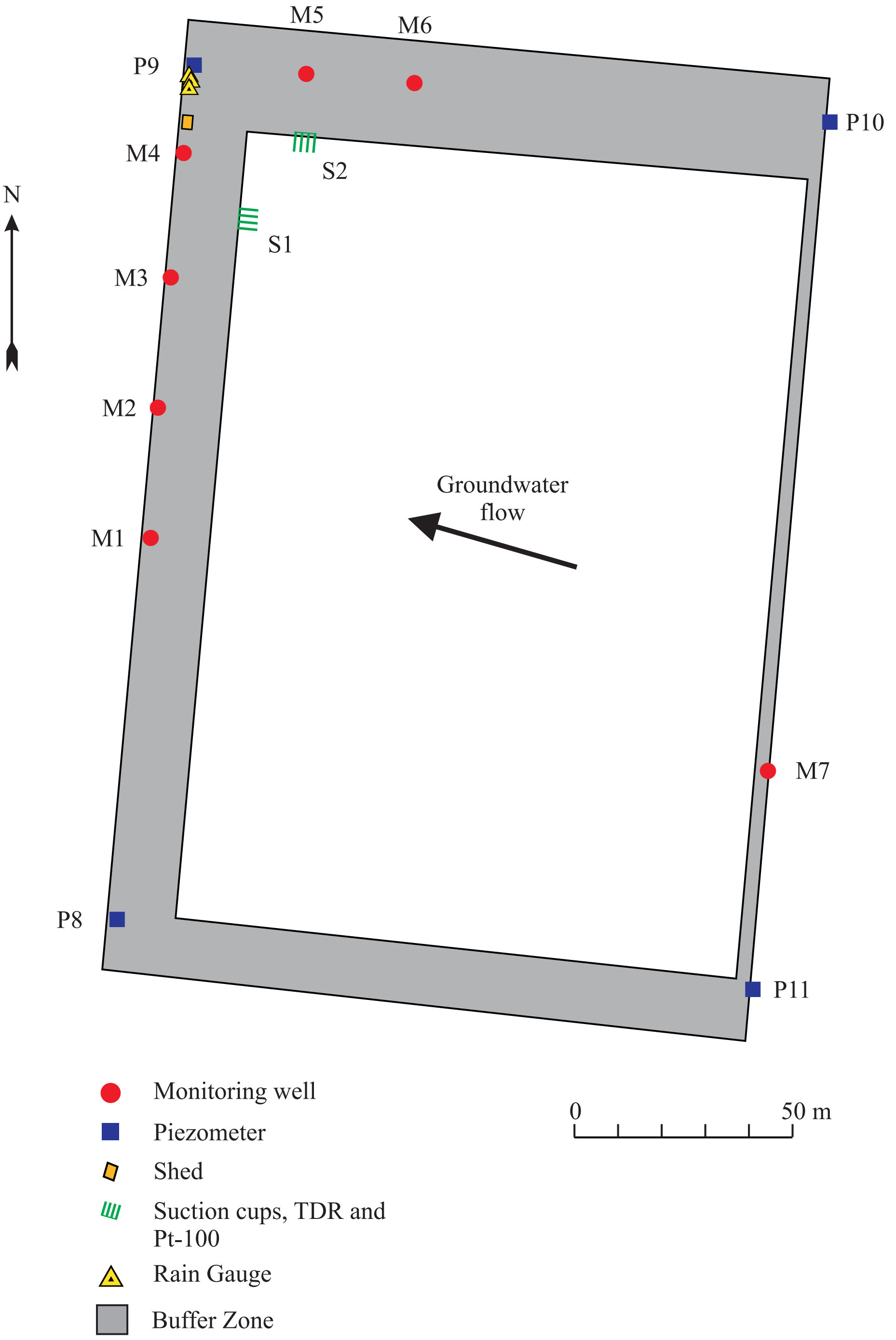


Figure 8. Overview of the Jyndevad test site. The innermost white area indicates the cultivated land, while the grey area indicates the surrounding buffer zone. The positions of the various installations are indicated, as is the direction of groundwater flow (by an arrow).

azoxystrobin. Due to a very dry summer the field was irrigated four times using 33, 27, 27 and 30 mm/ha on 31 May, 23, June 30 June and 13 July, respectively. The fungicide treatment done on 18 May did not suffice and a spraying with propiconazole was done on 10 June. Propiconazole was however not included in the monitoring programme. On 19 August the grain yield amounted to 5.77 t/ha (85% dry matter) and 2.65-t/ha of straw (100% dry matter) was harvested, grain yields being somewhat disappointing. The very low yields of grain may be attributed to the dry summer as well as problems with fungal diseases being resistant to the strobin.

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 2006 and to establish an annual water balance.

Due to the application of a newer version of MACRO than used in the previous reports (Kjær *et al.,* 2005c and Barlebo *et al.* in press.), the model for the Jyndevad site has been recalibrated for the monitoring period May 1999-June 2004 and validated for the monitoring period July 2004-June 2006 (Rosenbom *et al.* in prep.). For this purpose, the following time series have been used: the groundwater table measured in the piezometers located in the buffer zone, soil water content measured at three different depths (25, 60 and 110 cm b.g.s.) from the two profiles S1 and S2 (Figure 8), and the bromide concentration measured in the suction cups located 1 and 2 m b.g.s. Data acquisition, model set-up as well as results related to simulated bromide transport are described in Barlebo *et al.* (in press.) and Rosenbom *et al.* (in prep.).

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 (Figure 9). The dynamics of the simulated groundwater table was well described with MACRO 5.1 (Figure 9B). As noted earlier (Kjær *et al*., 2003), the model had some difficulty in capturing the degree of soil water saturation 1.1 m b.g.s. – a difference that is still apparent with the new model (Figure 9E). As in the Tylstrup scenario, the initial decrease in water saturation observed during the summer periods at 60 and 110 cm b.g.s. was less well captured.

Table 4. Annual water balance for Jyndevad (mm/yr). Precipitation is corrected to the soil surface according to the method of Allerup and Madsen (1979).

	Normal Precipitation [1]	Precipitation	Irrigation	Actual Evapotranspiration	Groundwater recharge [2]
1.7.99–30.6.00	995	1073	29	500	602
1.7.00–30.6.01	995	810	0	461	349
1.7.01–30.6.02	995	1204	81	545	740
1.7.02–30.6.03	995	991	51	415	627
1.7.03–30.6.04	995	937	27	432	531
1.7.04-30.6.05	995	1218	87	578	727
1.7.05-30.6.06	995	845	117	483	479

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

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

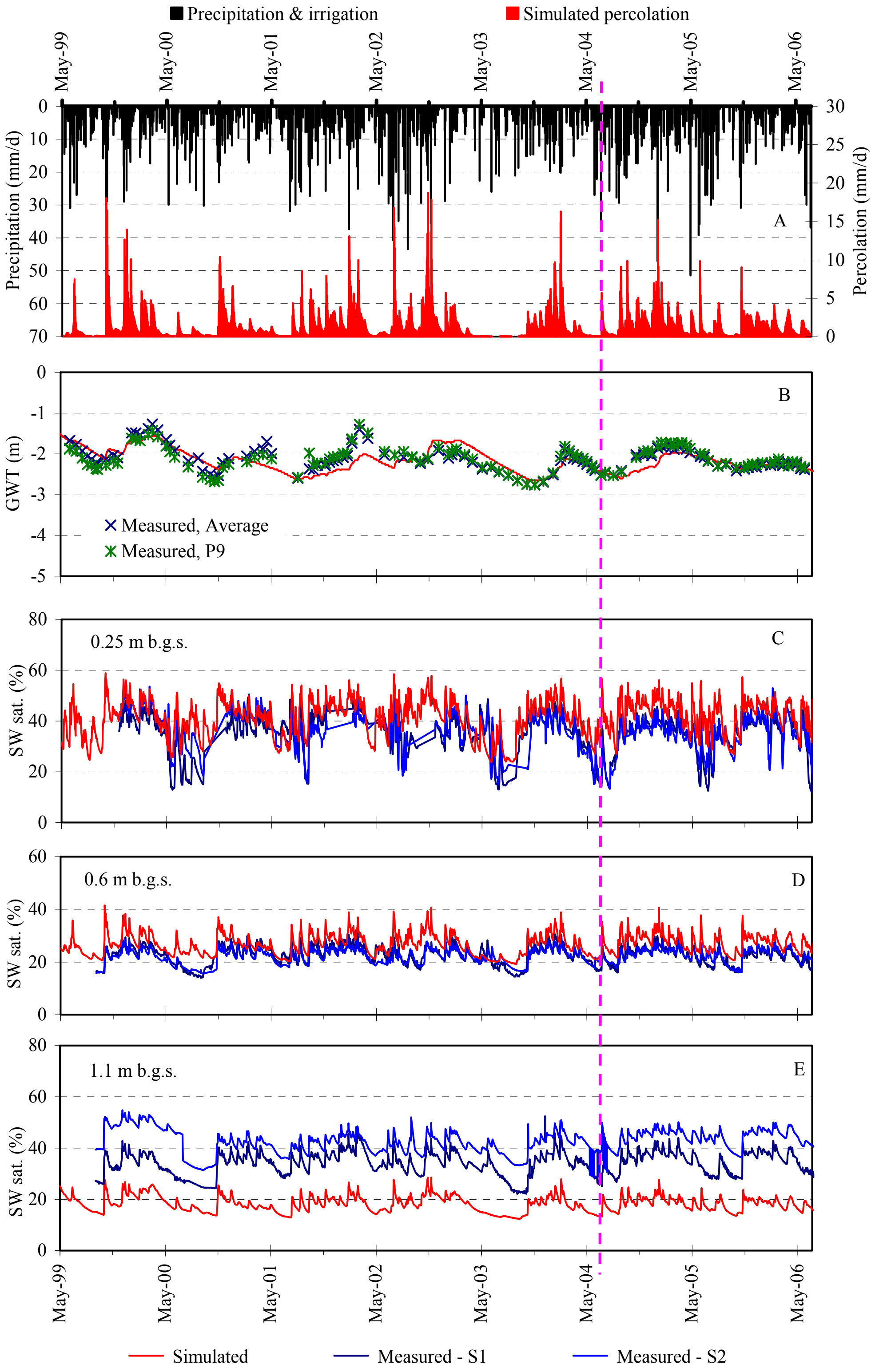


Figure 9. Soil water dynamics at Jyndevad: Measured precipitation, irrigation and simulated percolation 1 m b.g.s. (A), simulated and measured groundwater level (B), and simulated and measured soil water saturation (SW sat.) at three different soil depths (C, D and E). The measured data in B derive from piezometers located in the buffer zone. The measured data in C, D and E derive from TDR probes installed at S1 and S2 (see Figure 8).

The resulting water balance for Jyndevad for the seven monitoring periods is shown in Table 4. It is very similar to the balance calculated with MACRO 5.0 (Kjær *et al.*, 2005c). Here it should be noted that the hydraulic year July 2004-June 2005 had the highest precipitation and simulated actual evapotranspiration and the two latest hydraulic years were characterised by having higher irrigation values. Due to the wet hydraulic year of July 2004-June 2005 (Table 4), continuous percolation was simulated throughout the two last hydraulic years.

Table 4. Annual water balance for Jyndevad (mm/yr). Precipitation is corrected to the soil surface according to the method of Allerup and Madsen (1979).

	Normal Precipitation 1)	Precipitation	Irrigation	Actual Evapotranspiration	Groundwater recharge 2)
1.7.99–30.6.00	995	1073	29	500	602
1.7.00–30.6.01	995	810	0	461	349
1.7.01–30.6.02	995	1204	81	545	740
1.7.02–30.6.03	995	991	51	415	627
1.7.03–30.6.04	995	937	27	432	531
1.7.04-30.6.05	995	1218	87	578	727
1.7.05-30.6.06	995	845	117	483	479

3.2.2 Bromide leaching

Bromide has now been applied twice at Jyndevad. The bromide concentrations measured up to April 2003 (Figure 10 and Figure 11) relate to the bromide applied in autumn 1999, as described further in Kjær *et al.* (2003). Leaching of the bromide applied in March 2003 is evaluated in Rosenbom *et al.* (in prep.).

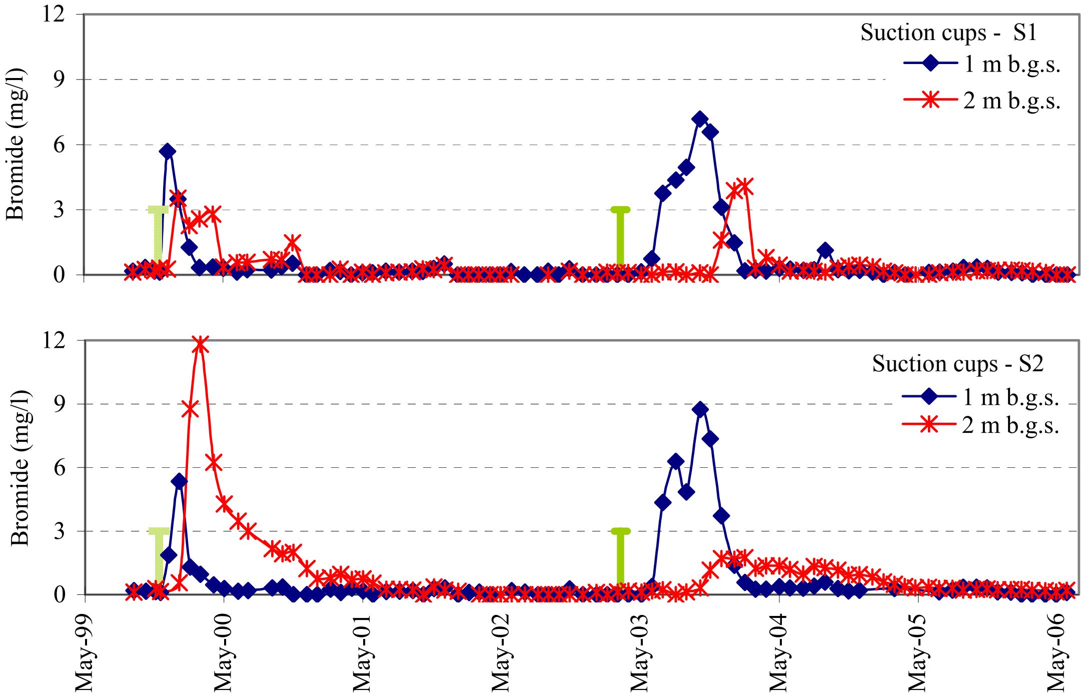


Figure 10. Bromide concentration in the unsaturated zone at Jyndevad. The measured data derive from suction cups installed (A) 1 m b.g.s. and (B) 2 m b.g.s. at locations S1 and S2 (Figure 8). The green vertical lines indicate the dates of bromide applications.

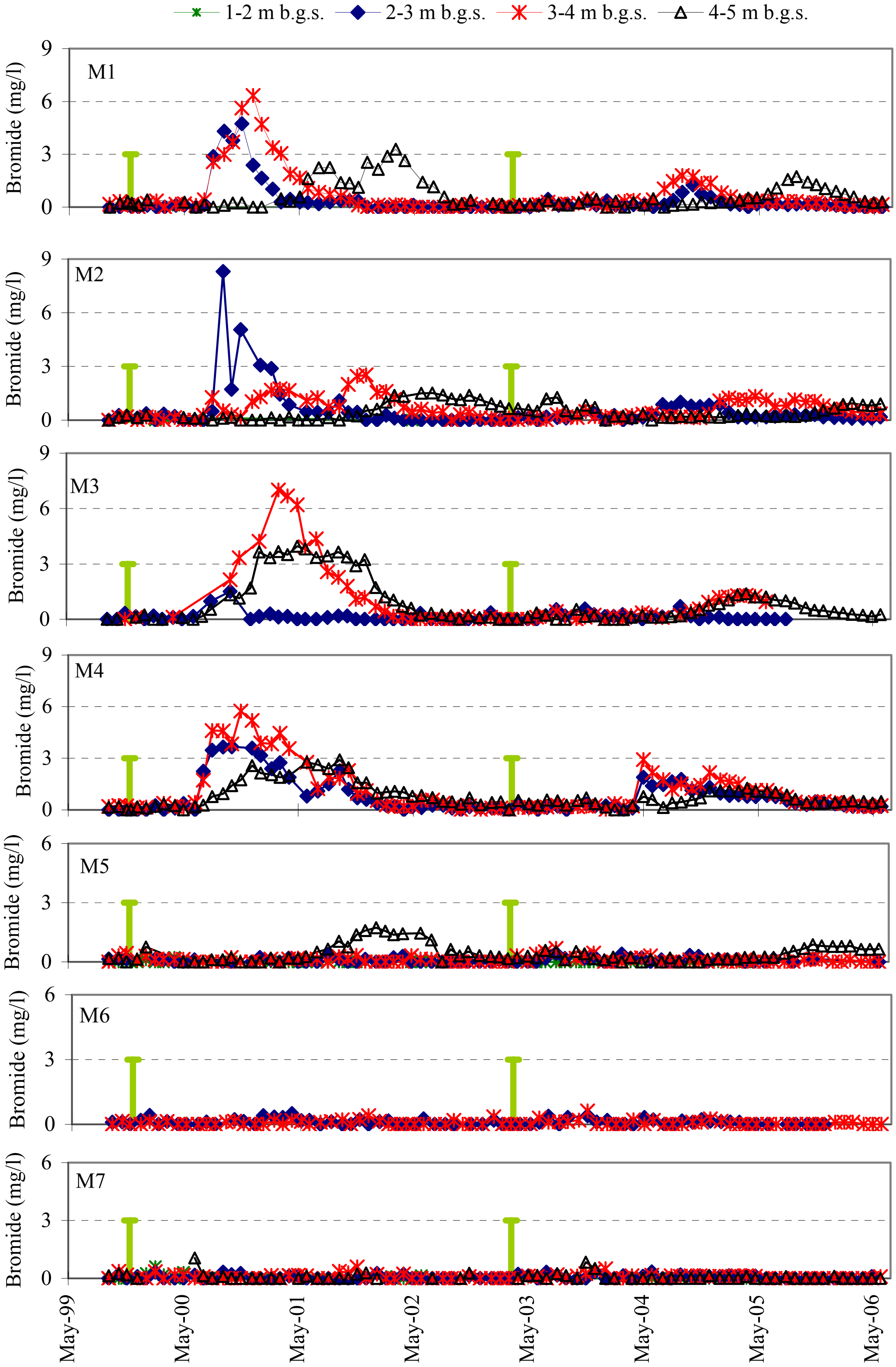


Figure 11. Bromide concentration in the groundwater at Jyndevad. The data derive from monitoring wells M1–M7. Screen depth is indicated in m b.g.s. The green vertical lines indicate the dates of bromide applications.

3.2.3 Pesticide leaching

Monitoring at Jyndevad began in September 1999 and presently encompasses several pesticides and their degradation products, as indicated in Table 5. Pesticide application during the two most recent growing seasons is shown together with precipitation and simulated precipitation in Figure 12. 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 percolation as simulated with the MACRO model. It should also be noted that as tribenuron methyl (applied here as Express), pyridate (applied here as Lido) and rimsulfuron (applied here as Titus) degrade rapidly, the leaching risk is more associated with their respective degradation products, triazinamin-methyl, PHCP, PPU and PPU-desamino. For the same reasons it is the degradation products and not the parent compounds that are monitored in the PLAP (Table 5). Pesticides applied later than April 2006 are not evaluated in this report and hence are not included in Table 5 and Figure 12.

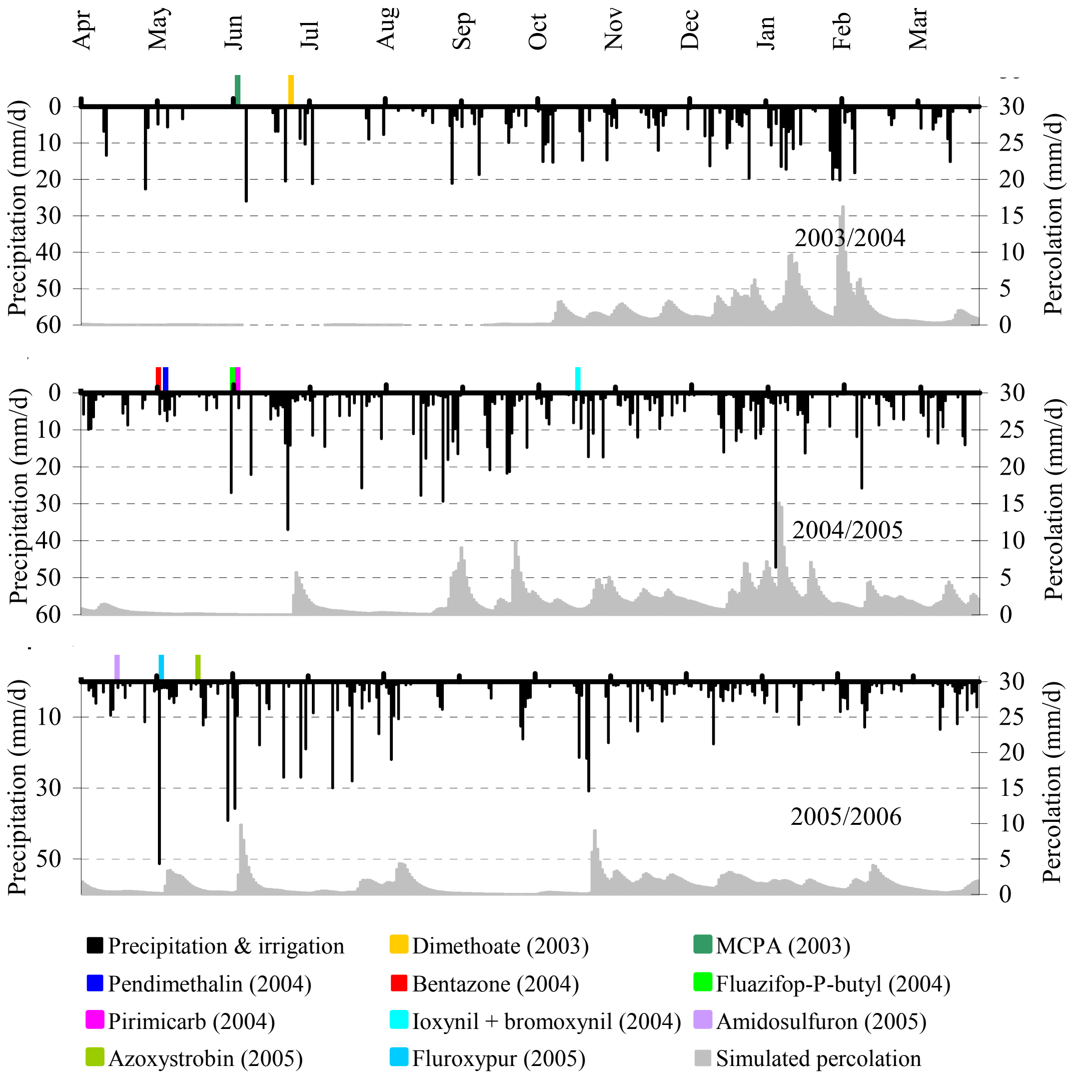


Figure 12. Pesticide application, precipitation and irrigation (primary axis) together with simulated percolation 1 m b.g.s. (secondary axis) at Jyndevad in 2003/2004 (upper), 2004/2005 (middle) and 2005/2006 (lower).

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

Crop and analysed pesticides	Application date	End of monitoring	Prec. (mm)	Perc. (mm)	1st month perc. (mm)	C_{mean} (µg/L)
Winter rye 2000						
Glyphosate (Roundup 2000)	Sep 99	Apr 02	2759	1607	139	<0.01 (0)
- *AMPA*						<0.01 (3)
Triazinamin-methyl [1] (Express)	Nov 99	Apr 02	2534	11451	86	<0.02 (0)
Propiconazole (Tilt Top)	Apr 00	Jul 02	2301	1061	3	<0.01 (0)
Fenpropimorph (Tilt Top)	Apr 00	Apr 02	2015	1029	3	<0.01 (2)
- *fenpropimorphic acid*						<0.01 (0)
Maize 2001						
Terbutylazine (Lido)	May 01	Jul 06†	4681	2421	4	<0.01 (0)
- *desethyl-terbutylazine*						<0.01–0.02 (42)
PHCP [2] (Lido)	May 01	Jul 03	2413	1366	4	<0.02 (0)
Potatoes 2002						
- *PPU* (Titus) [3]	May 02	Jul 06†	4436	2421	11	0.06[4]–0.13 (119)
- *PPU-desamido*		Jul 06†	4436	2421	11	0.01–0.03 63)
Spring barley 2003						
MCPA (Metaxon)	June 03	Jul 05	2340	1233	0	<0.01 (0)
- *4-chlor,2-methylphenol*						<0.01 (0)
Dimethoate (Perfekthion 500 S)	June 03	Jul 05	2278	1232	1	<0.01 (0)
Pea 2004						
Bentazone (Basagran 480)	May 04	Jul 06†	2459	1236	4	0.02-0.13 (25)
- *AIBA*						<0.01 (2)
Pendimethalin (Stomp)	May 04	Jul 06†	2459	1236	4	<0.01 (0)
Pirimicarb (Pirimor)	June 04	Jul 06†	2395	1233	27	<0.01 (0)
-Pirimicarb-desmethyl						<0.01 (1)
-Pirimicarb-desmethyl-formamido						<0.02 (0)
-fluazifop-P(free acid) [5] (Fusilade X-tra)	June 04	Jul 06†	2395	1233	27	<0.01 (0)
Winter wheat 2005						
Ioxynil (Oxitril CM)	Oct 04	Jul 06†	1857	1031	81	<0.01 (0)
Bromoxynil (Oxitril CM)	Oct 04	Jul 06†	1857	1031	81	<0.01 (0)
Amidosulfuron (Gratil 75 WG)	Apr 05	Apr 06	1070	515	33	<0.01 (3)
Fluroxypyr (Starane)	May 05	Jul 06†	1254	553	37	<0.02 (0)
Azoxystrobin (Amistar)	May 05	Jul 06†	4091	1176	49	<0.01 (0)
- *CyPM*						<0.02 (0)

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

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

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

[3] *Degradation product of rimsulfuron. The parent compound degrades too rapidly to be detected by monitoring*

[4] *Leaching increased the second year after application (see Figure 13)*

[5] *Degradation product of fluazifop-P-butyl. The parent compound degrades too rapidly to be detected by monitoring*

† Monitoring will continue during the following year. The values for prec. and perc. are accumulated up to July 2006

The leaching risk of pesticides applied in 1999, 2000 and 2001 has been evaluated in Kjær *et al.* (2003, 2004 and 2005).

The findings related to rimsulfuron are briefly summarized below. For a detailed description of the leaching pattern, including primary data and climate condition characterising the monitoring periods reference is made to Kjær *et al*. (2005c).

Two degradation products of *rimsulfuron*, *PPU* and *PPU-desamido*, were detected at 1 m depth in the suction cups at S1 and S2 (Figure 13). Both compounds were characterized by continuous leaching over a long period of time. Elevated concentrations, in particular of PPU, were still seen towards the end of the monitoring period, thus indicating that leaching of the compound from the uppermost meter of the soil has not yet ceased. Average yearly concentration of PPU reaching 0.1 µg/L were seen as long as three year after application and leached mass amounted to 37-40% of applied rimsulfuron (Figure 13 and Table 6). With an overall travel time of about 4 years PPU also reached the downstream monitoring screens. Elevated concentration of PPU was seen in M1 (sampled monthly), M2 (sampled half-yearly) but not in M4 (sampled monthly). Moreover PPU was also found in M7 receiving water from the upstream neighbouring field. The PPU found in this well is likely originating from the neighbouring upstream field. Firstly because the tracer test suggest that water sampled in M7 has not infiltrated at the PLAP site, and secondly because rimsulfuron was also applied at the neighbouring upstream area. Application rate of these upstream application is given in Appendix 5. In addition to the leaching observed at the PLAP site this result thus indicates that leaching also occurred at the neighbouring upstream field. Elevated concentrations of PPU were seen at the end of the monitoring period indication that transport to the monitoring well has not yet ceased. PPU-desamino was not detected in any of the monitoring wells.

Finally, it should be noted that the concentration of PPU is likely to be underestimated by 14 - 47% due to stability problems (Section 7.2.2). Results from the field-spiked samples thus indicated that PPU is unstable and tends to degrade further to PPU-desamido during storage and transport. Thus the observed PPU-desamido probably derives from degradation in the sample during subsequent storage and transport rather than from degradation occurring in the soil. As a consequence the concentration of PPU is likely to be underestimated, while that of PPU-desamido is likely to be overestimated.

The leaching risk of the pesticides applied in 2003 was found to be negligible, as neither MCPA, its degradation product 4-chlor-2-methylphenol nor dimethoate was detected in any of the analysed samples (Table 5). When evaluating the results it should be noted that precipitation input following the application of MCPA and dimethoate (applied on 3 June and 25 June 2003) amounted to 46 mm in June 2003 (39% lower than normal) and 46 mm in June 2003 (47% higher than normal) (Appendix 4). Despite of a few major events (daily precipitation reaching 20 mm/day) occurring shortly after application, percolation did not start until October (Figure 12).

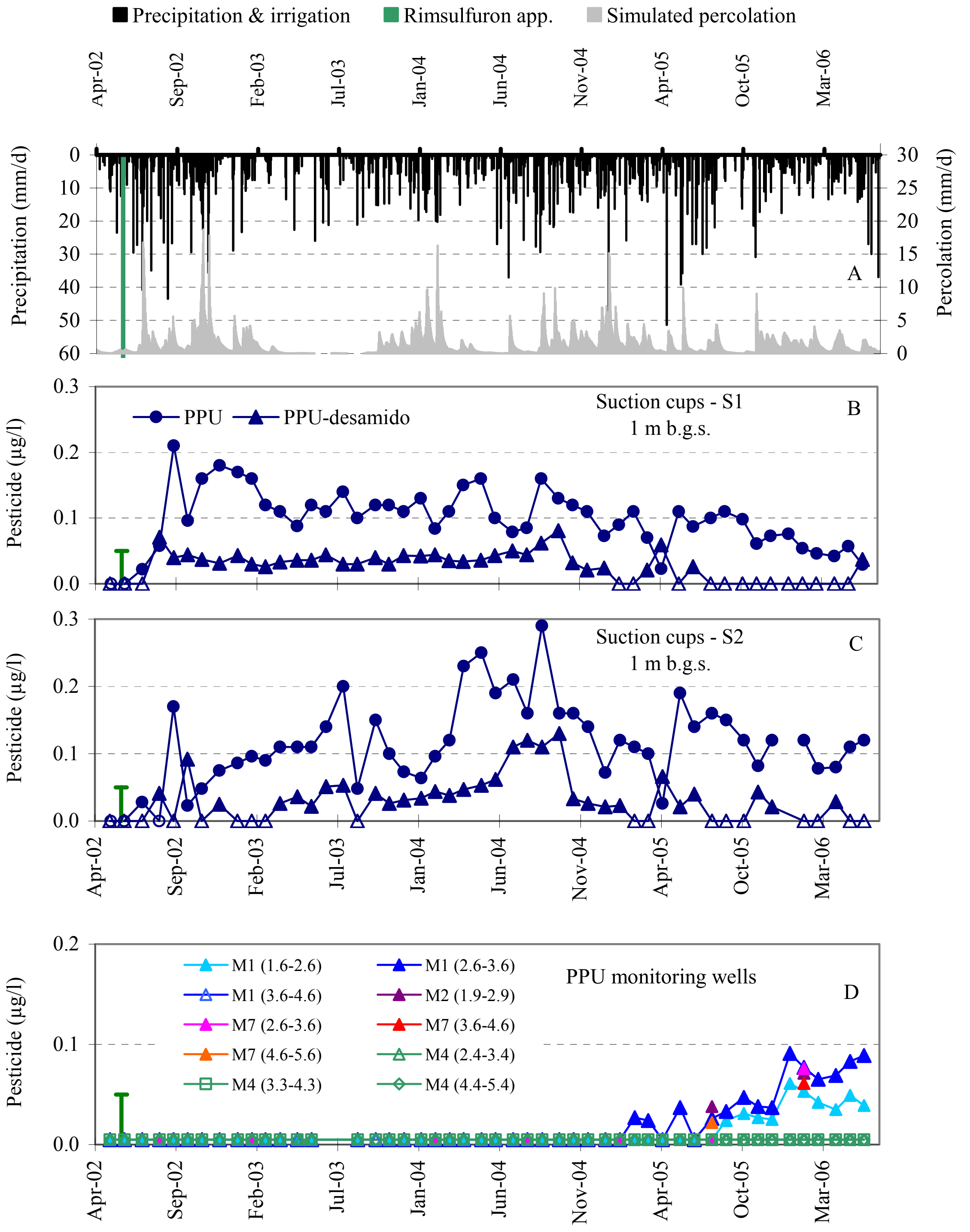


Figure 13. Precipitation, irrigation and simulated percolation 1 m b.g.s. (A) together with measured concentration of *PPU* and *PPU-desamido* in suction cups installed 1 m b.g.s. at location S1 (B) and S2 (C) at Jyndevad.The concentration of PPU in monitoring wells M1, M2 and M7 is given in D, the numbers in parentheses indicating the depths of the analysed screens. The green vertical line indicates the date of pesticide application. µg/L Open circles and triangles indicate concentrations below the detection limit of 0.02 µg/L.

Table 6. Percolation together with estimated average concentration (µg/L) of PPU and PPU-desamido 1 m b.g.s. at Jyndevad. Leached mass refers to the total mass (% of applied rimsulfuron) leached during the monitoring period 1.7.02–30.6.06.

	Percolation (mm/y)	PPU		PPU-desamido	
		Suction cup – S1	Suction cup – S2	Suction cup – S1	Suction cup – S2
1.7.02–30.6.03	648	0.13	0.06	0.03	<0.02
1.7.03–30.6.04	467	0.12	0.10	0.04	0.04
1.7.04–30.6.05	727	0.10	0.14	0.03	0.05
1.7.04–30.6.06	479	0.07	0.09	<0.02	<0.02
Leached mass[1)]		40%	37%	12-13%	12%

1) Expressed as rimsulfuron equivalent.

Among the four pesticides being applied during the 2004 growing season only bentazone leached, whereas the leaching of pirimicarb, pendimethalin and fluazifop-P (d*egradation product of fluazifop-P-butyl)* was found to be negligible. Apart from one sample (soil water sampled in suction cups at S2 on 3 August 2005) containing 0.011 µg/L pirimicarb-desmethyl, none of the latter three compounds have yet been detected.

Bentazone did however leach from the root zone. Concentration reaching 1.6 µg/L was found in suction cups of S1 only two months after application and concentration exceeding 0.1 µg/L was seen four months after application. Following this, the leaching decreased with measured concentrations all being below 0.1 µg/L (Figure 14). The rapid transport, allowing for the high detection of bentazone only two months after application, did not occur in the suction cups at S2. Although leaching was observed in S1, travel time through the uppermost meter of the soil was slower (four months) and measured concentrations were all below 0.1 µg/L. Bentazone have not yet been detected in the monitoring wells.

When evaluating the 2004 results it should be noted that precipitation input following the application of pendimethalin and bentazone (both applied on 5 May 2004) and fluazifop-p-butyl and pirimicarb (both applied on 3 June) amounted to 64 mm in May 2002 (30% lower than normal) and 127 mm in June 2002 (67% higher than normal) (Appendix 4). The number of large precipitation event as well as the total amount of percolation occurring during the first months after application of bentazone was much lower than that following the application of pirimicarb and fluazifop (Figure 12 and Table 5). Nevertheless only bentazone leached, presumably due to more sorption/degradation preventing leaching of the two former compounds. Moreover, the leaching risk was further reduced, as the fraction of applied pirimicarb/fluazifop reaching the soil surface was much lower than that of bentazone. While bentazone was applied on a rather bare soil (BBCH index of 15) the ground cover during the application of pirimicarb/fluazifop was much higher (BBCH index being 51).

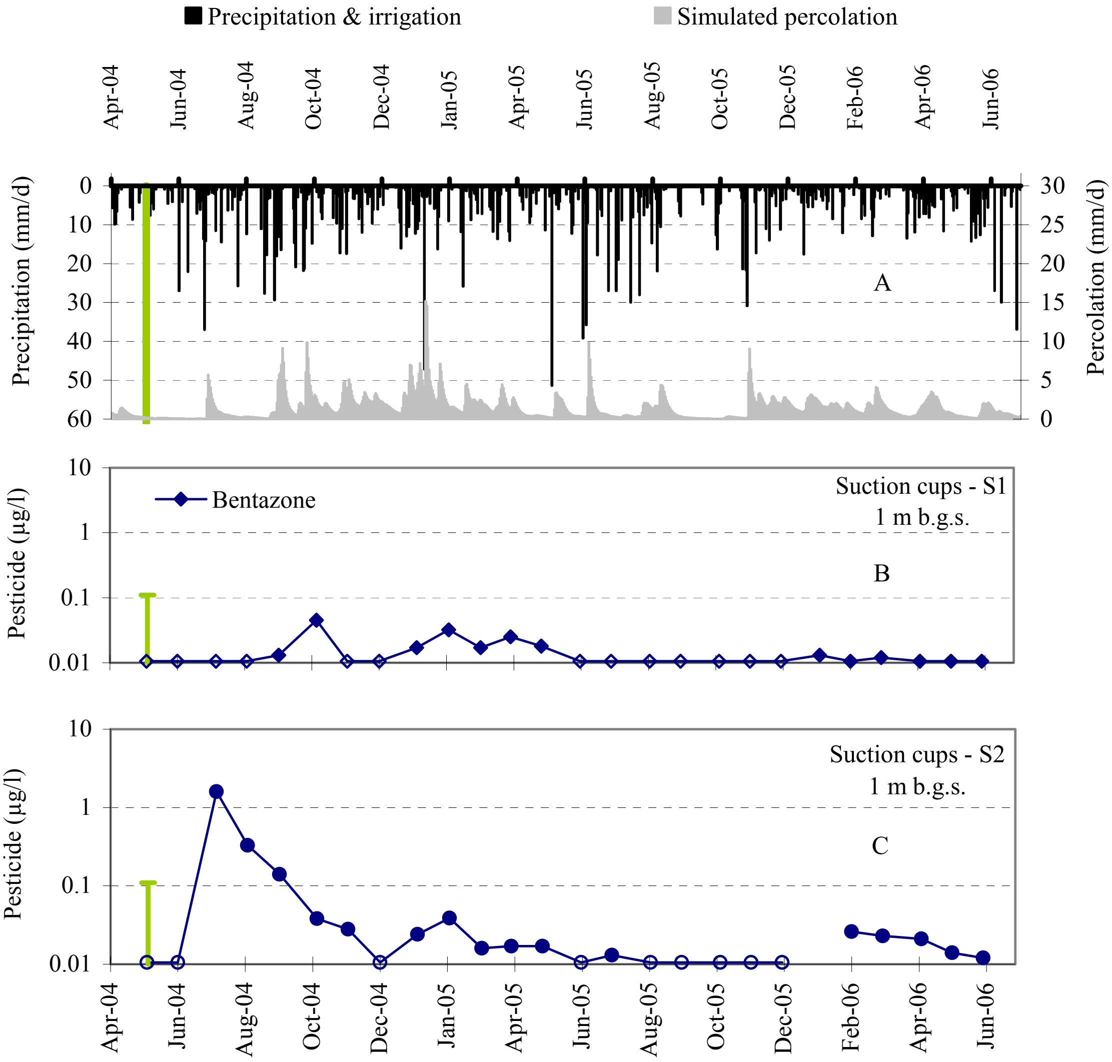


Figure 14 Precipitation, irrigation and simulated percolation 1 m b.g.s. together with measured concentration of bentazone at Jyndevad. The measured data derive from suction cups installed 1 m b.g.s. at location S1 and S2. The green vertical line indicates the date of pesticide application. Concentrations below the detection limit of 0.01 µg/L are indicated by open circles and squares.

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 north-western Jutland (Figure 1). The cultivated area is 1.69 ha (91 x 185 m) and slopes gently 1–2° to the north (Figure 15). Based on two profiles excavated in the buffer zone bordering the field the soil was classified as Alfic Argiudoll and Typic Hapludoll (Soil Survey Staff, 1999). The topsoil content of clay in the two profiles was 18.3 and 26.6%, and the organic carbon content was 3.4 and 2.8%, respectively. The geological description showed rather homogeneous clay till rich in chalk and chert, containing 20–35% clay, 20–40% silt and 20–40% sand. In some intervals the till was sandier, containing only 12–14% clay. Moreover, thin lenses of silt and sand were found in some of the wells. The gravel content was approx. 5%, but could be as high as 20%. A brief description of the sampling procedure is provided in Appendix 2. The monitoring design and test site are described in detail in Lindhardt *et al.* (2001) and the analysis methods in Kjær *et al.* (2002).

4.1.2 Agricultural management

Management practice during the 2003 - 2005 growing seasons is briefly summarized below and detailed in Appendix 3 (Table A3.3). For information about management practice during the first two monitoring periods see Kjær *et al.* (2003).

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

On 15 September 2003, some 5 weeks after harvesting the peas, the field was sprayed with glyphosate (Roundup Bio 4.0 l/ha). Winter wheat (cv. Deben) was sown on 26 September. On 29 October, when the wheat had 2 leaves, the herbicide prosulfocarb was applied. Herbicide treatment with MCPA was done on 12 May 2004 when the flag leaf was just visible. Fungus was treated with azoxystrobin on 14 June at the end of heading, and pests were treated with pirimicarb on 20 July, at the medium milk stage. Due to the high precipitation the winter wheat was not harvested until 23 August. The grain yield was 97.6 hkg/ha (85% dry matter), well above the average for this variety and year (Pedersen, 2004). 40.8 hkg/ha (100% dry matter) of straw was also removed from the field.

On 23 April 2005, the day before sowing of spring barley (cv Cabaret), pig slurry was injected to the field. The barley emerged 7 May. On 27 May, when two tillers were detectable, the herbicide fluroxypyr was applied. When at 30 June 20% of inflorescence had emerged, the crop was sprayed with the fungicide azoxystrobin. The pesticide pirimicarb was applied against aphids 14 July when the first grains had reached half their

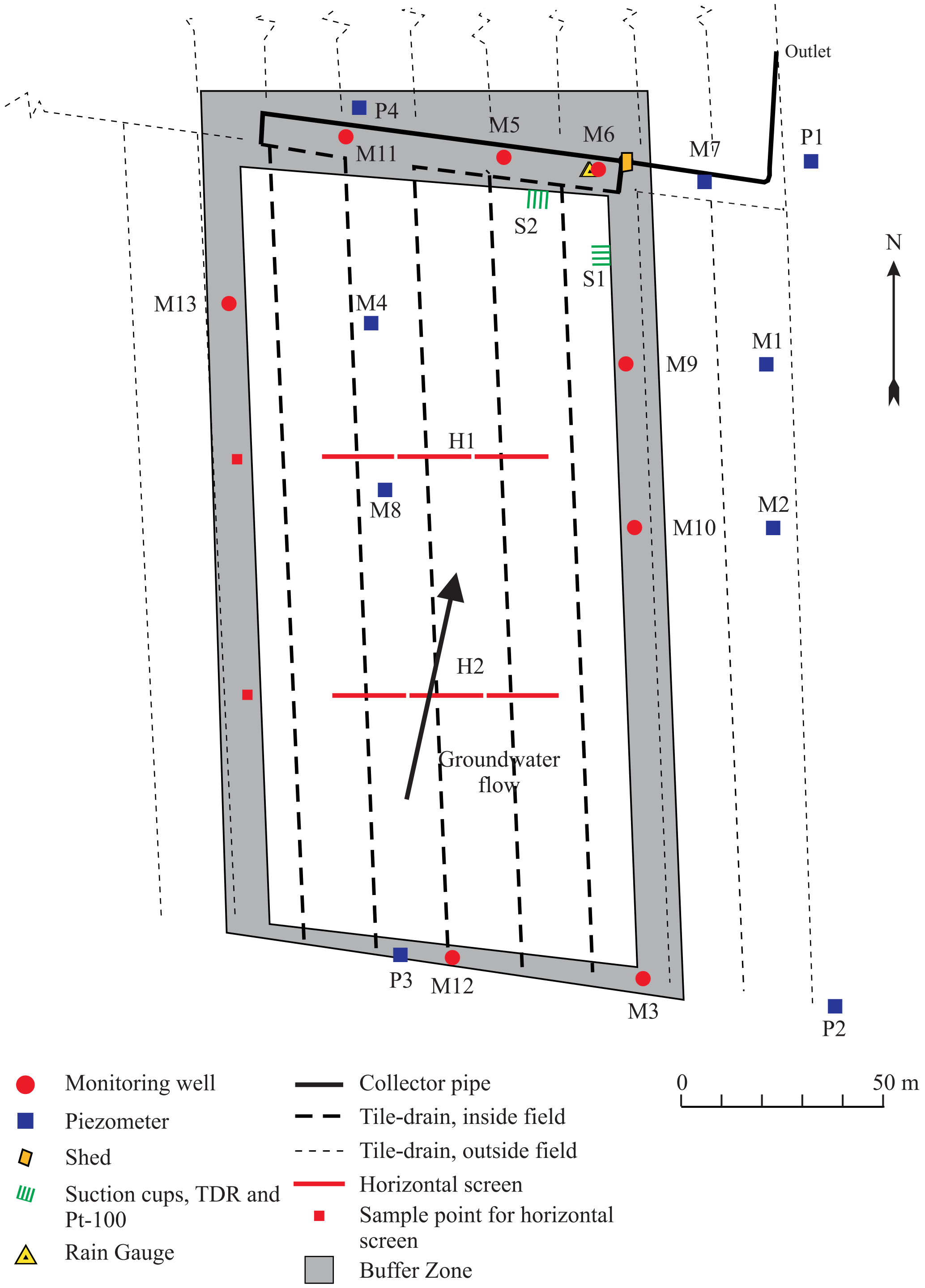


Figure 15. Overview of the Silstrup site. The innermost white area indicates the cultivated land, while the grey area indicates the surrounding buffer zone. The positions of the various installations are indicated, as is the direction of groundwater flow (by an arrow).

final size. The grain yield determined on 22 August amounted to 7.14 t/ha and that of straw to 2.96 t/ha being 85% and 100% of dry matter, respectively.

Within two hours after pig slurry had been trailer hose applied on 29 August 2005, the field was ploughed and on 1 September sown with winter rape (cv. Calypso). Before the emergence of the rape, the herbicide clomazone was sprayed on the bare soil. On 17 November, at the beginning of the winter, the herbicide propyzamid was applied. Weeds were sprayed again on 20 April using clopyralid, whereas pests were treated with alpha-cypermethrin on 5 May. This pyrethroid was however not included in the monitoring programme.

4.1.3 Model set-up and calibration

The MACRO model is applied to the Silstrup site covering the soil profile to a depth of 5 m b.g.s., always including the groundwater table. The model is used to simulate the water flow in the unsaturated zone during the full monitoring period April 2000–June 2006 and to establish an annual water balance.

Due to the application of a newer version of MACRO than used in the previous reports (Kjær *et al.,* 2005c, and Barlebo *et al.,* in press.) the model for the Silstrup site was recalibrated for the monitoring period May 1999- June 2004 and validated for the monitoring period July 2004-June 2006. For this purpose, the following time series have been used: the observed groundwater table measured in the piezometers located in the buffer zone, soil water content measured at three depths (25, 60 and 110 cm b.g.s.) from the two profiles S1 and S2 (Figure 15), and the measured drainage flow. Data acquisition, model set-up as well as results related to simulated bromide transport are described in Barlebo *et al*. (in press).

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 (Figure 16). As, in Kjær *et al*., 2005c, calibration to the much more fluctuating groundwater table, measured in piezometer P3, yielded a significantly better description of measured drainage. A delay in the initial increase in drainage flow in the autumn was still present both in the recalibration and the validation period (Figure 16B and 16C). As in the previous monitoring periods, the overall trends in soil water content were described reasonably well (Figure 16D, 16E, and 16F) and the model still tended to describe the subsoil as being dryer during the summer period than measured by the deeper TDR probes (Figure 16E and 16F).

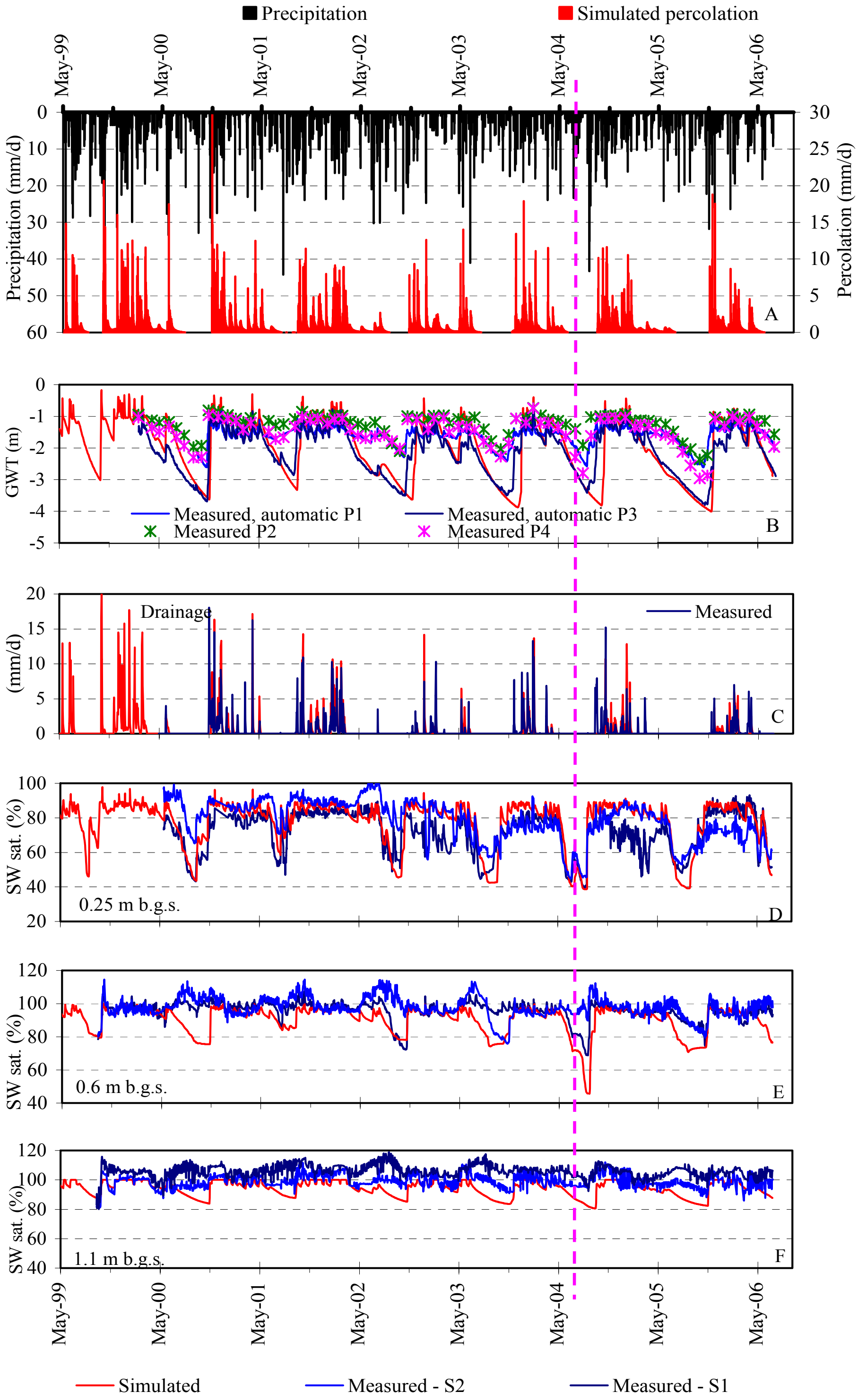


Figure 16. Soil water dynamics at Silstrup: Measured precipitation and simulated percolation 1 m b.g.s. (A), simulated and measured groundwater level GWT (B), simulated and measured drainage flow (C), and simulated and measured soil water saturation (SW sat.) at three different soil depths (D, E and 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 15). The broken vertical line indicates the beginning of the validation period (July 2004- June 2006).

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

	Normal precipitation 2)	Precipitation	Actual evapotrans-piration	Measured drainage	Simulated drainage	Groundwater recharge 3)
1.7.99–30.6.00 1)	976	1175	457	–	443	275 4)
1.7.00–30.6.01	976	909	413	217	232	279
1.7.01–30.6.02	976	1034	470	227	279	338
1.7.02–30.6.03	976	879	537	81	74	261
1.7.03–30.6.04	976	760	517	148	97	94
1.7.04–30.6.05	976	913	491	155	158	267
1.7.05–30.6.06	976	808	506	101	95	201

1) The monitoring is started in April 2000
2) Normal values based on time series for 1961–1990 corrected to soil surface
3) Groundwater recharge is calculated as precipitation - actual evapotranspiration - measured drainage
4) Where drainage flow measurements are lacking, simulated drainage flow is used to calculate groundwater recharge

Hydraulic conductivity and water content was measured downstream of the field (close to P1 and P4), but no such data were available upstream where P3 was located. As mentioned above, the calibration showed that the hydraulic conditions around P3 affected the measurements considerably. In order to model the measured values, the calibrated hydraulic conductivity curves were fitted less well to the measured data from P1 and P4 than from the other sites (Barlebo *et al.*, in press.).

The resulting water balance for the seven monitoring periods is shown in Table 7 (July to June). Apart from a better fit with measured drainage, there were no major differences between this balance and the one calculated with MACRO 5.0 (Kjær *et al.,* 2005c). Precipitation in the latest monitoring years, July 2004–June 2006, was within the precipitation range of the monitoring period (Appendix 4). Due to the very dry hydraulic year of July 2003- June 2004 (Table 7), drainage flow of the following hydraulic year became low, considering the precipitation of the year.

4.2.2 Bromide leaching

The bromide concentrations shown in Figure 17 and Figure 18 relate to the bromide applied in May 2000, as described in previous reports (Kjær *et al.* (2003 & 2004) and further evaluated in Rosenbom *et al.* (in prep) and Barlebo *et al.* (in press.).

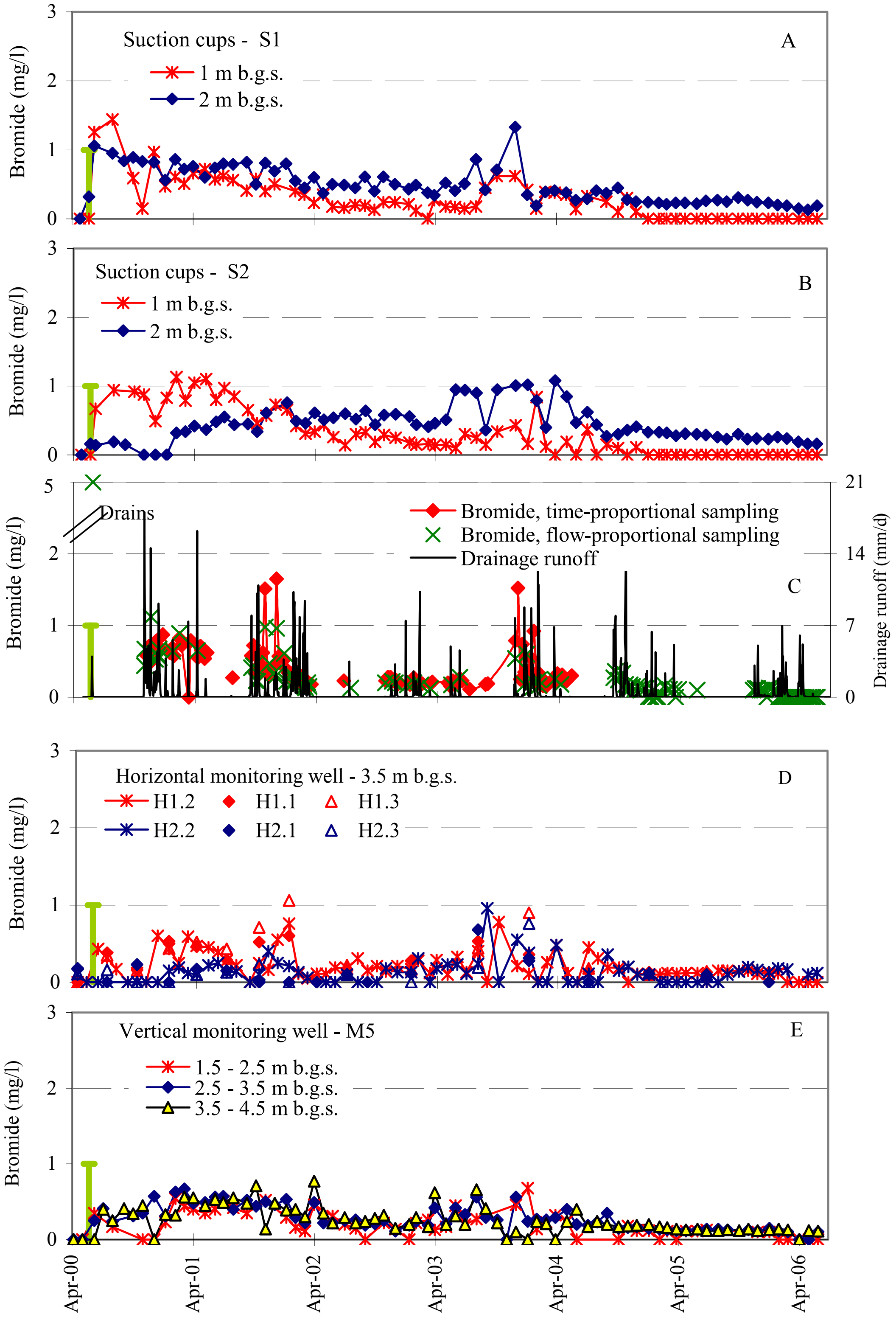


Figure 17. Bromide concentration at Silstrup. A and B refer to suction cups located at S1 and S2. The bromide concentration is also shown for drainage runoff (C), the horizontal monitoring wells H1 and H2 (D) and the vertical monitoring well M5 (E). The green vertical line indicates the date of bromide application.

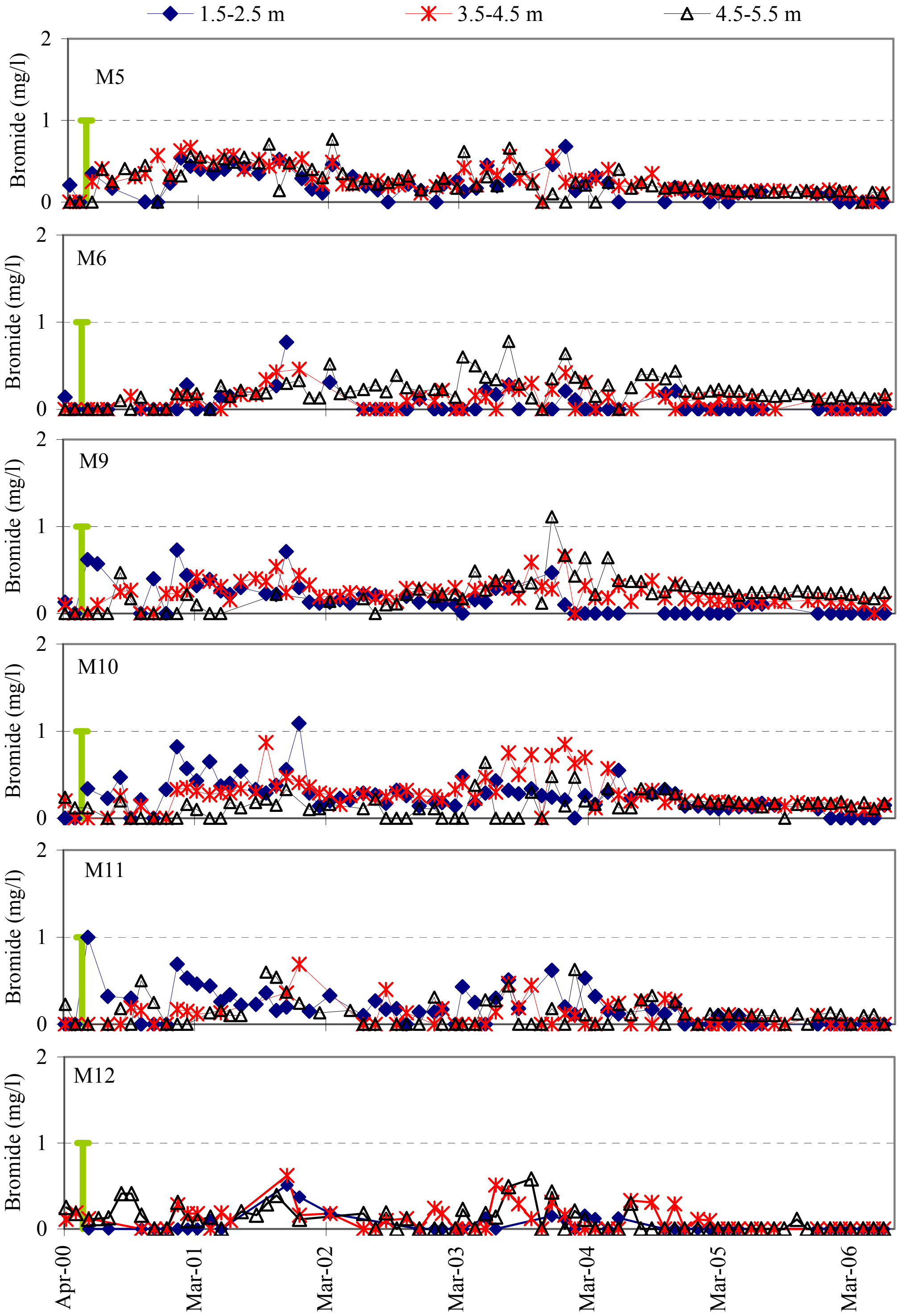


Figure 18. Bromide concentration at Silstrup. The data derive from the vertical monitoring wells (M5–M12). Screen depth is indicated in m b.g.s. The green vertical line indicates the date of bromide application.

4.2.3 Pesticide leaching

Monitoring at Silstrup began in May 2000 and presently encompasses severel pesticides and their degradation products, as indicated in Table 8. Pesticide application during the two most recent growing seasons is shown together with precipitation and simulated precipitation in Figure 19. It should be noted that precipitation in Table 8 is corrected to soil surface according to Allerup and Madsen (1979), whereas percolation (1 m b.g.s.) refers to accumulated percolation as simulated with the MACRO model. It should also be noted that as tribenuron methyl (applied here as Express) and pyridate (applied here as Lido) degrade rapidly, the leaching risk is more associated with their respective degradation products, triazinamin-methyl and PHCP. For the same reasons it is the degradation products and not the parent compounds that are monitored in the PLAP (Table 8).

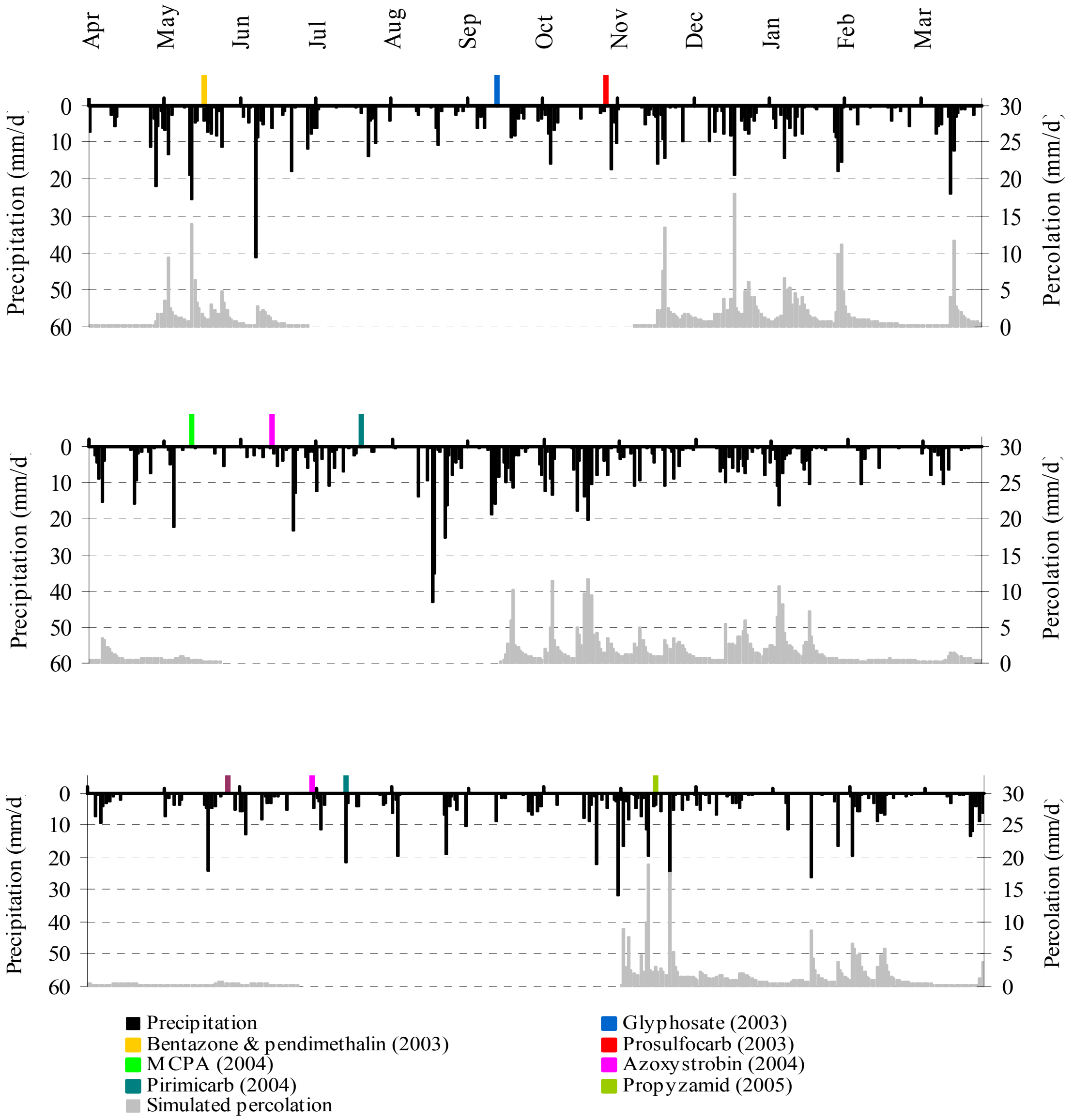


Figure 19. Pesticide application, precipitation and irrigation (primary axis) and simulated percolation 1 m b.g.s. (secondary axis) at Silstrup in 2003/2004 (upper), 2004/2005 (middle) and 2003/2004(lower). Pesticides applied later than April 2004 are not included.

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

Crop and analysed pesticides	Application date	End of monitoring	Prec. (mm)	Perc. (mm)	1st month perc. (mm)	C_{mean} (µg/L)
Fodder beet 2000						
Metamitron (Goltix WG)	May 00	Apr 03	2634	1328	53	0.05 (69)
- *metamitron-desamino*						0.06 (61)
Ethofumesate (Betanal Optima)	May 00	Apr 03	2634	1328	53	0.03 (24)
Desmedipham (Betanal Optima)	May 00	Apr 03	2634	1328	53	<0.01 (1)
- *EHPC*						<0.02 (0)
Phenmedipham (Betanal Optima)	May 00	Apr 03	2634	1328	53	<0.01 (0)
- *MHPC*						<0.02 (0)
- *3-aminophenol*						<0.02 (0)
Fluazifop-P-butyl (Fusilade X-tra)	Jun 00	Jul 02	1953	1019	5	<0.01 (0)
- *fluazifop (free acid)*						<0.02 (1)
Pirimicarb (Pirimor)	Jul 00	Jul 06†	5302	2329	1	0.01 (17)
- *pirimicarb-desmethyl*						<0.02 (1)
- *pirimicarb-desmethyl-formamido*						<0.02 (0)
Spring barley 2001						
Triazinamin-methyl 1) (Express)	May 01	Jul 03	1941	951	10	<0.02 (0)
Flamprop-M-isopropyl (Barnon Plus)	Jun 01	Jul 03	1928	944	3	<0.01 (13)
- *flamprop (free acid)*						<0.01 (7)
Propiconazole (Tilt Top)	Jun 01	Jul 03	1928	944	3	<0.01 (6)
Fenpropimorph (Tilt Top)	Jun 01	Jul 03	1928	944	3	<0.01 (0)
- *fenpropimorphic acid*						<0.01 (1)
Dimethoate (Perfekthion 500 S)	Jul 01	Jul 03	1882	937	3	0.02 (2)
Maize 2002						
Glyphosate (Roundup Bio)	Oct 01	Apr 06	3802	1694	44	<0.13 (71*)
- *AMPA*						0.06 (137*)
PHCP 2) (Lido 410 SC)	May 02	Jul 04	1764	738	6	0.06 (18)
Terbutylazine (Lido 410 SC)	May 02	Apr 06	3320	1327	6	0.07 (96)
- *desethyl-terbutylazine*		Apr 05				0.15 (269)
-2- hydroxy-terbutylazine		Apr 05				see text (26)
- *2-hydroxy-desethyl-terbutylazine*		Apr 05				see text (29)
- *desisopropyl-atrazine*		Apr 05				see text (47)

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

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

† Monitoring will continue during the following year. The values for prec. and perc. are accumulated up to July 2006

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

The leaching risk of pesticides applied during 2000, 2001 and 2002 has been evaluated in Kjær *et al.* (2003), Kjær *et al.* (2004) and Kjær *et al.* (2005c), respectively.

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

Crop and analysed pesticides	Application date	End of monitoring	Prec. (mm)	Perc. (mm)	1st month perc. (mm)	C_{mean} (µg/L)
Peas 2003						
Bentazone (Basagran 480)	May 03	Jul 06	2634	1055	44	0.26 (52)
- *AIBA*						<0.01 (0)
Pendimethalin (Stomp SC)	May 03	Apr 06	2634	1055	44	<0.01 (0)
Glyphosate (Roundup Bio)	Sep 03	Apr 06	2207	971	0	<0.01 (71*)
- *AMPA*						0.02 (137*)
Winter wheat 2004						
Prosulfocarb (Boxer EC)	Oct 03	Apr 06	2125	974	37	0.01 (6)
MCPA (Metaxon)	May 04	Jul 06	1797	710	4	<0.01 (0)
- *4-chlor,2-methylphenol*						<0.01 (0)
Azoxystrobin (Amistar)	Jun 04	Jul 06	1781	706	0	0.01 (6*)
- *CyPM*		Jul 06†	1781	706	0	0.09 (41*)
Pirimicarb (Pirimor G)	Jul 04	Jul 06†	1668	711	0	<0.01 (17*)
- *pirimicarb-desmethyl*						<0.01 (1*)
- *pirimicarb-desmethyl-formamido*						<0.02 (0)
Spring barley 2005						
Fluroxypyr (Starane 180)	May 05	Jul 06†	862	334	11	<0.02 (0)
Azoxystrobin (Amistar)	Jun 05	Jul 06	862	334	11	0.01 (6*)
- *CyPM*	Jun 05	Jul 06†	862	862	11	0.09 (41*)
Pirimicarb (Pirimor G)	Jul 05	Jul 06†	783	322	0	<0.01 (17*)
-pirimicarb-desmethyl						<0.01 (1*)
-pirimicarb-desmethyl-formamido						<0.01 (0*)
Propyzamid (Kerb 500 SC)	Nov 05	Jul 06†	451	264	74	0.22 (32)
-RH-24644						<0.01 (17)
-RH-24580						<0.01 (2)
-RH-24655						<0.01 (0)

† Monitoring will continue during the following year. The values for prec. and perc. are accumulated up to July 2006

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

Pendimethalin, a herbicide, was applied May 2003 and has been monitored since then without detections in any of the water sampled. *MCPA*, a herbicide, was used in May 2004. Neither the substance itself nor its metabolite, *4-chlor-2-methylphenol,* has been detected in any of the analysed samples. The insecticide *pirimicarb*, was applied in July 2004 as well as in July 2005. Neither the substance itself nor its two metabolites, pirimicarb-desmethyl and pirimicarb-desmethyl-formamido, were found in samples of groundwater. Pirimicarb and pirimicarb-desmethyl has however been found in samples from the monitoring wells (Table 8). The herbicide *fluroxypyr* was applied in May 2005 and monitoring will continue until July 2007. As of now it has been detected in any of the analysed samples.

Terbutylazine (Lido) was applied on the Silstrup field twice during 2002. The two first years of monitoring were reported by Kjær et al (2005c). Besides terbutylazine, at least four relevant degradation products are at risk of leaching. Unfortunately, however, only one of them, i.e. desethyl-terbutylazine, was included from the start of the monitoring. Literature findings suggest that desethyl-terbutylazine together with terbutylazine pose the primary risk, whereas the remaining degradation products will mainly be mobilized later on in the degradation pathway (Guzella *et al.,* 2003). During the first year (July 2002 – June 2003) contents of terbutylazine in the drainage water exceeded 0.1 µg/L several times (Figure 20B). In the second year (July 2003-June 2004) terbutylazine could still be found regularly, concentrations were however always less than 0.1 µg/L. In the third year (July 2004 - June 2005) there were only 4 detections of terbutylazin, concentrations ranging between 0.012 and 0.023 µg/L. Monitoring of terbutylazine was ended after the third year. The concentrations of the metabolite *desethyl-terbutylazine*, in the first year, were at a similar level to those of terbutylazine. However, during the second and third year concentrations were substantially higher, indicating a higher persistency (Figure 20B and Figure 20C). Evidence of higher persistence of desethyl terbutylazine was also seen from the groundwater monitoring data. While terbutylazine ceased to be detected at the end of 2003, desethyl-terbutylazine were detected in several monitoring screens throughout the monitoring period. Concentrations exceeding 0.1 g/l were only observed during the first three months after application, however (Appendix 6 and Appendix 7).

The concentrations of the remaining three metabolites are shown in Figure 21B, C and D. These were much lower than those of terbutylazine and desethyl-terbutylazine. However, since they were not included from the beginning, it is difficult to determine whether the low concentrations are due to leaching prior to the start of the monitoring, or a time lag in their formation as compared to that of desethyl-terbutylazine. Consequently their mean average concentrations have not been calculated. Re-evaluation of chromatograms revealed that desisopropyl-atrazine was not present at concentrations exceeding 0.03 µg/L, however. Among these three metabolites *desisopropyl-atrazine* appears to be the most persistence, being leached from the root zone and detected in groundwater monitoring wells during a longer period than the other metabolites (Figure 21, Appendix 6 and Kjaer et al. 2005 for details on groundwater detections).

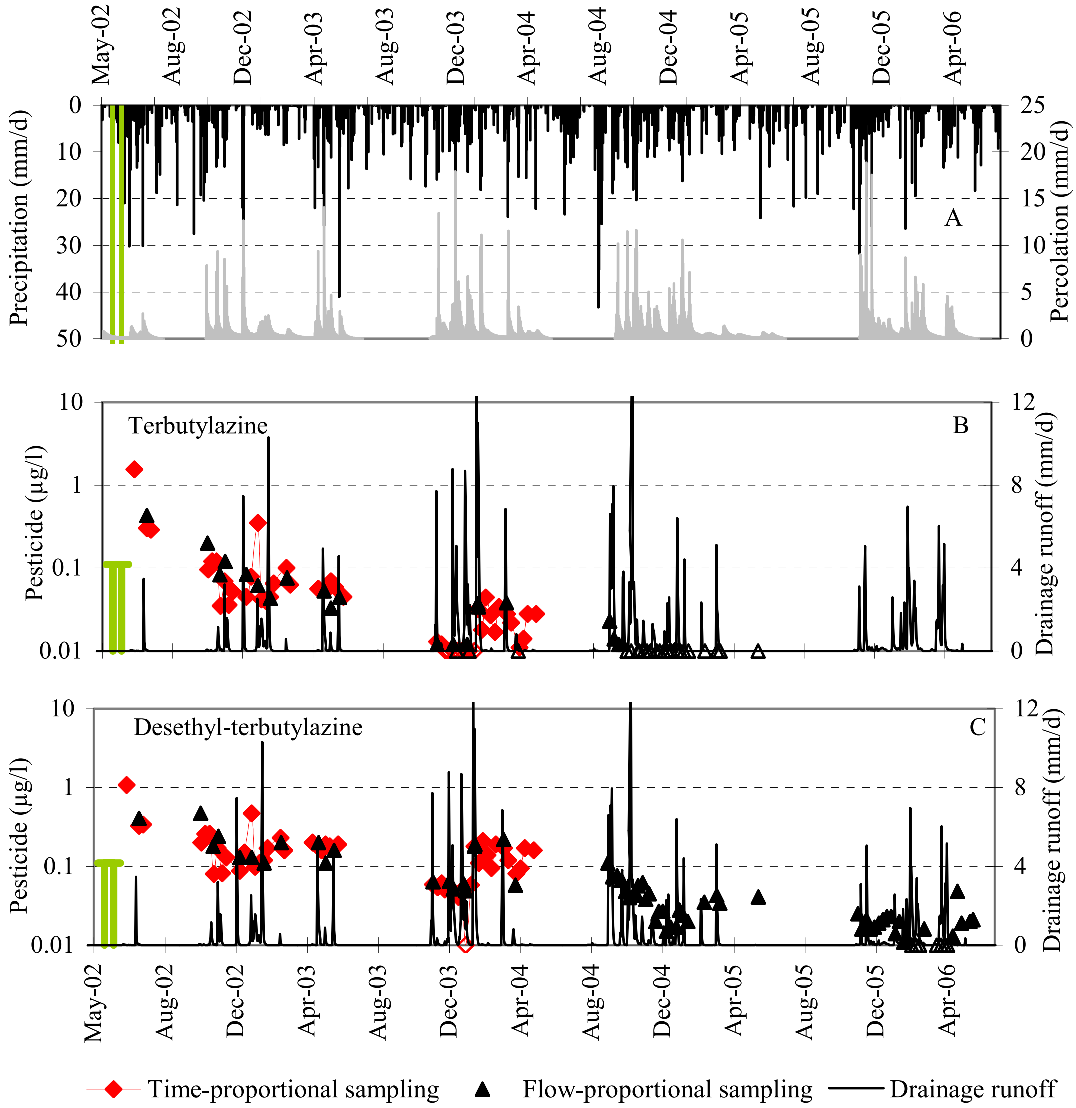


Figure 20. Precipitation and simulated percolation 1 m b.g.s (A) together with concentration of desethylterbutylazine (B) and terbutylazine (C) in the drainage runoff at Silstrup. The green vertical lines indicate the dates of application. Open diamonds indicate values below the detection limit of 0.01 µg/L.

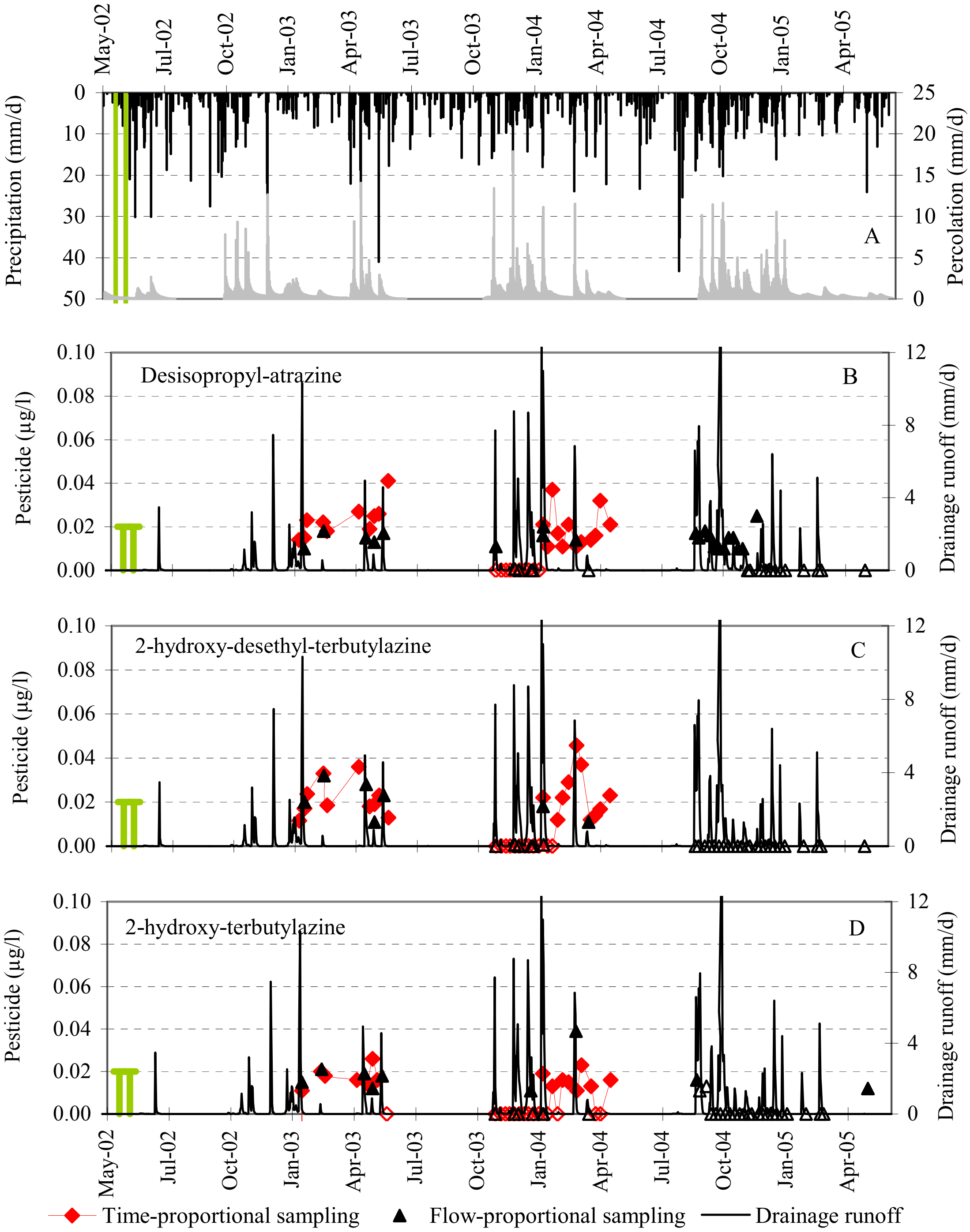


Figure 21. Precipitation and simulated percolation 1 m b.g.s. (A) together with concentration of desisopropylatrazine (B) and 2-hydroxy-desethyl-terbutylazine (C) and 2-hydroxy-terbutylazine (D) in the drainage runoff at Silstrup. The substances have been included in the monitoring programme since February 2003. The green vertical lines indicate the dates of terbutylazine application. Open diamonds indicate values below the detection limit of 0.01 µg/L.

The two herbicides *bentazone* and *pendimethalin* were applied in peas 17 May 2003. Neither pendimethalin nor AIBA, a degradation product of bentazone, could be detected in any of the water samples taken. The first detections of bentazone were done on 27 May, just 10 days after application. In a sample taken flow proportionally from the drains the content was 1.8 µg/L (Figure 22C), whereas a time proportional sample held 0.29 µg/L (Figure 22C). The concentration level increased further, with maximal 6.4 µg/L in a flow proportional sample taken 10 June. One week later concentrations peaked in the time proportional samples being 4.0 µg/L. Samples taken from M5 on the 3 June contained bentazone in the two uppermost filters (Figure 22D) and on 1 July the standards were exceeded in the three uppermost filters as well as in one filter of H1. The following 4 months bentazone could be found in H1 and M5, in which detections were done even in the deepest screen of M5 (4.5 to 5.5 m b.g.s.). Having disappeared from both the M5 and the H1, bentazone later was found at two occasions in M6, Figure 22D. It seems that the rapid movement of bentazone to the drainage depth and further down coincided with rather large rain events, in particular regarding the last incidence, , Figure 22 A. Out of the 31 drainage water samples taken between 24 November 2003 and 12 May 2004, 26 contained bentazone. At that time however, concentrations had decreased to less than 0.1 µg/L (Figure 22C). The average bentazone concentration in drainage water amounted to 0.26 µg/L within the first year after the application (Table 8).

The herbicide *prosulfocarb* was applied in the autumn on 29 October 2003 (Figure 22B), at which time there was no drainage water flow. One month later it was found in the drainage water, 0.082 µg/L in a time proportional sample, and 0.18 µg/L in a flow proportional sample. Furthermore, 0.027 µg/L was measured once in a horizontal screen of H1 located 3.5 m b.g.s. (Appendix 6). The last detection of prosulfocarb in drainage water was done on 2 February 2004 being 0.027 µg/L.

Figure 23 illustrates the findings in drainage water of *azoxystrobin* and its metabolite ***CyPM*.** Azoxystrobin was applied twice: 14 June 2004 and 30 June 2005. In both cases there was no drainage water flow when spraying. Azoxystrobin as well as CyPM were found in the first samples of drainage water taken midst September. The maximum concentration of azoxystrobin (0.034 µg/L) and CyPM (0.34 µg/L) was measured at the initial sampling. After the application on June 2004, six of the samples contained azoxystrobin. However, none of the samples following the June 2005 application had detectable amounts of azoxystrobin. Both applications of azoxystrobin caused leaching of the metabolite CyPM. Concentrations in drainage water followed the same pattern of high initial content followed be a steep drop, and finally a rice to a somewhat higher level (Figure 23B and 23C). Although the initial leaching was marked; the average, yearly concentrations did not exceed the 0.1µg/L in neither of the two years, Table 8. Neither azoxystrobin nor CyPM have been detected in the groundwater monitoring screens (Appendix 6).

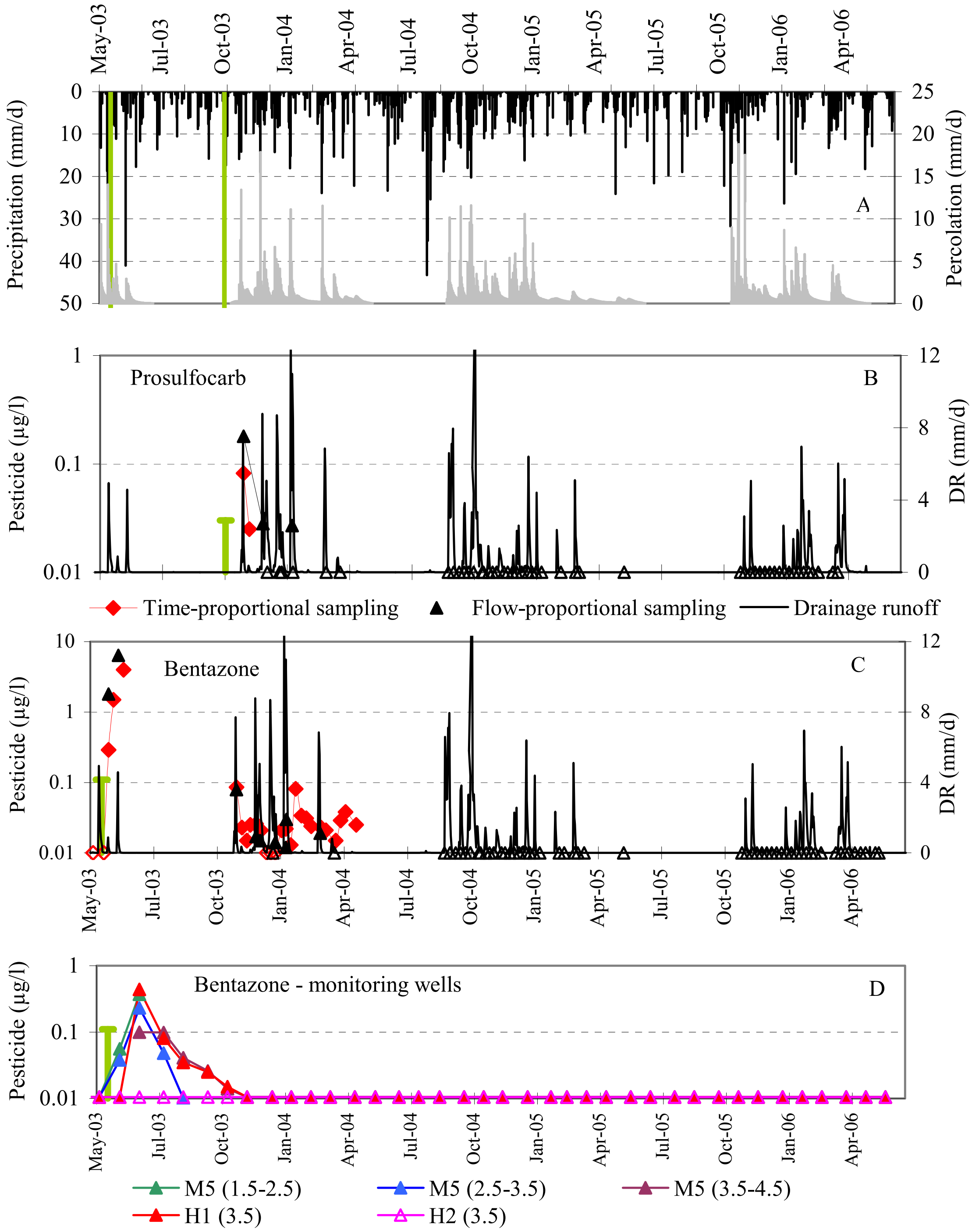


Figure 22. Precipitation and simulated percolation 1 m b.g.s. (A) together with the concentration of bentazone (B) and prosulfocarb (C) in the drainage runoff (DR on secondary axis) at Silstrup. The concentration of bentazone in groundwater monitoring wells M5, H1 and H2 is given in D, with numbers in parentheses indicating the screen depth. The green vertical lines indicate the dates of pesticide application. Open diamonds indicate values below the detection limit of 0.01 µg/L.

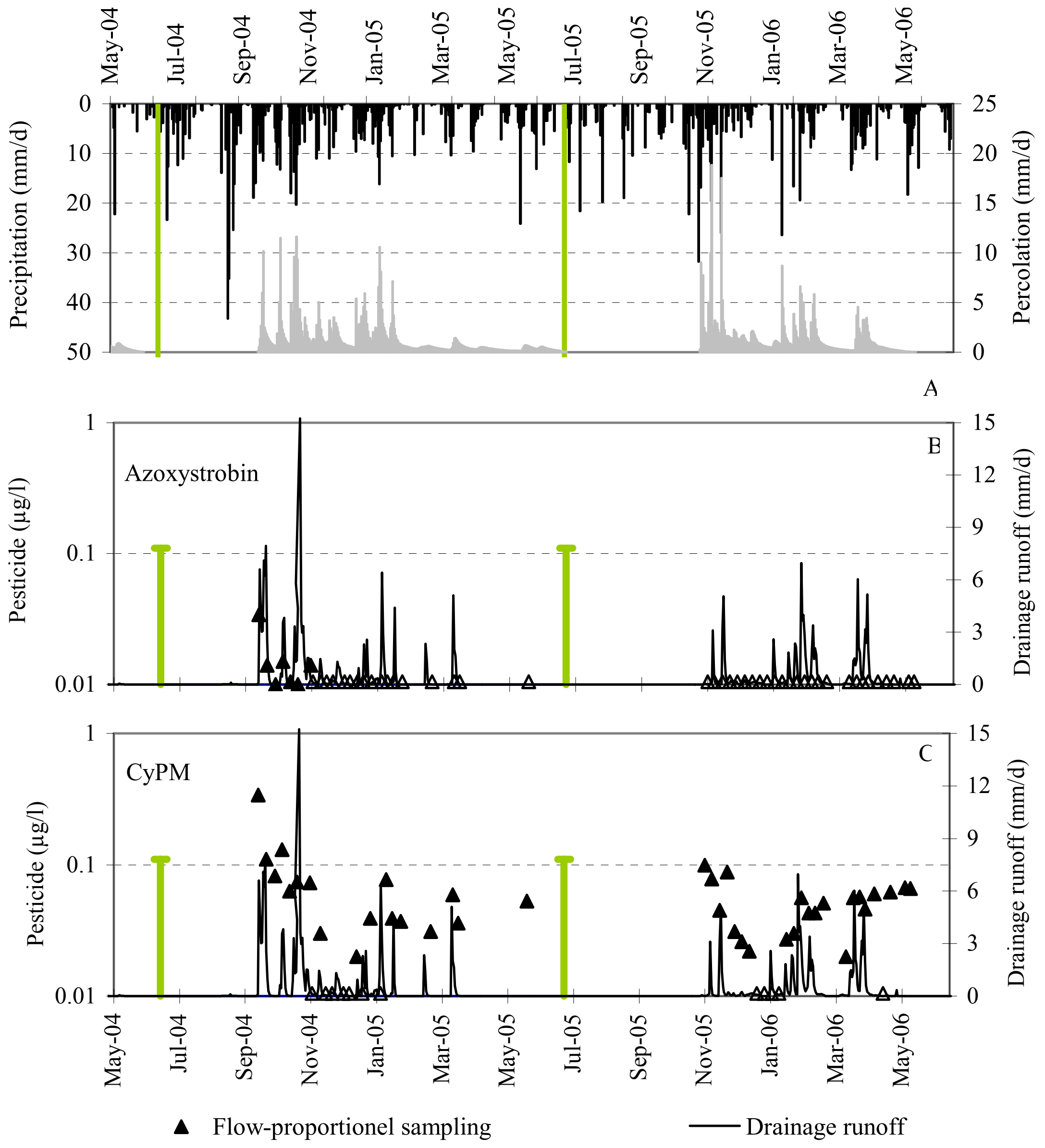


Figure 23 Precipitation and simulated percolation 1 m b.g.s. (A) together with the concentration of azoxystrobin (B) and CyPM (C) in the drainage runoff at Silstrup. The green vertical line indicates the date of azoxystrobin application. Open diamonds indicate values below the detection limit of 0.01 µg/L.

The most recent application of *glyphosate* at Silstrup was done 15 September 2003 (4.0 l/ha of Roundup Bio), at which time there was no flow of water in the tiles (Figure 25 B). On 24 November, at the onset of drainage water flow, concentrations in flow proportional samples were 0.023 µg/L of glyphosate and 0.065 µg/L of *AMPA*, Figure 25B and C. Whether these concentrations relates to the September 2003 application can not be determined, as both of the substances were present when drainage flow ended in July 2003 - due to the October 2001 application (Figure 25). The concentrations of both glyphosate and AMPA following the two applications deviated substantially. Concentrations in drainage flow, following the application of Roundup in 2003, were on average less than 0.01 µg/L of glyphosate and 0.02 µg/L of AMPA, significantly less than following the 2001 application. In the search for a possible explanation for the difference in leaching, it may be worthwhile looking at the difference in time of application. The application in 2001 was done late in the season - 25 October 2001 whereas in 2003 spraying was done 15 September. In 2001 the soil was moist and drainage flow had commenced when spraying. Within the first month following application percolation was 44 mm/ha, as compared to 0.0 mm/ha in 2003, Table 8. It seems that the time for degradation of the glyphosate from the second application at Silstrup was sufficient, as reflected in concentrations of AMPA always being higher than those of glyphosate, when comparing day by day. A higher persistence of AMPA can be seen, when comparing Figure 25 A and B for the period September 2004 - March 2005. In that period glyphosate was never above the level of detection whereas concentrations of AMPA varied between 0.011 and 0.037 µg/L. There have been only a few detections of AMPA and glyphosate in the groundwater monitoring screens (Table A7.1 in Appendix 7).

Propyzamid, a herbicide applied late autumn/beginning of the winter 2005 has, together with its 3 metabolites RH24580, RH 24644 and RH24655, been monitored for less than a year. Therefore a final evaluation awaits an additional year of monitoring. In Figure 24 it can be seen that loss of this substance relates to propyzamid, followed by RH24644 and RH 24580 whereas RH24655 has not been found at all. Only propyzamid leached in concentrations above 0.1µg/L. Of the metabolites only RH24644 has been detected in groundwater samples, 0,032 µg/L in H1 (3.5 m b.g.s.) and 0.016 in M5 (1.5-2.5 m b.g.s.). Both findings were done 1 December 2005 (data not shown). Propyzamid has been found in the groundwater 9 times. Twice, the drinking water standard has been exceeded being 0.14 µg/L in H1 (3.5 m b.g.s.) and 0.11µg/L in M5 (1.5-2.5 m b.g.s.) both taken on 1 December 2005 when also drainage water had its peak concentration (Figure 24).

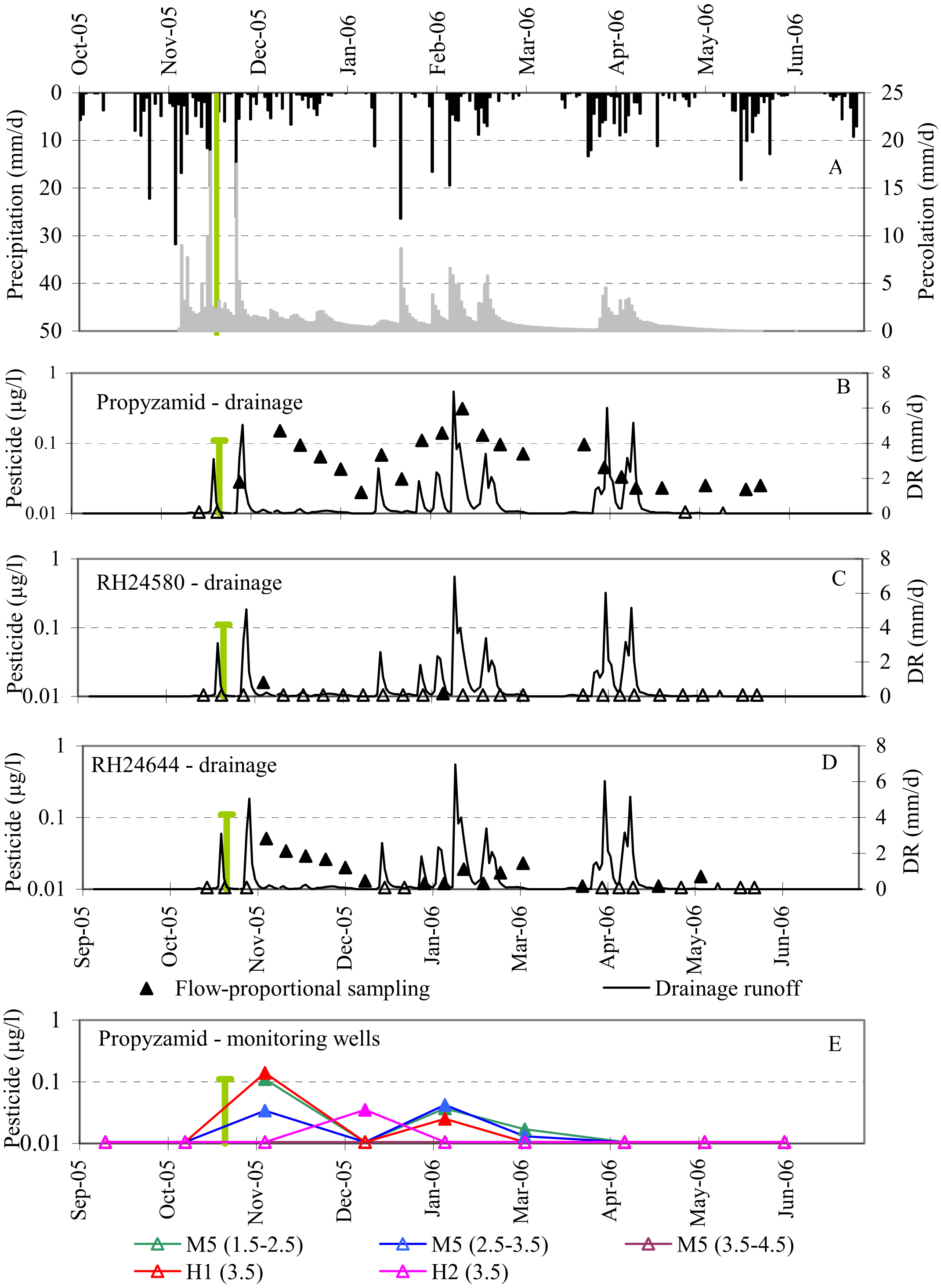


Figure 24. Precipitation and simulated percolation 1 m b.g.s. (A) together with the concentration of propyzamid (B) and RH24580 (C) and RH 24644 (D) in the drainage runoff at Silstrup. The concentration of propyzamid in monitoring well M5, H1 and H2 is given in E, the numbers in parentheses indicating the screen depth. Open diamonds indicate values below the detection limit of 0.01 µg/L. The green vertical line indicates the date of propyzamid application.

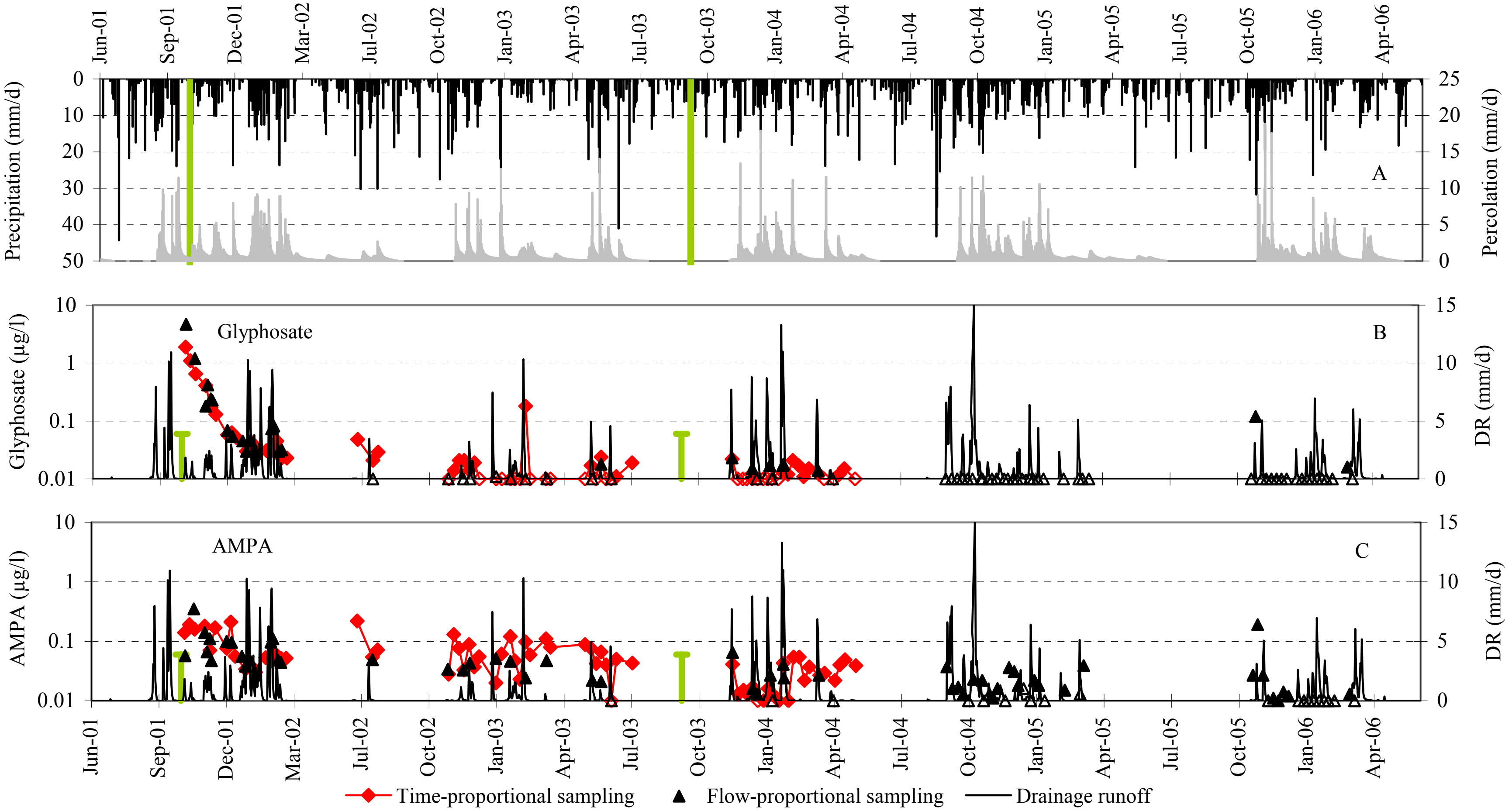


Figure 25. Precipitation and simulated percolation 1 m b.g.s. (A) together with concentration of glyphosate (B) and AMPA (C) in the drainage runoff at Silstrup. The green vertical line indicates the dates of applications. DR.: Drainage runoff.

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 hill-island, i.e. a glacial moraine preserved from the Weischselian Glaciation. Estrup has thus been exposed to weathering, erosion, leaching and other geomorphologic processes for a much longer period than that of the other sites. The test field covers a cultivated area of 1.26 ha (105 x 120 m) and is virtually flat (Figure 26). The site is highly heterogeneous with considerable variation in both topsoil and aquifer characteristics (Lindhardt *et al.* (2001). 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 clay content of 10–20% and an organic carbon content of 1.7–7.3%. The site is also characterized by a C-horizon of low permeability. The saturated hydraulic conductivity in the C-horizon is 10^{-8} m/s, which is about two orders of magnitude lower than that at the other loamy sites (Table 1). The geological structure is complex comprising a clay till core with deposits of different age and composition (Lindhardt *et al.* (2001). A brief description of the sampling procedure is provided in Appendix 2. The monitoring design and test site are described in detail in Lindhardt *et al.* (2001) and the analysis methods in Kjær *et al.* (2002). Please note that the geological conditions only allowed one of the planned horizontal wells to be installed as drilling in sand proved impossible.

5.1.2 Agricultural management

Management practice during the 2003 - 2005 growing seasons is briefly summarized below and detailed in Appendix 3 (Table A3.4). For information about management practice during the first two monitoring periods see Kjær *et al.* (2003).

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

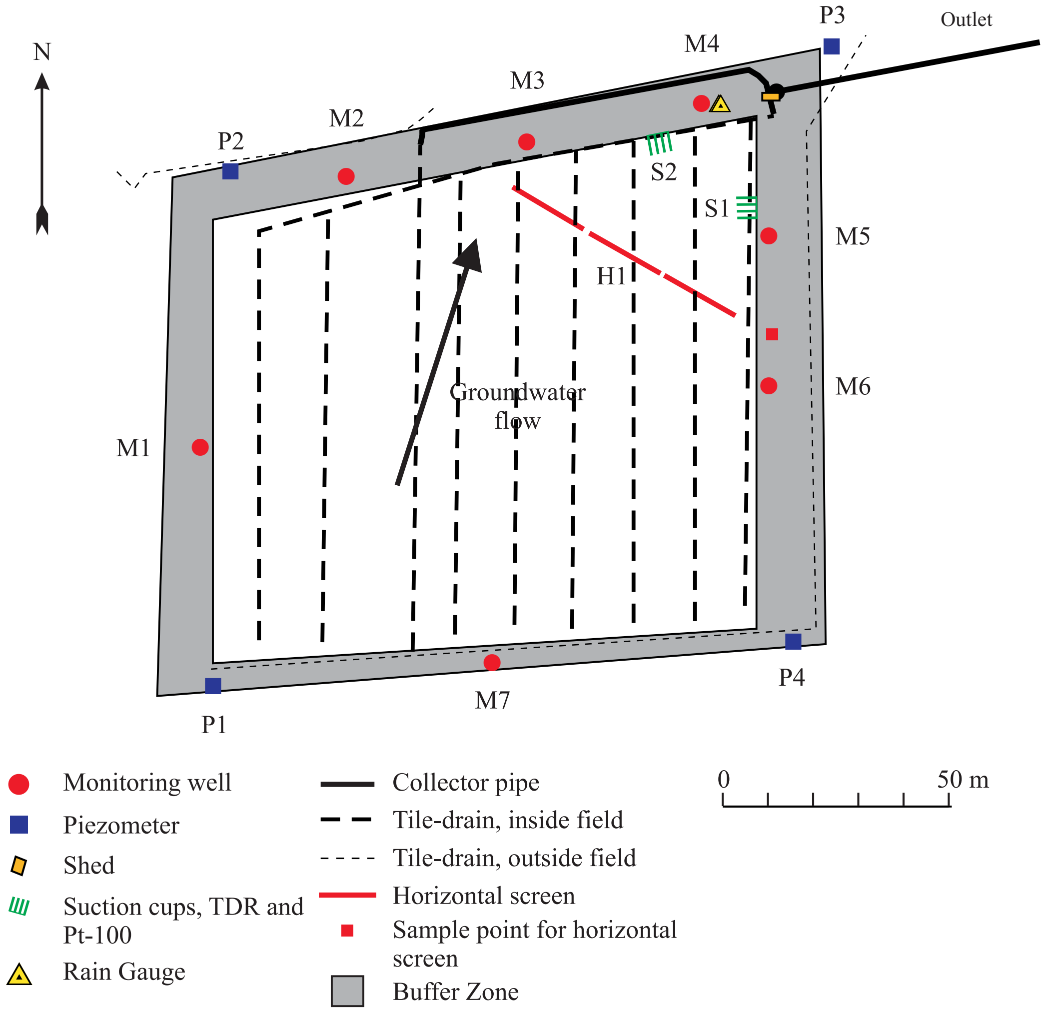


Figure 26. Overview of the Estrup site. The innermost white area indicates the cultivated land, while the grey area indicates the surrounding buffer zone. The positions of the various installations are indicated, as is the direction of groundwater flow (by an arrow).

The field was ploughed four days after the beets were harvested and on 14 April 2004 a crop of spring barley (cv. Prestige) was sown. When the barley had 3 leaves unfolded the herbicide fluroxypyr was used. On 22 June, when 70% of inflorescence had emerged, azoxystrobin was sprayed against fungi. The barley was harvested on 29 august yielding 5.13 t/ha of grain (85% dry matter) whereas 1.19 t/ha of straw (100% dry matter) was removed from the field on 7 September. Grain yields were slightly below average compared to Petersen (2004).

Sow slurry was injected and the field was ploughed on 18 April 2005. On 13 May the field was sown with maize (cv. Tassilo), which 26 May, at emergence, were sprayed with the herbicide terbutylazine. A mixture of terbutylazine and bentazone was used when 4 leaves had unfolded - 8 June. The maize was harvested as a whole crop on 13 October yielding 14.34 t/ha of 100% dry matter similar to experiments (Pedersen 2005). In order to further evaluate the transport of the strongly sorbing compound glyphosate, pendimethalin and a tracer of bromide were applied on 9 November.

5.1.3 Model set-up and calibration

The MACRO model is applied to the Estrup site covering the soil profile to a depth of 5 m b.g.s., always including the groundwater table. The model is used to simulate the water flow in the unsaturated zone during the monitoring period from July 2000–June 2006 and to establish an annual water balance.

Due to the application of a newer version of MACRO than used in the previous reports (Kjær *et al.,* 2005c, and Barlebo *et al.,* in press.), the model for the Estrup site has been recalibrated for the monitoring period July 2000-June 2004 and validated for the monitoring period July 2004-June 2006. For this purpose, the following time series have been used: the observed groundwater table measured in the piezometers located in the buffer zone, measured drainage flow and soil water content measured at two depths (25 and 40 cm b.g.s.) from the soil profile S1 (Figure 27). 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 (data not shown). No explanation can presently be given for the unreliable data, and they have been excluded from the analysis. The data from the soil profile S2 have also been excluded due to a problem of water ponding above the TDR probes installed at S2, as mentioned in Kjær *et al.* (2003). Because of the erratic TDR data, calibration data are limited at this site. Data acquisition, model set-up as well as results related to simulated bromide transport are described in Barlebo *et al.* (in press.) and Rosenbom *et al.* (in prep.).

5.2 Results and discussion

5.2.1 Soil water dynamics and water balances

The model simulations were generally consistent with the observed data (which were limited compared to other PLAP sites, as noted above), indicating a good model description of the overall soil water dynamics in the unsaturated zone (Figure 27). The model provided an acceptable simulation of the overall level of the groundwater table. Compared to the simulations made with MACRO 5.0 (Kjær *et al.*, 2005c), the groundwater table fluctuated more, and the falling groundwater table during the dry summer periods was better described (Figure 27B). This was also more consistent with the automatic measurements (Figure 27B) in piezometer P1 situated upstream (Figure 26). A drop in measured groundwater table was seen after short periods of low precipitation (Figure27A). The simulated groundwater table still did not seem as sensitive to these short periods of low precipitation and tended not to drop as much as the measured values. Since the TDR data are limited in the subsoils, a more detailed study of dynamics in these layers is difficult. Nothing special is noted for the groundwater table in the latest monitoring period (July 2004–June 2006). As in previous years (Kjær *et al.*, 2005c), the simulated groundwater table often fluctuates slightly above the drain depth during periods of drainage flow.

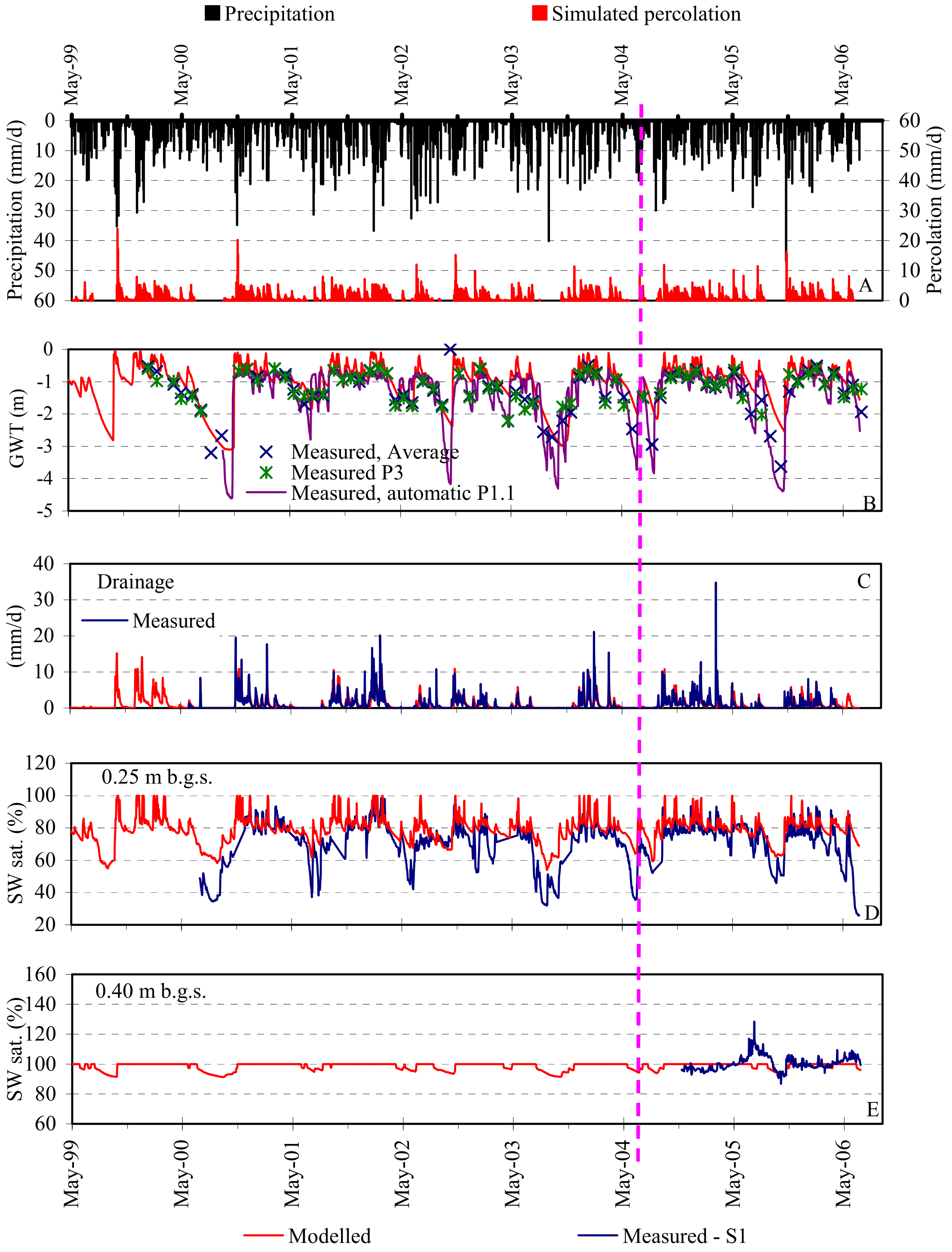


Figure 27. Soil water dynamics at Estrup: Measured precipitation and simulated percolation 0.6 m b.g.s. (A), simulated and measured groundwater level (B), simulated and measured drainage flow (C), and simulated and measured soil saturation (SW sat.) at two different soil depths (D and E). The measured data in B derive from piezometers located in the buffer zone. The measured data in D and E derive from TDR probes installed at S1 (see Figure 26). The broken vertical line indicates the beginning of the validation period (July 2004- June 2006).

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).

	Normal precipitation [2)]	Precipitation	Actual evapotrans-piration	Measured drainage	Simulated drainage	Groundwater recharge [3)]
1.7.99–30.6.00 [1)]	968	1173	466	–	553	154 [4)]
1.7.00–30.6.01	968	887	420	356	340	111
1.7.01–30.6.02	968	1290	516	505	555	270
1.7.02–30.6.03	968	939	466	329	346	144
1.7.03–30.6.04	968	928	499	298	312	131
1.7.04–30.6.05	968	1087	476	525	468	86
1.7.05–30.6.06	968	897	441	258	341	199

[1)] *Monitoring started in April 2000*

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

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

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

The simulated drainage (Figure 27C) matched the measured drainage flow quite well. Drainage runoff over the whole monitoring period was high as compared to that of the other three till sites, being investigated in the PLAP. –This being due to a significantly lower permeability of the C-horizon than that of the overlying A and B horizons (Kjær *et al.*, 2003). Precipitation in the latest monitoring year, July 2004–June 2006, was within the precipitation range of the monitoring period, Table 9.

5.2.2 Bromide leaching

Bromide has now been applied twice at Estrup. The bromide concentrations measured up to October 2006 (Figure 28 and Figure 29) relate to the bromide applied in spring 2000, as described further in Kjær *et al.* (2003). Leaching of the bromide applied in November 2005 is evaluated in Rosenbom *et al.* (in prep.).

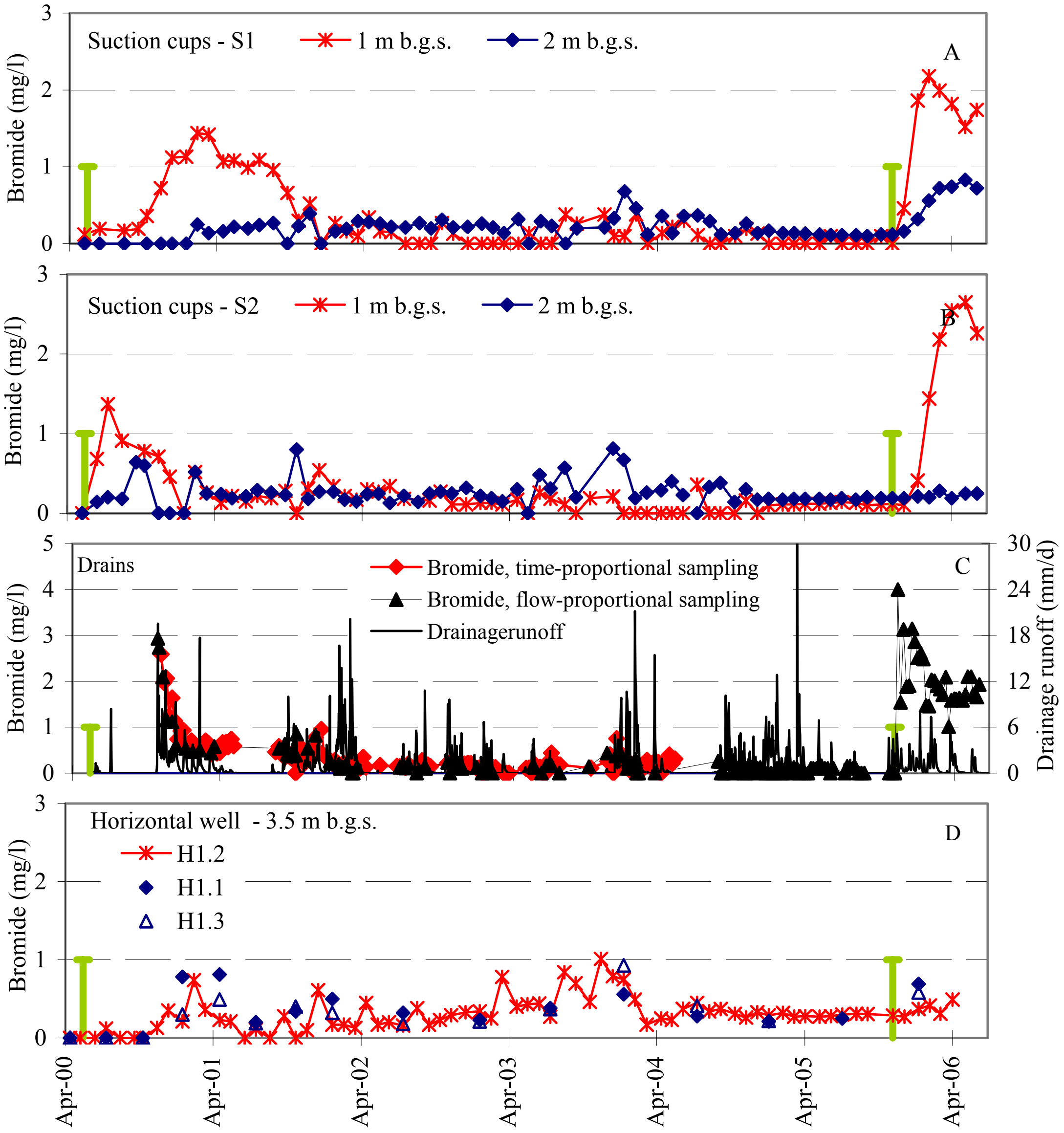


Figure 28. Bromide concentration at Estrup. A and B refer to suction cups located at S1 and S2, respectively. The bromide concentration is also shown for drainage runoff (C) and the horizontal monitoring well H1 (D). The green vertical line indicates the date of bromide application.

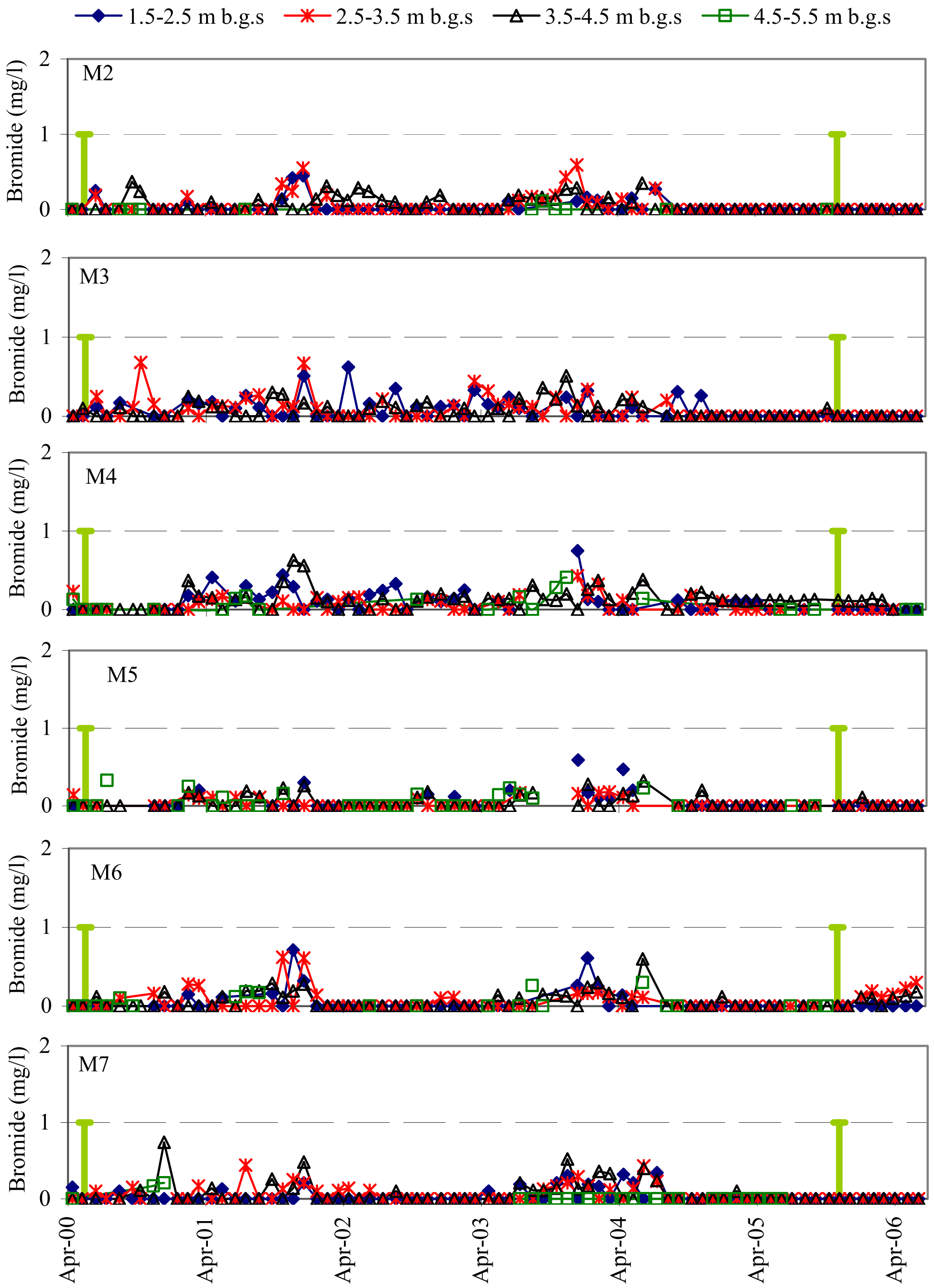


Figure 29. Bromide concentration at Estrup. The data derive from the vertical monitoring wells (M2–M7). Screen depth is indicated in m b.g.s. The green vertical line indicates the date of bromide application.

5.2.3 Pesticide leaching

Monitoring at Estrup began in May 2000 and presently encompasses several pesticides and their degradation products, as indicated in Table 10. Pesticide application during the three most recent growing seasons is shown together with precipitation and simulated precipitation in Figure 30. It should be noted that precipitation in is corrected to the soil surface according to Allerup and Madsen (1979), whereas percolation (0.6 m b.g.s.) refers to accumulated percolation as simulated with the MACRO model (Section 5.2.1). Moreover, pesticides applied later that April 2006 are not evaluated in this report and hence are not included in Table 10.

Table 10. Pesticides analysed at Estrup with the product used shown in parentheses. Degradation products are in italics. Precipitation (prec.) and percolation (perc.) are accumulated from the date of first application until the end of monitoring. 1st month perc. refers to accumulated percolation within the first month after application. C_{mean} refers to average leachate concentration in the drainage water within the first drainage season after application (See Appendix 2 for calculation methods). The number of pesticide-positive samples is indicated in parentheses.

Crop and analysed pesticides	Application date	End of monitoring	Prec. (mm)	Perc. (mm)	1st month perc. (mm)	C_{mean} (µg/L)
Spring barley 2000						
Metsulfuron-methyl (Ally)	May 00	Apr 03	2990	1456	29	<0.01(1)
- *triazinamin*						<0.02(1)
Flamprop-M-isopropyl (Barnon Plus)	May 00	Apr 03	2914	1434	2	0.02(20)
- *flamprop (free acid)*						0.01(13)
Propiconazole (Tilt Top)	Jun 00	Apr 05	4938	2294	0	0.01(27*)
Fenpropimorph (Tilt Top)	Jun 00	Jul 02	2211	1048	0	<0.01(1)
- *fenpropimorphic acid*						<0.02(0)
Dimethoate (Perfekthion 500 S)	Jun 00	Jul 02	2211	1048	0	<0.01(0)
Pea 2001						
Glyphosate (Roundup Bio)	Oct 00	Jul 06†	5780	2867	123	0.54(208*)
- *AMPA*						0.17(248*)
Bentazone (Basagran 480)	May 01	Jul 06†	5783	2457	9	0.03 (105*)
- *AIBA*						<0.02 (2)
Pendimethalin (Stomp)	May 01	Jul 03	2208	1096	9	<0.01(37*)
Pirimicarb (Pirimor)	Jun 01	Jul 05	4251	1995	10	0.01(40*)
- *pirimicarb-desmethyl*						<0.02(0)
- *pirimicarb-desmethyl-formamido*						<0.02(26*)
Winter wheat 2002						
Ioxynil (Oxitril CM)	Nov 01	Jul 03	1580	860	52	0.04(20)1)
Bromoxynil (Oxitril CM)	Nov 01	Jul 03	1580	860	52	0.01(3)1)
Amidosulfuron (Gratil 75 WG)	Apr 02	Jul 04	2148	928	8	<0.01 (0)
MCPA (Metaxon)	May 02	Jul 04	2091	928	0	<0.01(12)
- *4-chlor,2-methylphenol*						<0.01(1)
Propiconazole (Tilt 250 EC)	May 02	Apr 05	2920	1336	39	0.02 (27*)
Pirimicarb (Pirimor)	Jun 02	Jul 05	2982	1403	58	0.01(40*)
- *pirimicarb-desmethyl*						<0.02(0)
- *pirimicarb-desmethyl-formamido*		Apr 06				<0.02(26*)

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

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

† Monitoring will continue during the following year. The values for prec. and perc. are accumulated up to July 2006

1) Drainage runoff commenced about two and a half months prior to the application of ioxynil and bromoxynil, and the weighted concentrations refer to the period from the date of application until 1 July 2002

Table 10 continued. Pesticides analysed at Estrup with the product used shown in parentheses. Degradation products are in italics. Precipitation (prec.) and percolation (perc.) are accumulated from the date of first application until the end of monitoring. 1st month perc. refers to accumulated percolation within the first month after application. C_{mean} refers to average leachate concentration in the drainage water within the first drainage season after application (See Appendix 2 for calculation methods). The number of pesticide-positive samples is indicated in parentheses.

Crop and analysed pesticides	Application date	End of Monitoring	Prec. (mm)	Perc. (mm)	1st month perc. (mm)	C_{mean} (µg/L)
Fodder beet 2003						
Glyphosate (Roundup Bio)	Sep 02	Jul 06†	3586	1790	0	0.43(179*)
- *AMPA*						0.19(225*)
Ethofumesate (Betanal Optima)	May 03	Apr 06	2901	1371	50	0.11(35)
Metamitron (Goltix WG)	May 03	Apr 06	2901	1371	50	1.1(42)
-*metamitron-desamino*						0.21(49)
Pirimicarb (Pirimor)	Jul 03	Jul 05	2071	939	0	<0.01(40*)
- *pirimicarb-desmethyl*		Jul 05				<0.01(0)
- *pirimicarb-desmethyl-formamido*		Apr 06				0.12 (26*)
Spring barley 2004						
Fluroxypyr (Starane)	May 04	Jul 06	2073	1030	0	<0.02 (2)
Azoxystrobin (Amistar)	Jun 04	Jul 06†	2006	1038	38	0.12 (36)
- *CyPM*						0.23 (60)
Maize 2005						
Terbutylazine (Inter-Terbutylazin)	May 05	Jul 06†	937	479	32	0.48 (44)
- *desethyl-terbutylazine*						0.31 (45)
- *2-hydroxy-terbutylazine*						0.11 (41)
- *desisopropyl-atrazine*						0.02 (47)
- *2-hydroxy-desethyl-terbutylazine*						0.24 (41)
Bentazone (Laddok TE)	Jun 05	Jul 06†	892	457	9	0.18 (105)
- *AIBA*						<0.01 (2)
Glyphosate (Roundup Bio	Nov 05	Jul 06†	487	350	68	4.04(208*1))
-*AMPA*						0.42 (248*1))
Pendimethalin (Stomp)	Nov 05	Jul 06†	487	350	68	3.13 (37*1))

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

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

† Monitoring will continue during the following year. The values for prec. and perc. are accumulated up to July 2006

1) Drainage runoff commenced about two weeks prior to the application of glyphosate and pendimethalin and the weighted concentrations refer to the period from the date of application until 1 July 2006

The leaching risk of pesticides applied during 2000, 2001 and 2002 has been evaluated in Kjær *et al.* (2003), Kjær *et al.* (2004) and Kjær *et al.* (2005c), respectively.

The pesticides applied during 2003 all leached during the monitoring period. Ethofumesate, metamitron and its degradation product metamitron-desamino thus leached from the root zone into the drainage water at average concentrations exceeding 0.1 µg/L (Figure 31). Leaching has hitherto been confined to the depth of the drainage system and the compounds have not been detected in deeper monitoring screens (Appendix 6). It should be noted that these compounds also leached from the root zone at Silstrup and Faardrup, reaching both drainage system and groundwater monitoring screens (Appendix 6). Average concentrations in drainage water were not as high as at Estrup, although concentrations exceeding 0.1 µg/L were observed in both drainage system and groundwater monitoring screens during a 1–4-month period (see Kjær *et al.*, 2002 and Kjær *et al.*, 2004 for details).

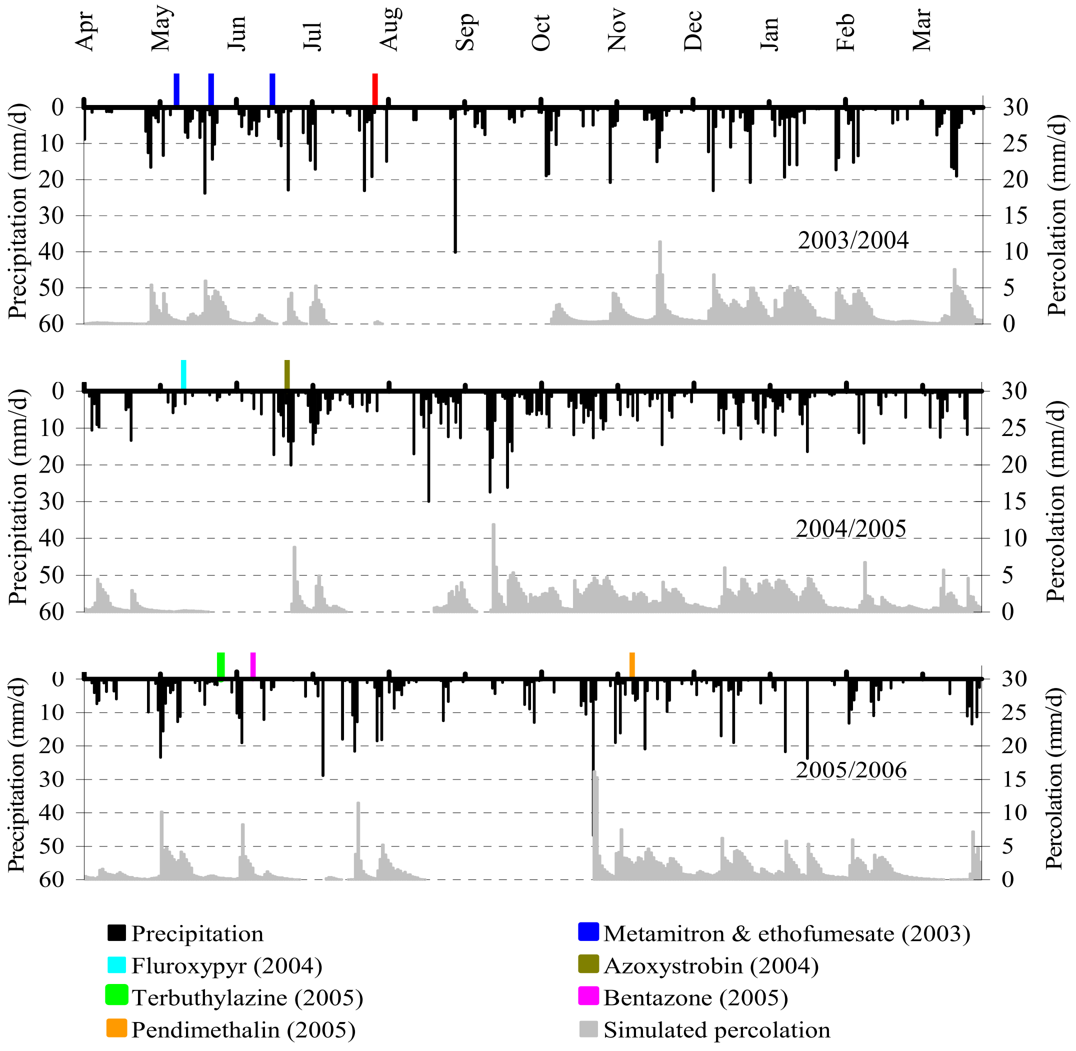


Figure 30. Pesticide application and precipitation (primary axis) together with simulated percolation 0.6 m b.g.s. (secondary axis) at Estrup in 2003/2004 (upper), 2004/2005 (middle) and 2005/2006 (lower). Pesticides applied later than April 2006 are not included.

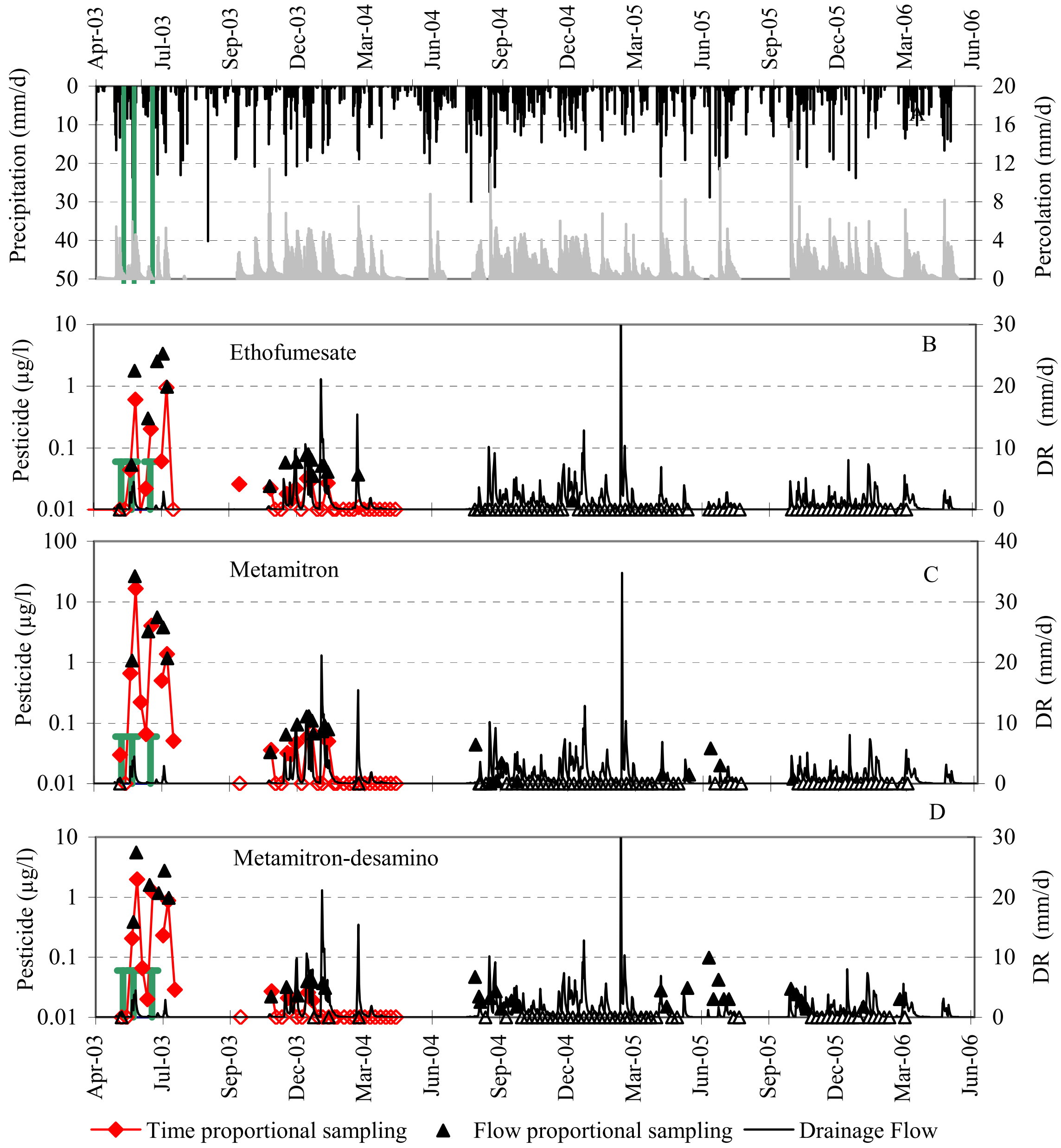


Figure 31 Precipitation and simulated percolation (A) together with concentration of ethofumesate (B), metamitron (C) and metamitron-desamino (D) in the drainage runoff (DR on secondary axis) at Estrup in 2003/2006. The green vertical lines indicate the dates of applications. Open diamonds and triangles indicate values below the detection limit of 0.01 µg/L.

Pirimicarb-desmethyl-formamido (degradation product of pirimicarb) also leached from the root zone into the drainage water at average concentrations exceeding 0.1 µg/L (Figure 32). Leaching has hitherto been confined to the depth of the drainage system, and pirimicarb-desmethyl-formamido has not been detected in deeper monitoring screens. A similar high leaching of pirimicarb-desmethyl-formamido has not been observed with any of the previous applications of pirimicarb at the five PLAP sites (Kjær *et al.*, 2004).

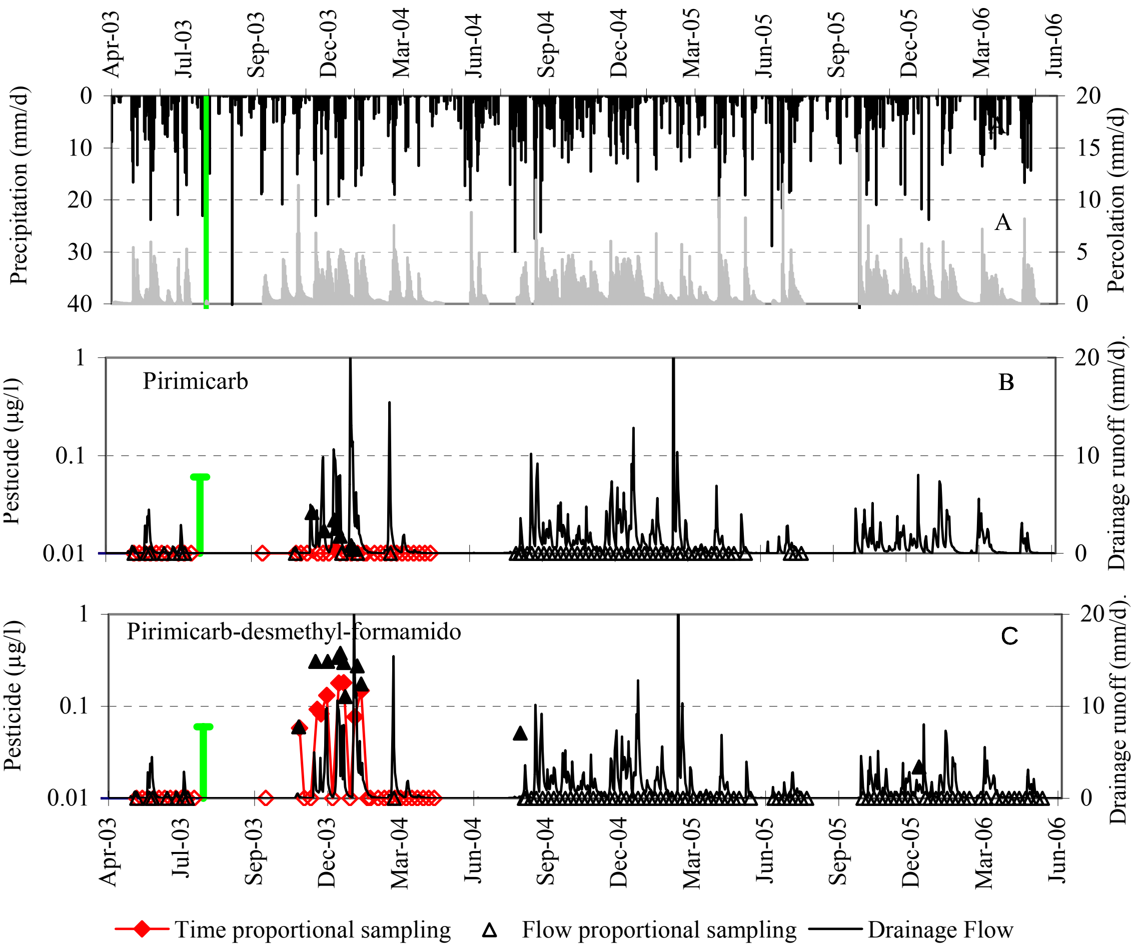


Figure 32. Precipitation and simulated percolation (A) together with concentration of pirimicarb (B) and pirimicarb-desmethyl-formamido (C) in the drainage runoff at Estrup in 2003/2006. The green vertical lines indicate the dates of application. Open diamonds and triangles indicate values below the detection limit of 0.01 µg/L.

When evaluating these results it should be noted that precipitation input following the application of ethofumesate and metamitron (May-June 2003) was much higher than normal (Appendix 5). May and June 2003 were characterized by high precipitation (111 mm and 94 mm, respectively) that exceeded the monthly normal by 76% and 23%, respectively. Percolation the first month after application amounted to 50 mm. Although high, this percolation pattern is not unusual for the Estrup region, similar high percolation thus occurred during the summer of 2002 (Table 10). On the contrary pirimicarb was applied in July, when precipitation input was close to normal and was counterbalanced by actual evapotranspiration such that no percolation occurred during the first month after the pesticide application (Table 10).

Of the pesticides applied in 2003 the leaching risk of fluroxypyr was found to be negligible at Estrup. Apart from one sample from the drainage system (0.03 µg/L) and another from a groundwater monitoring well (0.06 µg/L) fluroxypyr was not detected in any of the analysed samples. Azoxystrobin, as well as its degradation product CyPM, did however leach from the root zone entering the tile-drains in average concentration exceeding 0.1

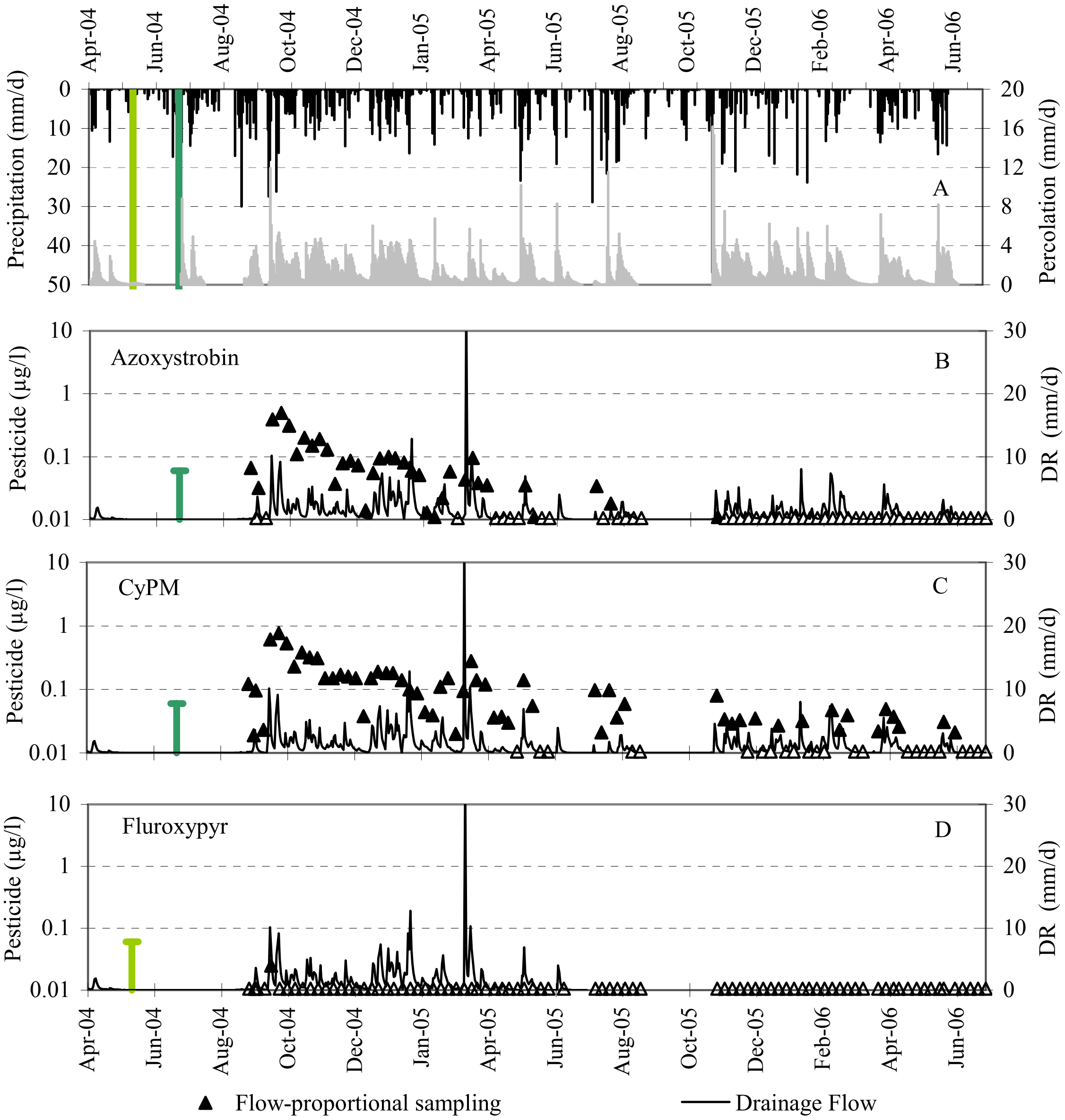


Figure 33. Preciption and simulated percolation (A) together with concentration of azoxystrobin (B), CyPM (C) and fluroxypyr (D) in the drainage runoff (DR on secondary axis) at Estrup in 2004/2006. The green vertical lines indicate the dates of applications. Open diamonds and triangles indicate values below the detection limit of 0.01 µg/L.

µg/L (Figure 33). Leaching of azoxystrobin was confined within a seven months period whereas the leaching of CyPM continued throughout the second year after application. Similar to previous observed leaching patterns, also the leaching of azoxystrobin and its degradation product was confined to the depth of the drainage system, as none of these compounds were detected in the groundwater monitoring wells situated beneath the drainage system. Precipitation following the application of fluroxypyr was close to normal and was counterbalanced by the evapotranspiration such that no percolation occurred during the first month after pesticide application (Table 10). Precipitation following first the month after application of azoxystrobin amounted to 132 mm/ha with corresponding percolation being 38 mm/ha. Although high, this is not unusual for the Estrup region, however, as similar patterns have been seen during the period of 1990–2004 (data not shown).

The leaching risk of pesticides applied in 2005 will not be evaluated until the 2007 monitoring results become available, i.e. when two years of monitoring data have been collected. It should be noted, though, that all of the applied pesticides leached, as illustrated in Figure 34 – Figure 37) and Appendix 6 (Table A6.4) and Appendix 8.

Detection frequency of glyphosate, which were applied three times at the Estrup site (Figure 37), has increased in the groundwater monitoring wells during the monitoring period. During the last year (July 2005 – June 2006) glyphosate was thus detected in 16% of the 82 analysed groundwater samples, with two samples containing more than 0.1 µg/L glyphosate (Appendix 8; Table A8.1). Nevertheless, pesticide leaching pattern at Estrup is generally confined to the depth of the drainage system. Apart from 21 samples containing 0.01–0.67 µg/L glyphosate, pesticides have only sporadically been detected in groundwater monitoring screens below the depth of the drainage system (Appendix 6 and 8). Due to decreased hydraulic conductivity and lower degree of preferential flow, transport of water and solutes at Estrup was much slower beneath the drainage system than above it. Slow transport may allow for dispersion, dilution, sorption and degradation, thereby further reducing the deep transport. Compared to the other loamy soils investigated, the retention characteristics at Estrup suggest that the C-horizon (situated beneath the drainage depth) is less permeable with a lower degree of preferential flow occurring through macropores (See Kjær *et al.* 2005c for details).

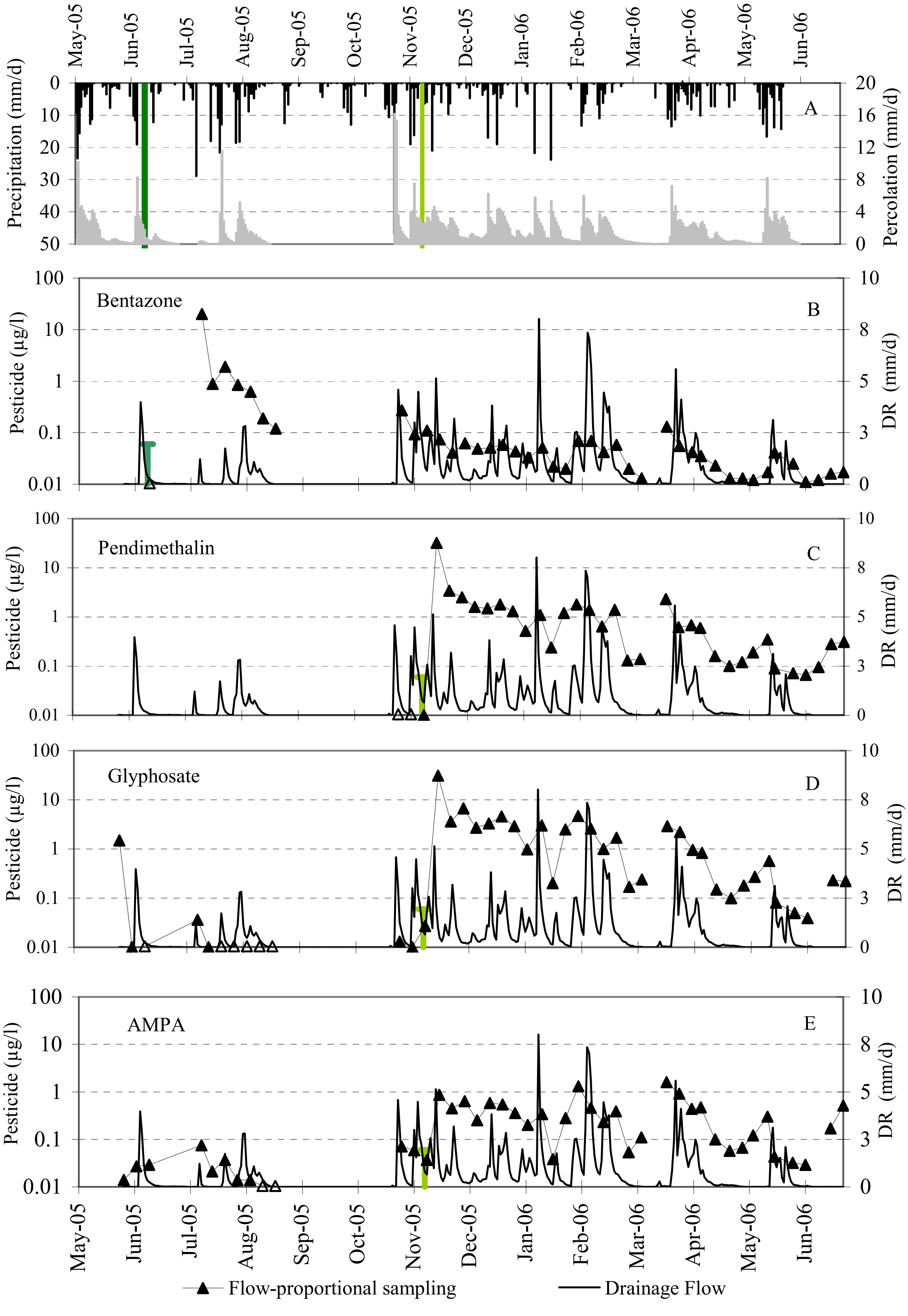


Figure 34. Precipitation and simulated percolation (A) together with concentration of bentazone (B), pendimethalin (C), glyphosat (D) and AMPA (E) in the drainage runoff (DR on secondary axis) at Estrup in 2005/2006. The green vertical lines indicate the dates of applications. Open diamonds and triangles indicate values below the detection limit of 0.01 µg/L.

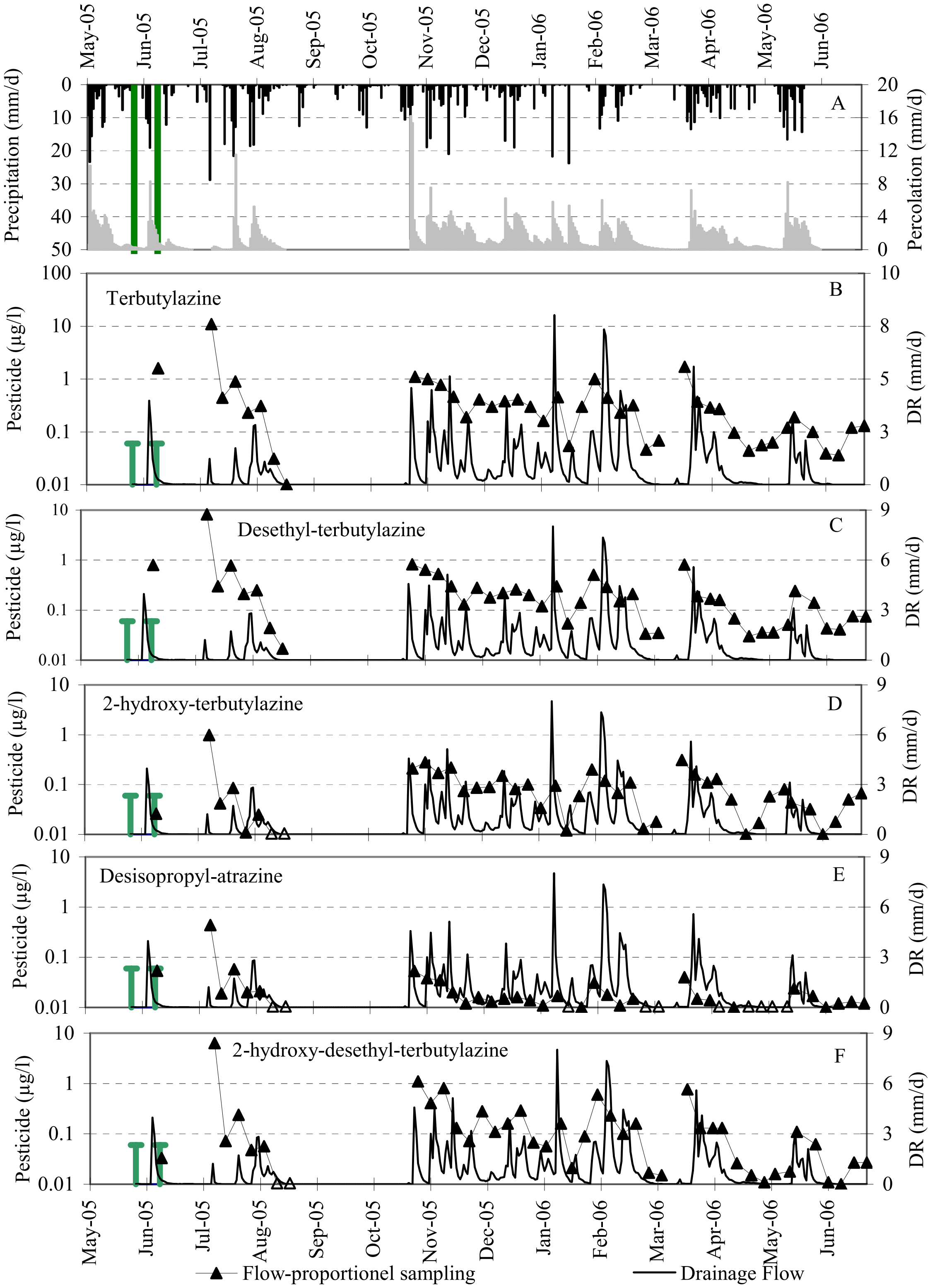


Figure 35 Precipitation and simulated percolation (A) together with concentration of terbutylazine (B), desethyl-terbutylazine (C), 2-hydroxyl-terbutylazine (D), desisopropyl-atrazine (E) and 2-hydroxy-desethyl-terbutylazine (F) in the drainage runoff (DR on secondary axis) at Estrup in 2005/2006. The green vertical lines indicate the dates of applications. Open triangles indicate values below the detection limit of 0.01 µg/L.

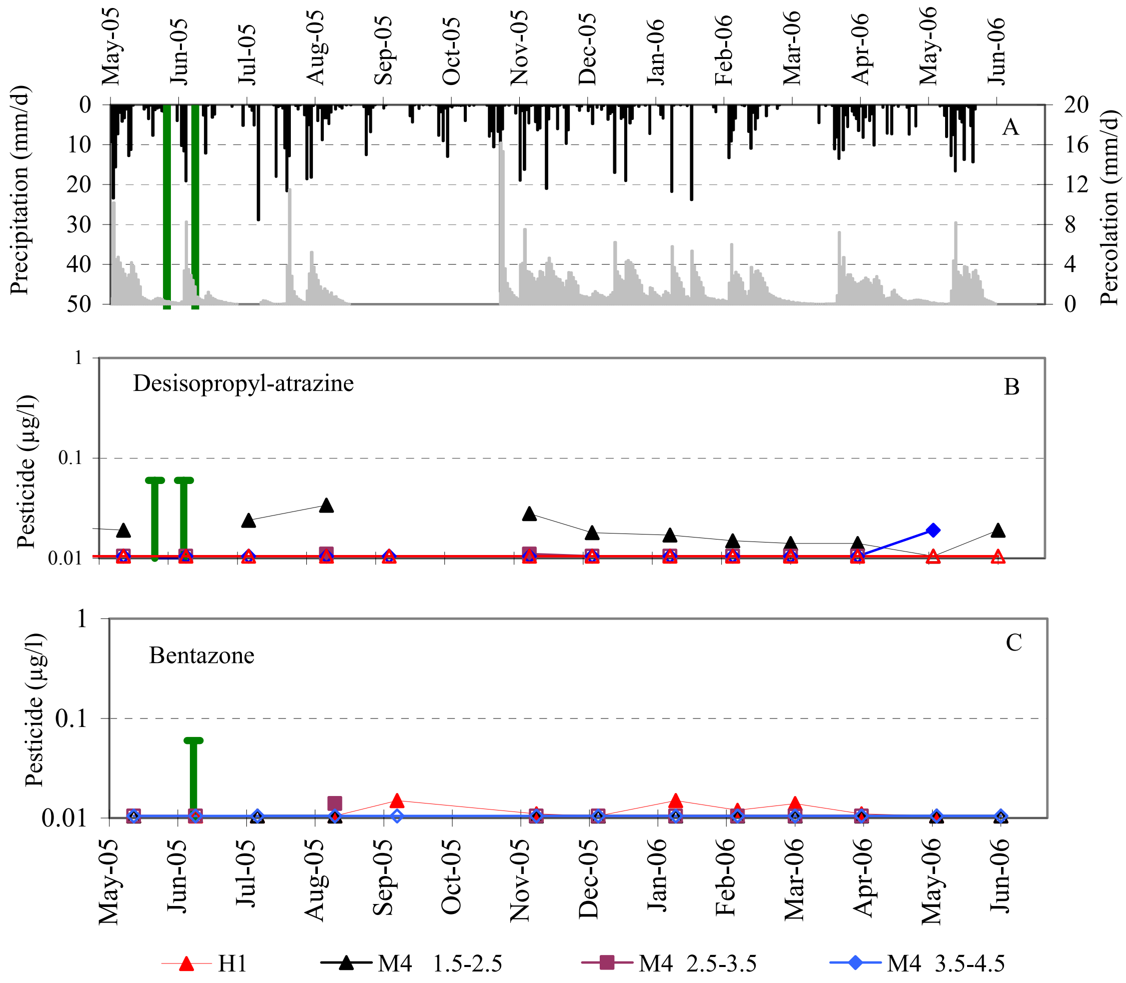


Figure 36. Precipitation and simulated percolation (A) together with concentration of desisopropylatrazine (B) and bentazone (C) in groundwater monitoring screens at Estrup in 2005/2006. The green vertical lines indicate the date of applications, and numbers in parentheses the screen depth.

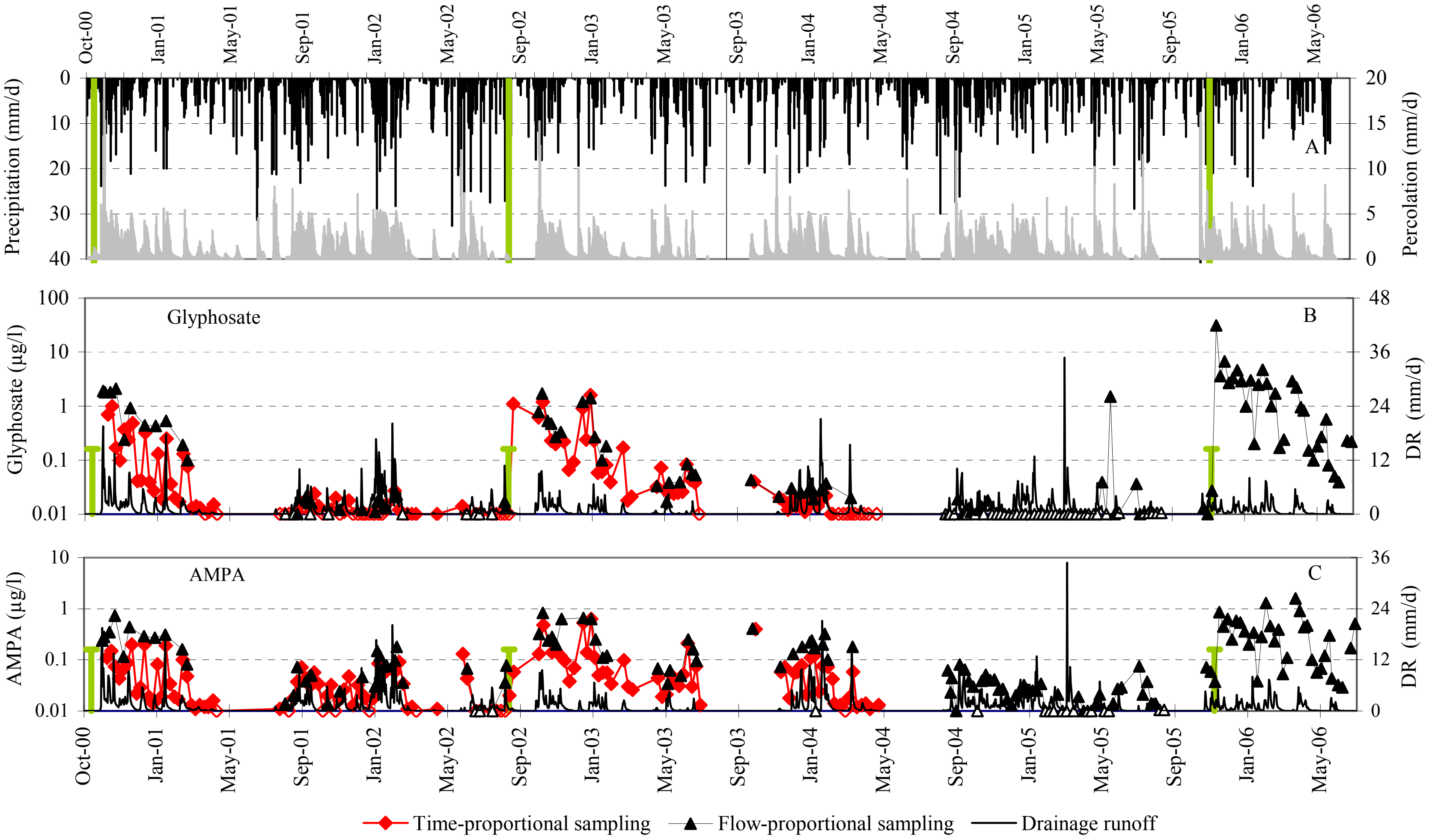


Figure 37. Precipitation and simulated percolation (A) together with the concentration of glyphosate (B) and AMPA (C) in the drainage runoff (DR. on secondary axis) at Estrup. Data represent a four-year period including three applications of glyphosate as indicated by the green vertical lines. Open diamonds and triangles indicate values below the detection limit of 0.01 µg/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° (Figure 38). Based on three profiles in the buffer zone bordering the field, the soil was classified as Haplic Vermudoll, Oxyaquic Hapludoll and Oxyaquic Argiudoll (Soil Survey Staff, 1999). The topsoil is characterized as sandy loam with 14–15% clay and 1.4% organic carbon. Within the upper 1.5 m numerous desiccation cracks coated with clay are present. The test field contains glacial deposits dominated by sandy till to a depth of about 1.5 m overlying a clayey till. The geological description shows that small channels or basins filled with meltwater clay and sand occur both interbedded in the till and as a large structure crossing the test field (Lindhardt *et al.,* 2001). The calcareous matrix and the reduced matrix begin at 1.5 m and 4.2 m b.g.s., respectively. 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 was located 1–2 and 2–3 m b.g.s. in the lower and upper parts of the area, respectively. During fieldwork within the 5 m deep test pit it was observed that most of the water entering the pit came from an intensely horizontally fractured zone in the till at a depth of 1.8–2.5 m. The intensely fractured zone could very well be hydraulically connected to the sand fill in the deep channel, which might drain part of the percolation. The bromide tracer study showed that virtually none of the applied bromide reached the vertical monitoring well (M6) located in the sand-filled basin (Figure 39 and Figure 42), however, thus indicating that hydraulic contact with the surface in the "basin" does not differ from that in other parts of the test field, and that the basin is a small pond filled with sediments from local sources. A brief description of the sampling procedure is provided in Appendix 2. The monitoring design and test site are described in detail in Lindhardt *et al.* (2001) and the analysis methods in Kjær *et al*. (2002).

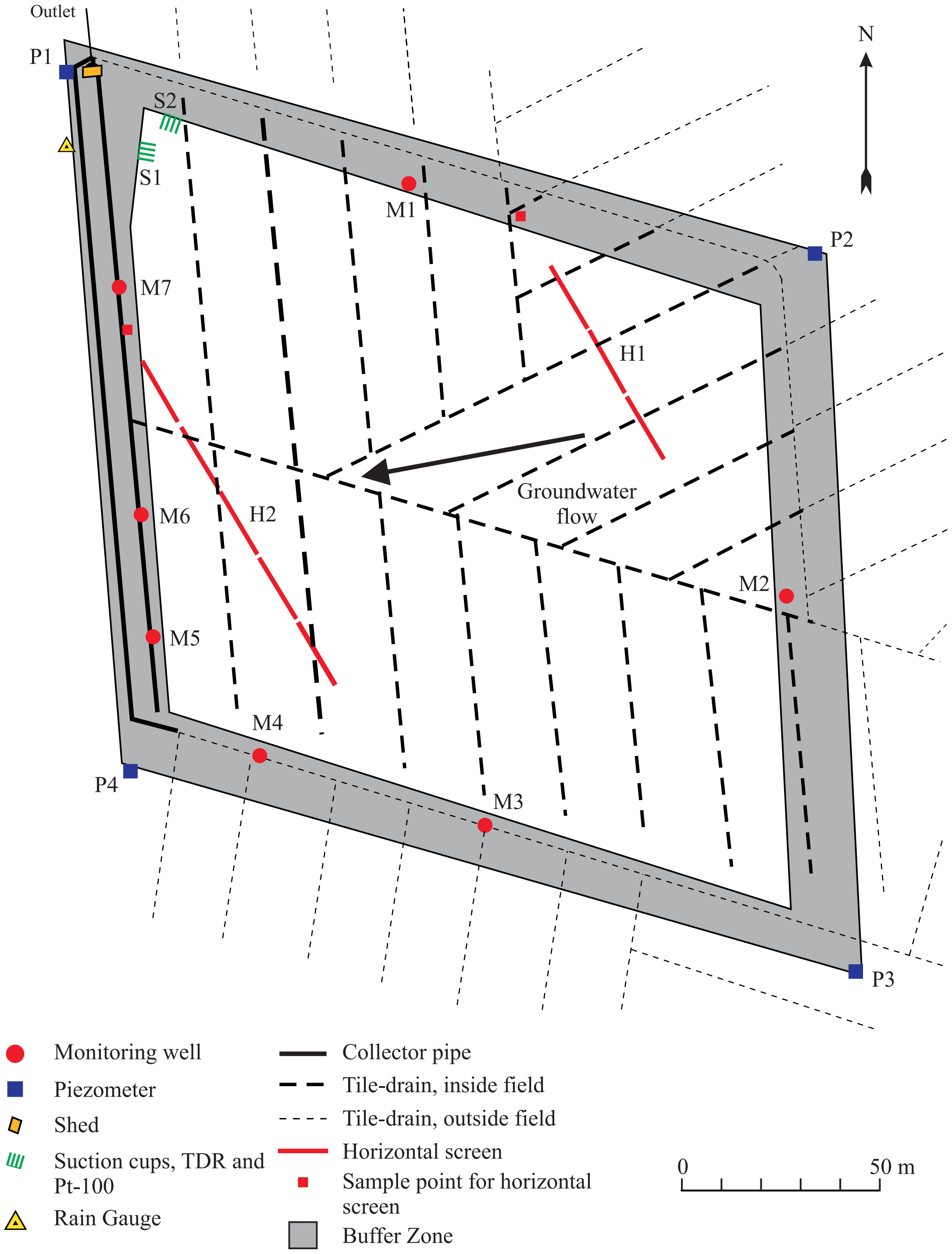


Figure 38. Overview of the Faardrup site. The innermost white area indicates the cultivated land, while the grey area indicates the surrounding buffer zone. The positions of the various installations are indicated, as is the direction of groundwater flow (by an arrow).

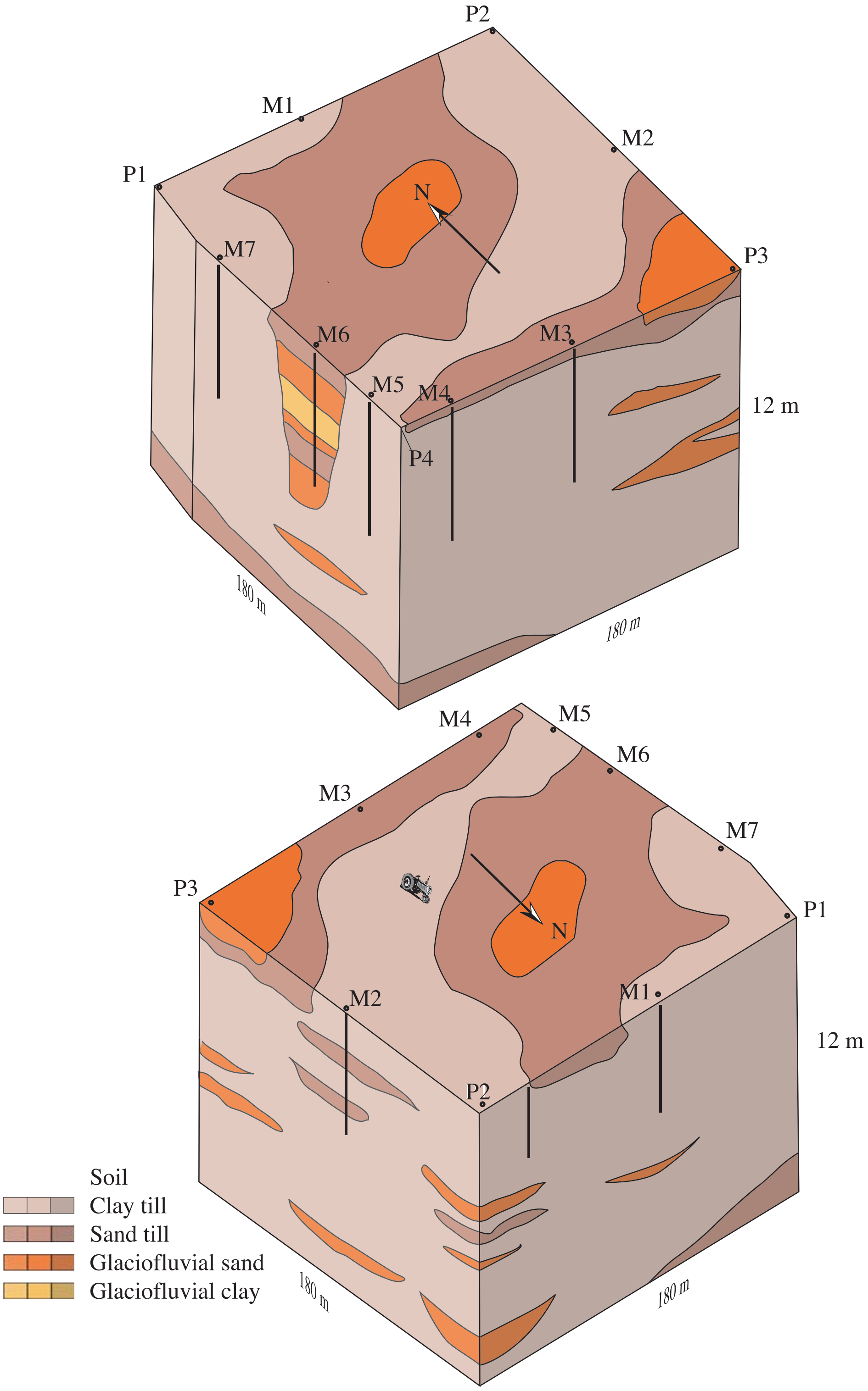


Figure 39. Geological description of Faardrup (Lindhardt *et al.* 2001).

6.1.2 Agricultural management

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

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

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

The field was ploughed in the autumn of 2004 and sown with maize (cv. Nescio) on 26 April 2005. At emergence, 17 May, weeds were treated with terbutylazine and further, when two leaves had unfolded, with a mixture of terbutylazine and bentazone. Whole crop yields on 28 September was 16.0 t/ha of 100% dry matter, being very high, this particular cultivare was however not included in the Farmer's experiments (Pedersen, 2005).

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 2006 and to establish an annual water balance.

Due to application of a newer version of MACRO than used in the previous report (Kjær *et al.,* 2005c, and Barlebo *et al.,* in press.) the model for the Faardrup site was recalibrated for the monitoring period July 1999-June 2004 and validated for the monitoring period July 2004-June 2006. For this purpose, the following time series were used: observed groundwater table measured in the piezometers located in the buffer zone, water content measured at three depths (25, 60 and 110 cm b.g.s.) from the two profiles S1 and S2

(Figure 38) and measured drainage flow. Data acquisition and model set-up are described in Barlebo *et al. (*in press.) and Rosenbom *et al.* (in prep.).

Due to electronic problems and periods with snow, precipitation measured at Flakkebjerg located 3 km east of Faardrup was used for the monitoring periods: July 1999–June 2002, July 2003 – June 2004, and in January and February of both 2005 and 2006. Precipitation measured locally at Faardrup was used for the rest of the monitoring period.

6.2 Results 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 (Figure 40). The dynamics and level of the measured groundwater table were well described by the present model. Furthermore, the measured, quick rise in groundwater table after the summer period 2005 was delayed in the simulation. The level and dynamics of the soil water saturation in all three horizons were generally well described by the model (D, E and F). Though, in 0.25 m b.g.s., the model did not capture the rise in water saturation in the autumn of 2003 and the drop in water saturation in the spring 2005.

The drainage flow simulated with MACRO 5.1 did not quit match the measured drainage flow (Figure 40C). As with the simulations made by use of the earlier versions of MACRO (Kjær *et al*., 2005c, and Barlebo *et al.,* in press.), the simulated peak at the onset of the drainage flow in the monitoring period was less well described. This is probably attributable to the above-mentioned problems with the groundwater table. The drainage runoff season in the latest monitoring period July 2005–June 2006 was very short, like in the period July 2003-June 2004 (Figure 40C) and consequently, the drainage negligible, Table 11. The resultant annual water balance for Faardrup is shown for each monitoring period (July–June) in Table 11. Compared with the previous monitoring years, the hydraulic year July 2005–June 2006 was characterised by having the lowest, measured, annual drainage flow, the lowest annual precipitation. For information about the water balance in previous monitoring periods see Kjær *et al.* (2005c).

Table 11. Annual water balance for Faardrup (mm/year). Precipitation is corrected to the soil surface according to the method of Allerup and Madsen (1979).

	Normal precipitation [1]	Precipitation [2]	Actual evapotranspiration	Measured drainage	Simulated drainage	Groundwater recharge [3]
1.7.99–30.6.00	626	715	572	192	152	-50
1.7.00–30.6.01	626	639	383	50	34	206
1.7.01–30.6.02	626	810	515	197	201	98
1.7.02–30.6.03	626	636	480	49	72	107
1.7.03–30.6.04	626	685	498	36	24	151
1.7.04–30.6.05	626	671	529	131	80	11
1.7.05–30.6.06	626	595	435	28	0	132

[1] *Normal values based on time series for 1961–1990*

[2] *For 1.7.99–30.6.02, measured at the DIAS Flakkebjerg meteorological station located 3 km from the test site (see text)*

[3] *Groundwater recharge is calculated as precipitation - actual evapotranspiration - measured drainage*

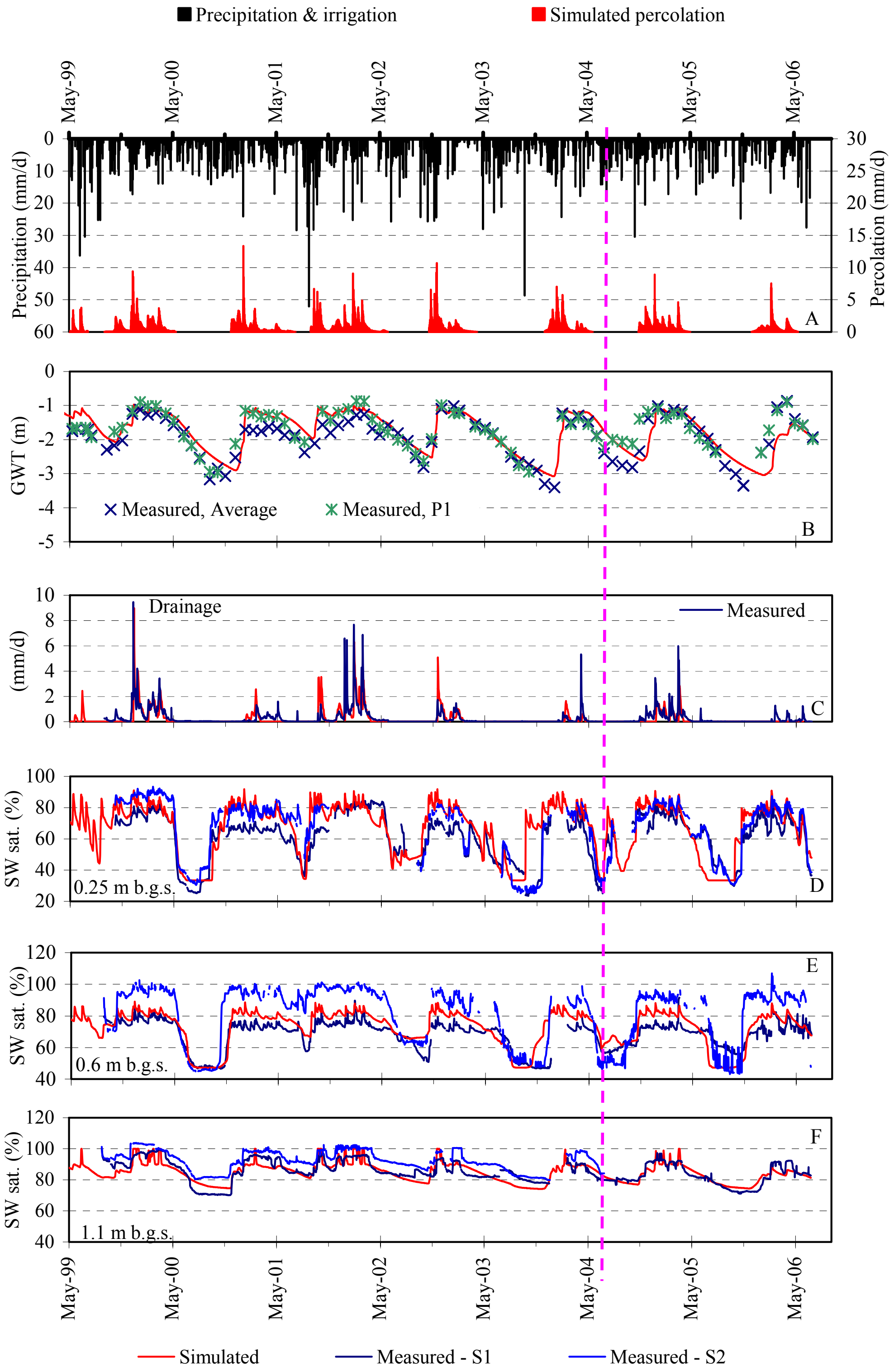


Figure 40. Soil water dynamics at Faardrup: Measured precipitation and simulated percolation 1 m b.g.s. (A), simulated and measured groundwater level GWT (B), simulated and measured drainage flow (C) and simulated and measured soil water saturation (SW sat.) at three different soil depths (D, E, and 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 (Figure 38). The broken vertical line indicates the beginning of the validation period (July 2004-June 2006).

6.2.2 Bromide leaching

The bromide concentration shown in Figure 41 and Figure 42 relate to the bromide applied in May 2000, as described further in Kjær *et al.* 2003, and further evaluated in Rosenbom et al. (in prep).

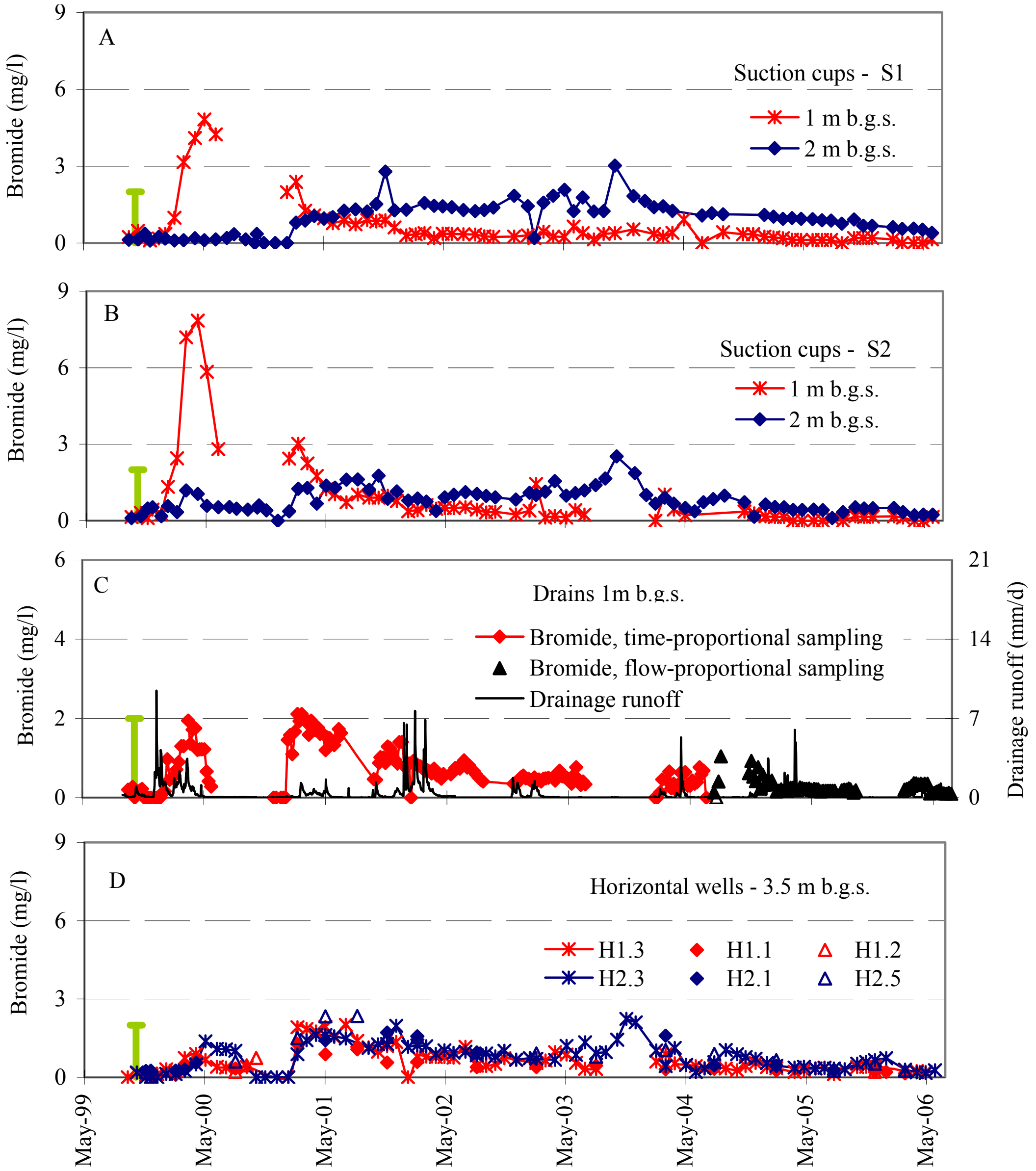


Figure 41. Bromide concentration at Faardrup. A and B refer to suction cups located at S1 and S2. The bromide concentration is also shown for drainage runoff (C) and the horizontal monitoring wells (D). The green vertical line indicates the date of bromide application.

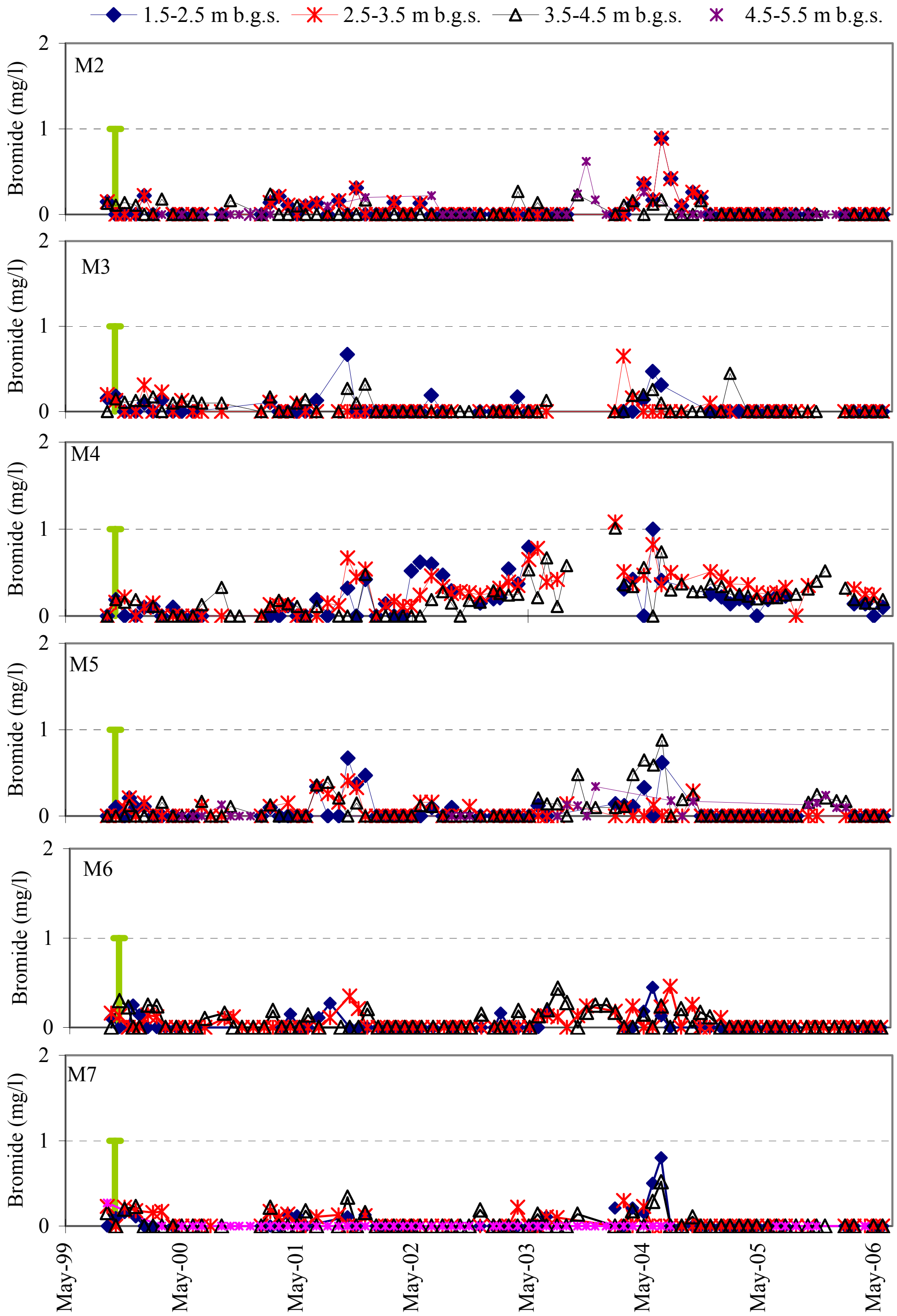


Figure 42. Bromide concentration at Faardrup. The data derive from the vertical monitoring wells (M2–M7). Screen depth is indicated in m b.g.s. The green vertical line indicates the date of bromide application.

6.2.3 Pesticide leaching

Monitoring at Faardrup began in September 1999 and presently encompasses severels pesticides and their degradation products, as indicated in Table 12. Pesticide application during the two most recent growing seasons is shown together with precipitation and simulated precipitation in Figure 43. 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 tribenuronmethyl (applied here as Express) degrades rapidly, the leaching risk is more associated with its degradation product, triazinamin-methyl. For the same reason it is the degradation product and not the parent compound that is monitored in the PLAP (Table 12).

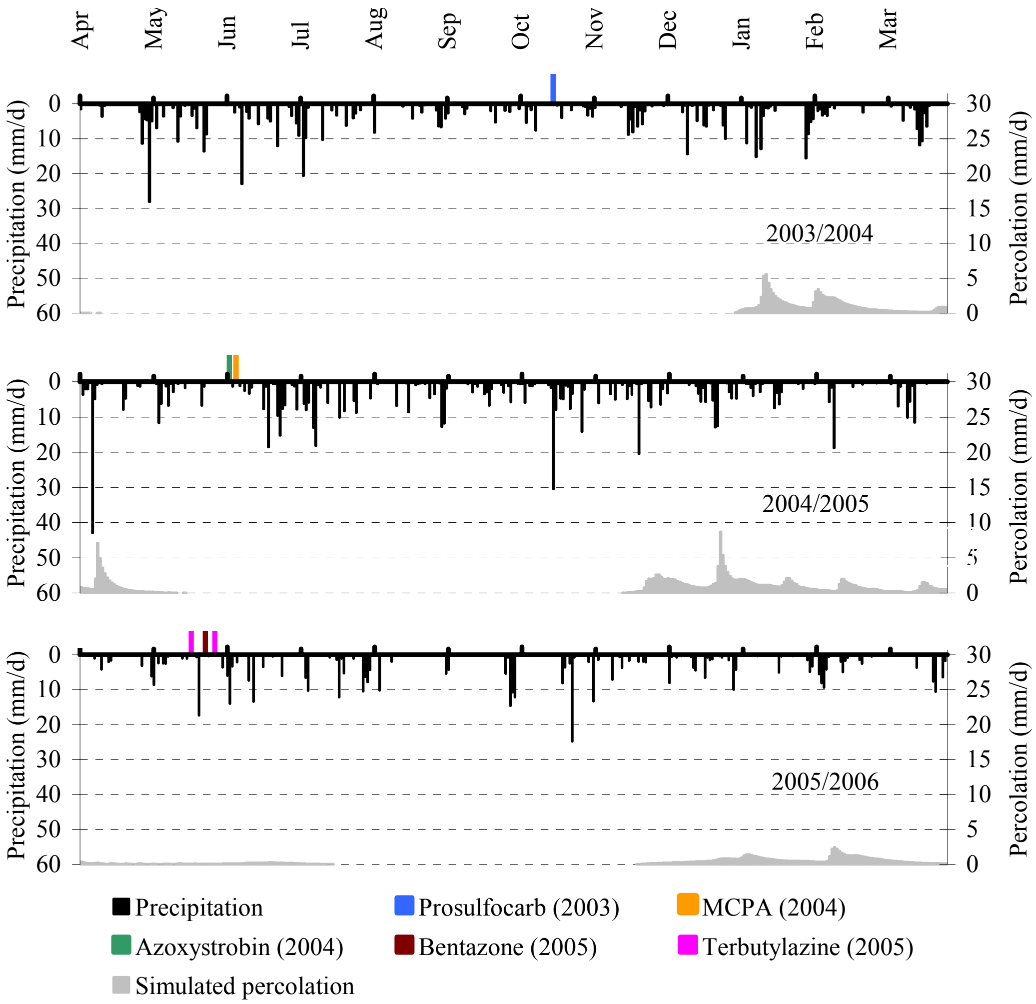


Figure 43. Pesticide application, precipitation (primary axis) together with simulated percolation (secondary axis) at Faardrup in 2003/2004 (upper), 2004/2005 (middle) and 2005/2006 (lower). Pesticides applied later than April 2006 are not included.

Table 12. Pesticides analysed at Faardrup with the product used shown in parentheses. Degradation products are in italics. Precipitation (prec.) and percolation (perc.) are accumulated from the date of first application (app. date) until the end of monitoring. 1st month perc. refers to accumulated percolation within the first month after application. C_{mean} refers to average leachate concentration in the drainage water the first drainage season after application (See Appendix 2 for calculation methods). The number of pesticide-positive samples is indicated in parentheses.

Crop and analysed pesticides	Application date	End of monitoring	Prec. (mm)	Perc. (mm)	1st month perc. (mm)	C_{mean} (µg/L)
Winter wheat 1999						
Glyphosate (Roundup 1999)	Aug 99	Apr 03	2526	947	0	<0.01(8*)
- *AMPA*						<0.01(17*)
Bromoxynil (Briotril)	Oct 99	Apr 02	1738	751	35	<0.01(0)
Ioxynil (Briotril)	Oct 99	Apr 02	1738	751	35	<0.01(2)
Fluroxypyr (Starane 180)	Apr 00	Apr 02	1408	494	7	<0.01(2)
Propiconazole (Tilt Top)	May 00	Jul 03	2151	669	0	<0.01(1*)
Fenpropimorph (Tilt Top)	May 00	Jul 02	1518	491	0	<0.01(1)
- *fenpropimorphic acid*						<0.01(0)
Pirimicarb (Pirimor G)	Jun 00	Jul 03	2066	684	0	<0.01(9*)
- *pirimicarb-desmethyl*						<0.01(9*)
- *pirimicarb-desmethyl-formamido*						<0.02(5*)
Sugar beet 2001						
Glyphosate (Roundup 2000)	Oct 00	Jul 03	1747	709	0	<0.01(8*)
- *AMPA*						0.01(17*)
Metamitron (Goltix WG)	May 01	Jul 03	1512	507	4	0.01(35)
- *metamitron-desamino*						0.01(63)
Ethofumesate (Betanal Optima)	May 01	Jul 03	1512	507	4	0.06(45)
Desmedipham (Betanal Optima)	May 01	Jul 03	1512	507	4	<0.01(0)
- *EHPC*						<0.02(0)
Phenmedipham (Betanal Optima)	May 01	Jul 03	1512	507	4	<0.01(2)
- *MHPC*						<0.02(3)
Fluazifop-P-butyl (Fusilade X-tra)	Jun 01	Jul 03	1460	503	0	<0.01(0)
- *fluazifop (free acid)*						0.02(17)
Pirimicarb (Pirimor G)	Jul 01	Jul 03	1460	503	1	<0.01(9*)
- *pirimicarb-desmethyl*						<0.01(9*)
- *pirimicarb-desmethyl-formamido*						<0.02(5*)
Spring barley 2002						
Flamprop-M-isopropyl (Barnon Plus)	May 02	Jul 04	1337	333	0	<0.01(1)
- *Flamprop-M (free acid)*						<0.01(1)
MCPA (Metaxon)	May 02	Jul 04	1358	337	4	<0.01(2*)
- *4-chlor,2-methylphenol*						<0.02(1*)
- *Triazinamin-methyl* 1) (Express)	May 02	Jul 04	1358	337	4	<0.02(0)
Dimethoate (Perfekthion 500 S)	Jun 02	Jul 04	1328	333	0	<0.01(0)
Propiconazole (Tilt 250 EC)	Jun 02	Jul 04	1328	333	0	<0.01(1*)

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

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

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

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

Table 12 continued. Pesticides analysed at Faardrup with the product used shown in parentheses. Degradation products are in italics. Precipitation (prec.) and percolation (perc.) are accumulated from the date of first application (app. date) until the end of monitoring. 1st month perc. refers to accumulated percolation within the first month after application. C_{mean} refers to average leachate concentration in the drainage water the first drainage season after application (See Appendix 2 for calculation methods). The number of pesticide-positive samples is indicated in parentheses.

Crop and analysed pesticides	Application date	End of monitoring	Prec. (mm)	Perc. (mm)	1st month perc. (mm)	C_{mean} (µg/L)
Winter rape 2003						
Clomazone (Command CS)	Aug 02	Apr 05	1655	543	4	<0.02(1)
-propanamide-clomazone (FMC65317)						<0.02(1)
Winter wheat 2004						
Prosulfocarb (Boxer EC)	Oct 03	Apr 06†	1462	449	0	<0.01 (0)
MCPA (Metaxon)	Jun 04	Jul 06	1274	293	0	<0.01 (2*)
- *4-chlor,2-methylphenol*						<0.01(1*)
Azoxystrobin (Amistar)	Jun 04	Jul 06†	1247	293	0	<0.01 (3)
- *CyPM*						<0.01 (4)
Maize 2005						
Terbutylazine (Inter-Terbutylazin)	May 05	Jul 06†	631	96	0	0.67 (49)
- *desethyl-terbutylazine*						0.59 (51)
- *2-hydroxy-terbutylazine*						0.04 (20)
- *desisopropyl-atrazine*						0.03 (38)
- *2- hydroxy-desethyl-terbutylazine*						0.07 (10)
Bentazone (Laddok TE)	May 05	Jul 06†	612	97	0	2.82 (28)
- *AIBA*						<0.01 (1)

Systematic chemical nomenclature for the analysed pesticides is given in Appendix 1
** Pesticide has been applied twice, and the findings are not necessarily related to one specific application*
† Monitoring will continue during the following year. The values for prec. and perc. are accumulated up to July 2004

The leaching risk of pesticides applied during 2000, 2001 and 2002 has been evaluated in Kjær *et al.* (2003), Kjær *et al.* (2004) and Kjær *et al.* (2005c), respectively.

The leaching risk of pesticides applied in 2003 and 2004 was found to be negligible at Faardrup. Apart from one sample (drainage water sampled on 15 July 2004) containing 0.23 µg/L *MCPA* and 0.24 µg/L *4-chlor,2-methylphenol* and another (drainage water sampled on 23 June 2005) containing 0.012 µg/L MCPA, as well as four drainage water samples containing between 0.02 – 0.06 µg CyPM, none of the applied pesticides or the degradation products listed in Table 12 have yet been detected.

The leaching risk of pesticides applied in 2005 will not be evaluated until the 2007 monitoring results become available, i.e. when two years of monitoring data have been collected. It should be noted, though, that applied compounds did leach from the root zone reaching both drainage system and the groundwater monitoring screens as illustrated in Figure 44, Figure 45 and Figure 46 and Table A6.5 in Appendix 6.

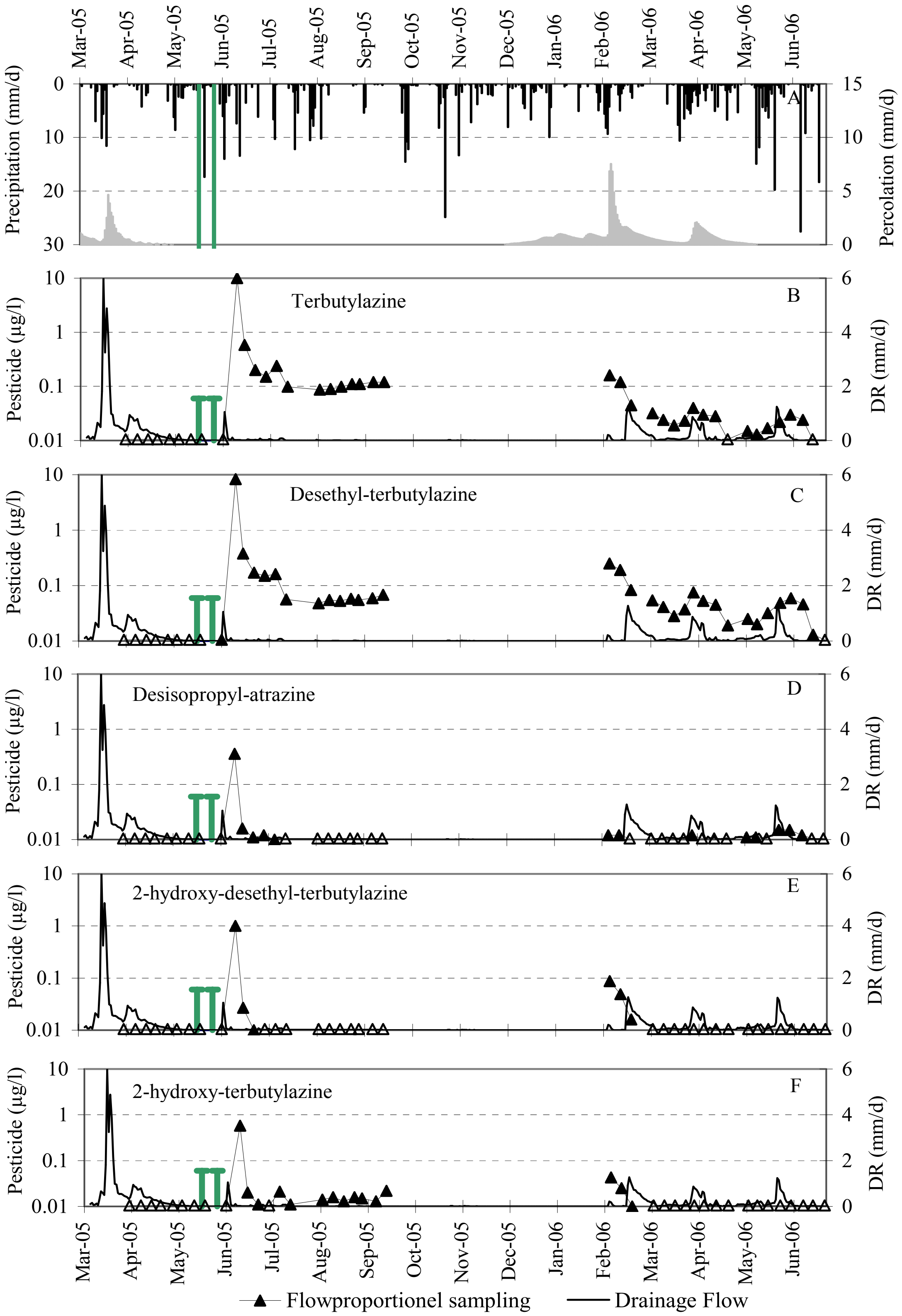


Figure 44. Precipitation and simulated percolation (A) together with concentration of terbutylazine (B), desethyl-terbutylazine (C), 2-hydroxyl-terbutylazine (D), desisopropyl-atrazine (E) and 2-hydroxy-desethyl-terbutylazine (F) in the drainage runoff (DR on secondary axis) at Faardrup in 2005/2006. The green vertical lines indicate the dates of applications. Open triangles indicate values below the detection limit of 0.01 µg/L.

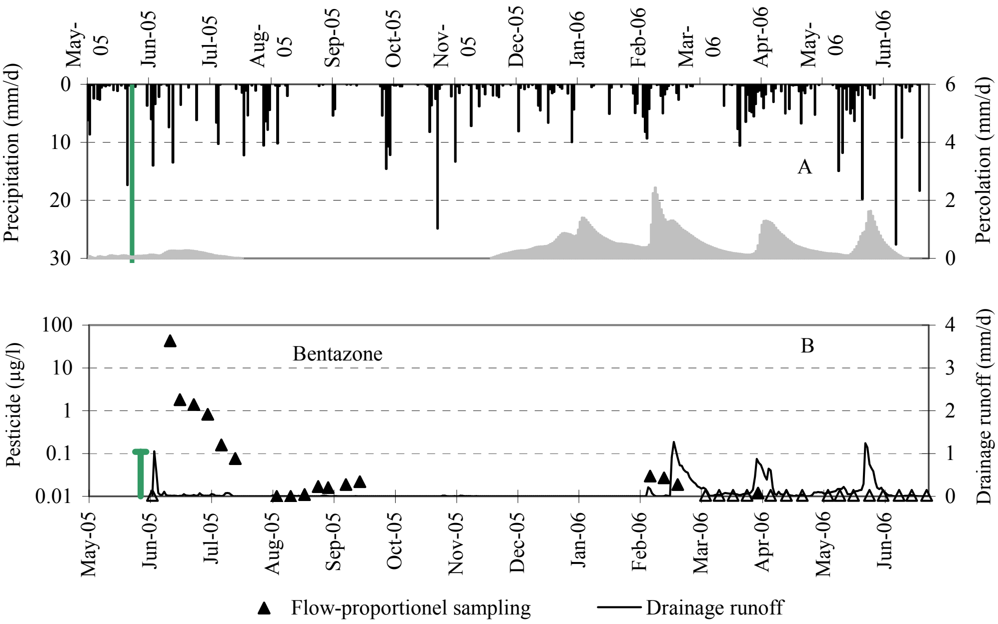


Figure 45. Precipitation and simulated percolation (A) together with concentration of bentazone (B) in the drainage runoff at Faardrup in 2005/2006. The green vertical lines indicate the date of application. Open diamonds indicate values below the detection limit of 0.01 µg/L.

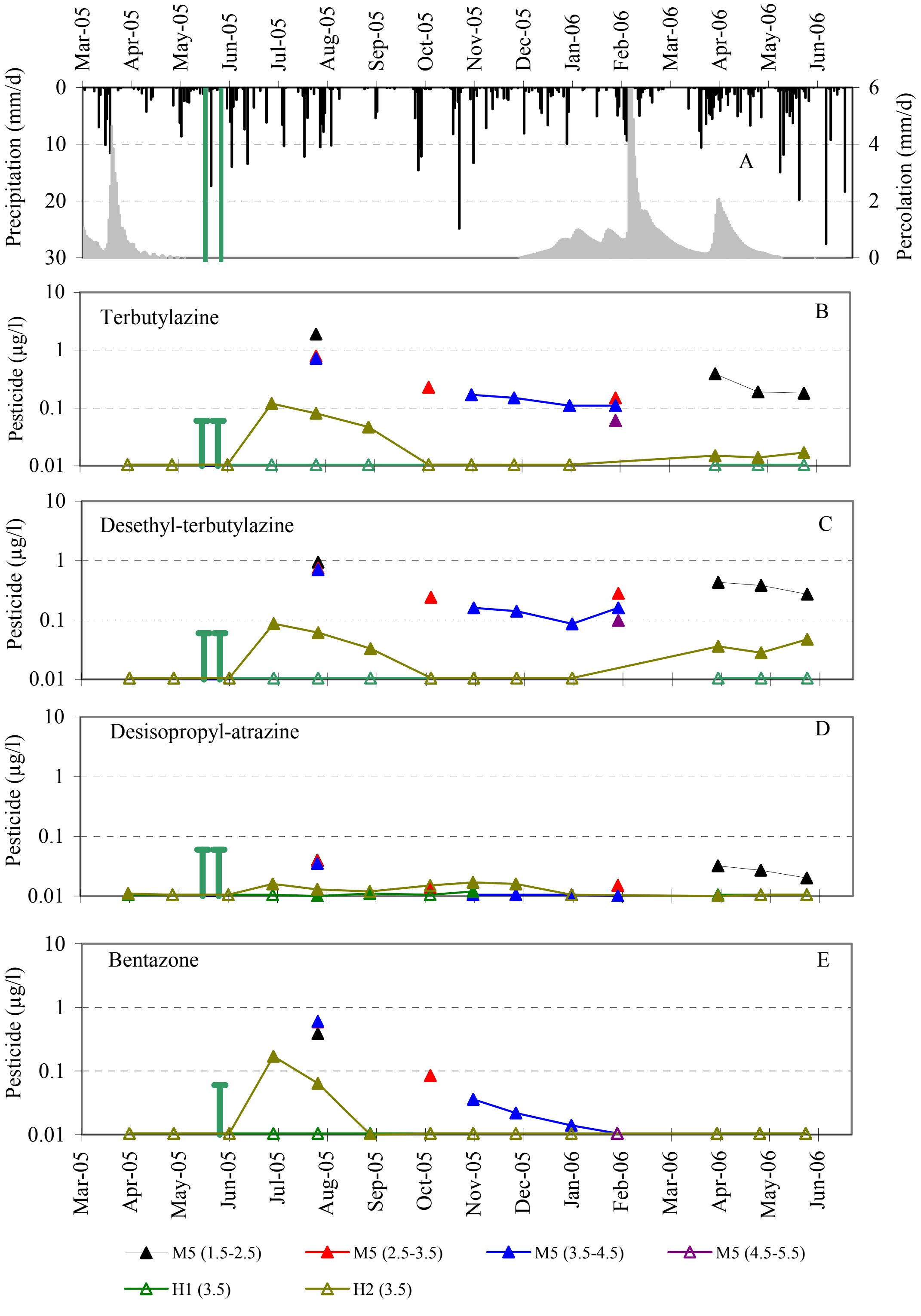


Figure 46. Precipitation and simulated percolation (A) together with concentration of terbutylazine (B), desethyl-terbutylazine (C), 2-hydroxyl-terbutylazine (D) and bentazone in monitoring well M5, H1 and H2 at Faardrup. None of the pesticides were detected in monitoring well M4 (monitored monthly), M2 and M6 (the latter two monitored monthly). The green vertical lines indicate the dates of applications, numbers in parentheses screen depth and open triangles values below the detection limit of 0.01 µg/L.

7 Pesticide analysis quality assurance

Reliable results and scientifically valid methods of analysis are essential for the integrity of the present monitoring programme. Consequently, the field monitoring work has been supported by intensive quality assurance entailing continuous evaluation of the analyses employed. Two types of sample are used in the quality control – samples with known pesticide composition and concentration are used for *internal monitoring* of the laboratory method, while *external spiked samples* are used to incorporate additional procedures such as sample handling, transport and storage. Pesticide analysis quality assurance (QA) data for the period July 2004–June 2006 are presented below, while those for the preceding monitoring periods are given in Kjær *et al.* (2002, 2003, 2004 and 2005).

7.1 Materials and methods

The pesticide analyses were carried out at commercial laboratories selected on the basis of a competitive tender. Until 1 October 2004 the analysis were done by two different laboratories, which merged into a single laboratory (laboratory 1) from October 2004. Accordingly, the results from the internal and external quality control are evaluated only for laboratory 1, as very few analyses have been performed by the former laboratory (laboratory 2) during the period covered in this report.

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 Nationwide Monitoring and Assessment Programme for the Aquatic and Terrestrial Environments (NOVANA).

7.1.1 Internal QA

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

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

Table 13. Pesticide concentrations in the spike solution and in the high-level and low-level external control samples used in the two monitoring period

Compound and period	Spike solution (mg/l)	High-level control (ng/l)	Low-level control (ng/l)
01.07.04 – 30.06.05			
AMPA	1	117	50
Azoxystrobin	1	117	50
Bentazone	1	117	50
Bromoxynil	1	117	50
Clomazone	1	117	50
Dimethoate	1	117	50
Ethofumesate	1	117	50
Flamprop (free acid)	1	117	50
Flamprop-M-isopropyl	1	117	50
Fluazifop (free acid)	1	117	50
Fluroxypyr	1	117	50
Glyphosate	1	117	50
Ioxynil	1	117	50
MCPA	1	117	50
Metamitron	1	117	50
Pendimethalin	1.3	152	65
Pirimicarb	1.3	152	65
Propiconazole	1	117	50
Prosulfocarb	1	117	50
PPU	1	117	50
Terbutylazine	1	117	50
Desethyl-terbutylazine	1.3	152	65
01.07-05 – 30.06.06			
AMPA	1	117	50
Azoxystrobin	1	117	50
Bentazone	1	117	50
Bromoxynil	1	117	50
CyPM	1	117	50
Ethofumesate	1	117	50
Fluazifop (free acid)	1	117	50
Fluroxypyr	1	117	50
Glyphosate	1	117	50
Ioxynil	1	117	50
MCPA	1	117	50
Metamitron	1	117	50
Pendimethalin	1.3	152	65
Pirimicarb-desmethyl-formamido	1.3	152	65
Prosulfocarb	1	117	50
PPU	1	117	50
Desethyl-terbutylazine	1.3	152	65

7.1.2 External QA

Every fourth month, two external control samples were analysed at the laboratories along with the various water samples from the five test sites. Two stock solutions of different concentrations were prepared from two standard mixtures in ampoules prepared by Dr. Ehrenstorfer, Germany (Table 13). Fresh ampoules were used for each set of low- and high-standard solutions. 150 µl or 350 µl 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 two days before a sampling day. The pesticide concentration in the solution is indicated in Table 13. 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.

7.2 Results and discussion

7.2.1 Internal QA

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

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

Table 14. Internal QA of pesticide analyses carried out in the period 01.07.04 – 30.06.05. Results of the test for normality, one-way analysis of variance (ANOVA), and the estimated values of standard deviations (w: within-day, b: between-day, t: total – see text for details), and number of duplicate samples (n) is given for each pesticide. Degradation products are indicated with 'D' following the compound name. For tests the P value $\alpha=0.05$ was used. Only data for $n\geq3$ are included.

Pesticide/Degradation product		Normal distribution $\alpha=0.05$	Significant S_b between-day contribution ANOVA $\alpha=0.05$	S_w (μg/L)	S_b (μg/L)	S_t (μg/L)	Ratio Sb/Sw	n
AMPA	D			0.006	0.004	0.007	0.58	26
Azoxystrobin		yes	yes	0.002	0.004	0.005	2.02	50
Bentazone		yes	yes	0.003	0.006	0.006	2.38	40
Bromoxynil			yes	0.008	0.017	0.018	2.23	12
4-Chlor-2-methylphenol	D	yes	yes	0.005	0.008	0.009	1.59	56
Clomazone			yes	0.003	0.007	0.008	2.62	41
Desethyl-terbutylazine	D		yes	0.004	0.013	0.014	2.90	36
Desisopropyl-atrazine	D		yes	0.004	0.016	0.016	4.08	31
Dimethoate		yes	yes	0.005	0.009	0.010	1.75	22
Ethofumesate		yes	yes	0.003	0.002	0.004	0.72	36
Flamprop (free acid)	D	yes	yes	0.004	0.012	0.013	2.76	12
Flamprop-M-isopropyl		yes	yes	0.002	0.007	0.007	3.92	12
Fluazifop-P (free acid)	D	yes	yes	0.004	0.006	0.007	1.28	21
Glyphosate		yes		0.005	0.003	0.006	0.53	26
2-hydroxy-desethyl-terbutylazine	D	yes	yes	0.005	0.013	0.014	2.58	32
2-hydroxy-terbutylazine	D	yes	yes	0.008	0.014	0.016	1.83	30
Ioxynil			yes	0.007	0.016	0.018	2.15	12
MCPA			yes	0.008	0.011	0.014	1.39	55
Metamitron		yes	yes	0.004	0.005	0.006	1.43	33
Metribuzin-desamino-diketo	D		yes	0.005	0.008	0.009	1.41	8
Metribuzin-diketo	D			0.012	0.002	0.012	0.14	7
Pendimethalin			yes	0.004	0.009	0.010	2.45	37
Pirimicarb			yes	0.004	0.007	0.008	1.99	50
Pirimicarb-desmethyl-formamido	D		yes	0.009	0.014	0.017	1.48	26
PPU	D	yes	yes	0.005	0.013	0.014	2.53	22
PPU-desamido	D		yes	0.003	0.015	0.015	5.11	24
Propanamid-clomazon	D		yes	0.003	0.006	0.007	2.20	41
Propiconazole			yes	0.004	0.006	0.007	1.41	35
Prosulfocarb			yes	0.007	0.020	0.021	2.88	52
Terbutylazine			yes	0.007	0.005	0.009	0.67	33

As the error associated with the analytical result is likely to be highly dependent on the compound analysed, the QA applied is pesticide-specific. The results of the internal QA statistical analysis for each pesticide are presented Table 14 and Table 15. For reference, estimated S_b values are listed for all pesticides, including those for which the between-day variance is not significantly greater than the within-day variance. ANOVA details and variance estimates are also included, even in the case of pesticides where the requirement for normality is not fulfilled. Such data should obviously be interpreted with caution.

Table 15. Internal QA of pesticide analyses carried out in the period 01.07.05 – 30.06.07. Results of the test for normality, one-way analysis of variance (ANOVA), and the estimated values of standard deviations (w: within-day, b: between-day, t: total – see text for details), and number of duplicate samples (n) is given for each pesticide. Degradation products are indicated with ‘D’ following the compound name. For tests the P value α=0.05 was used. Only data for n≥3 are included.

Pesticide/Degradation product		Normal distribution α=0.05	Significant S_b between-day contribution ANOVA α=0.05	S_w (µg/L)	S_b (µg/L)	S_t (µg/L)	Ratio Sb/Sw	n
Amidosulfuron		yes		0.011	0.007	0.013	0.66	6
AMPA	D	yes	yes	0.003	0.006	0.007	2.20	14
Azoxystrobin		yes	yes	0.002	0.008	0.008	4.75	38
Bentazone		yes	yes	0.002	0.006	0.006	2.30	40
Bromoxynil		yes	yes	0.003	0.004	0.005	1.48	9
4-Chlor-2-methylphenol	D	yes	yes	0.003	0.006	0.007	2.20	36
Clomazone		yes	yes	0.002	0.006	0.006	3.31	21
Clopyralid		yes		0.002	0.003	0.004	1.41	3
Desethyl-terbutylazine	D		yes	0.002	0.013	0.013	8.09	38
Desisopropyl-atrazine	D		yes	0.003	0.013	0.013	4.94	42
Dimethoate		yes	yes	0.002	0.003	0.003	2.06	7
Ethofumesate		yes	yes	0.001	0.007	0.007	5.27	27
Flamprop (free acid)	D	yes	yes	0.004	0.009	0.010	2.09	4
Flamprop-M-isopropyl		yes	yes	0.002	0.004	0.004	2.61	4
Fluazifop-P (free acid)	D	yes	yes	0.006	0.007	0.010	1.14	16
Glyphosate		yes	yes	0.004	0.006	0.008	1.49	14
2-hydroxy-desethyl-terbutylazine	D	yes	yes	0.005	0.006	0.008	1.27	41
2-hydroxy-terbutylazine	D	yes	yes	0.004	0.008	0.009	1.94	42
Ioxynil		yes	yes	0.004	0.005	0.006	1.28	9
MCPA			yes	0.013	0.010	0.016	0.82	36
Metamitron		yes	yes	0.003	0.009	0.009	3.21	23
Metribuzin-desamino-diketo	D	yes	yes	0.003	0.005	0.006	1.59	7
Metribuzin-diketo	D	yes	yes	0.001	0.006	0.006	5.92	7
Pendimethalin			yes	0.002	0.007	0.008	3.16	34
Propanamide-clomazon	D	yes	yes	0.001	0.008	0.008	7.36	21
Pirimicarb		yes	yes	0.002	0.005	0.005	2.59	31
Pirimicarb-desmethyl-formamido	D		yes	0.002	0.022	0.022	11.86	18
PPU	D	yes		0.004	0.008	0.009	2.16	25
PPU-desamido	D	yes	yes	0.007	0.013	0.014	1.91	15
Propiconazole		yes	yes	0.002	0.002	0.003	1.20	7
Propyzamid		yes	yes	0.002	0.005	0.006	2.28	27
Prosulfocarb		yes	yes	0.005	0.008	0.009	1.76	25
Terbutylazine		yes	yes	0.001	0.008	0.008	7.37	37

As a “rule of thumb” the between-day standard deviation should be no more than double the within-day standard deviation. From Table 14 and Table 15 it can be seen that S_b/S_w ratios greater than two were observed for several compounds. Overall, the results indicate that day-to-day variation makes a significant contribution. Among the pesticides or degradation products meeting the normality requirement, the S_b/S_w ratio is highest for terbutylazine, ethofumesate, metribuzin-diketo and propanamide-clomazon. Regarding these compounds, however, very low values of S_w rather than critical values of S_b caused the high ratios, as S_t did not exceed the average value for any of these compounds.

The total standard deviations (S_t) of the various analyses of pesticides and degradation products lie within the range 0.004–0.022 µg/L (only data with $n \geq 3$ are included in the analysis). The overall mean S_t was 0.010 µg/L. Analysing S_t with a *t*-test revealed no significant differences between pesticides and degradation products (*t*-test, equal variances, $\alpha=0.05$). The pesticide and degradation products with the poorest reproducibility were bromoxynil, ioxynil, prosulfocarb, and pirimicarb-desmethyl-formamido. However, only pirimicarb-desmethyl-formamido had poor reproducibility in both years.

7.2.2 External QA

Table 16 provides an overview of the recovery of all externally spiked samples based on one to three observations. Recovery of the spiked samples is generally good (>70%). Exceptions are MCPA, fluroxypyr, pendimethalin, prosulfocarb, CyPM and PPU for which recovery was low at some of the field sites.

As the results for each field site are based on only one to three observations, this should not be interpreted too rigorously. However, the data may indicate possible recovery problems for pesticides at one or several sites.

Recovery of MCPA is generally low. Recoveries are 40 - 70% in more than half of the samples and only few results exceed 80%. Differing from that, a considerable variation is observed for CyPM, fluroxypyr, pendimethalin and prosulfocarb. Recovery of these compounds are low or very low in some samples, whereas it exceeds 100% in other samples. The low recovery cannot be related to specific fields, sampling time, etc.

A possible explanation for the low recovery could be degradation of the spiked compound during transport, storage or analysis. In agreement with this hypothesis, the degradation product PPU-desamido was observed in several samples even though this substance is not included in the spike solution (indicated by asterisks in Table 16). As PPU-desamido was not detected in the blank sample matrix used for spiking, its presence in the spiked samples is likely to derive from the added PPU, the primary degradation product of rimsulfuron degradation. The secondary degradation product PPU-desamido was observed in all the samples spiked with PPU at the high-level, and in a few of the low-level spiked samples. However, the concentration of PPU-desamido in the high-level spiked samples was rather close to the detection limit, which may explain its absence in most of the low-level spiked samples. Since the recovery of PPU was similar in the high- and low-level spiked samples, degradation of PPU probably occurred in the low-level samples as well even if PPU-desamido was not detected. The measured concentration of PPU-desamido corresponds to 14–47% of the added amount of PPU. Consequently, the concentration of PPU detected at Jyndevad and Tylstrup (Figure 7 and Figure 13) may be underestimated to some extent. In the same way, metamitron-desamino was detected in a few samples in concentrations corresponding to 10-20% of the added amount of metamitron.

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

	Tylstrup		Jyndevad		Silstrup		Estrup		Faardrup		Average
	Low	High	Low	High	Low	High	Low	High	Low	High	
01.07.04 – 30.06.05											
AMPA					95	82	83	93			88
Azoxystrobin			102	103	97	100	78	81	102	105	94
Bentazone	96	103	130	111	96	99	104	120	94	94	105
Bromoxynil	82	84	87	86							85
Clomazone									88	97	94
Desethyl-terbutylazine	98	99	114	151	97	117	108	105	98	92	113
Dimethoate	77	91	93	98							89
Ethofumesate							97	97			97
Flamprop (free acid)	79	82									80
Flamprop-M-isopropyl	90	97									93
Fluazifop (free acid)	80	88	88	95							88
Fluroxypyr	83	80	112	111	54	48	71	58			75
Glyphosate					100	98	95	83			93
Ioxynil	74	75	81	78							77
MCPA			58	60	64	71			56	57	61
Metamitron *							96	87			92
Pendimethalin			66	62	64	53					61
Pirimicarb			69	78	88	92	82	84			93
Propiconazole							76	77			76
Prosulfocarb					69	67			84	77	73
PPU *	86	72	109	100							90
Terbutylazine	88	94			105	105	106	103	106	94	102
01.07.05 – 30.06.06											
AMPA					98	86	71	71			76
Azoxystrobin			85	91	85	90	93	84	73	77	85
Bentazone	103	94	102	103	93	91	97	87	86	88	94
Bromoxynil			82	84							83
CyPM			75	80	75	74	85	73	61	76	76
Desethyl-terbutylazine	92	86	106	108	107	108	101	92	94	95	99
Ethofumesate							102	85			93
Fluazifop (free acid)	83	85	77	84							83
Fluroxypyr			101	83	95	91	77	58	110	111	86
Glyphosate					102	79	87	83			86
Ioxynil			74	81							78
MCPA					63	56			80	69	66
Metamitron *							99	81			90
Pendimethalin			73	77			70	69			72
Pirimicarb-desmethyl-formamido			91	92	96	90	95	84			92
PPU *	73	58	161	110							95
Prosulfocarb					91	129			92	94	103

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

Since August 2005 PPU was frequently detected in the upstream well at Jyndevad from which water was collected for the spiked samples. The findings of PPU in this well do originate from the neighbouring field. PPU-desamido was not detected in the sample matrix. A possible background level of PPU at about 0.022 µg/L may explain the high recoveries of PPU in some of the spiked samples from this field compared to recoveries from Tylstrup (see Table 17). The recoveries listed in Table 16 are not corrected for eventual background level, since blank samples were not delivered for analysis parallel with the spiked samples. However, except from PPU at Jyndevad no other contamination is observed in the upstream samples used for spiking. Blank samples will be included in the control sampling set onwards.

In a total of 195 blank samples, one pesticide degradation product was detected in a single sample, thus indicating that in general 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.

During the 2004/2006 monitoring period a total of 9 pesticides and 12 degradation products were detected in samples from the experimental fields, and the external and internal QA data relating to these particular pesticides/degradation products are of special interest. These data (when available) are therefore illustrated in Appendix 9.

Table 17. Recovery of PPU at Tylstrup and Jyndevad. PPU was frequently detected in the blank sample matrix used for spiking at Jyndevad, which may explain the higher recoveries at this site compared to Tylstrup. The secondary degradation product, PPU-desamido, was detected in most of the spiked samples at both sites, but not in the blank samples.

	Tylstrup		**Jyndevad**	
	low	**high**	**low**	**high**
10.11.2004		58		
01.12.2004			106	111
02.02.2005				94
09.02.2005	100	94		
01.06.2005			112	94
08.06.2005	72	62		
02.11.2005			62	63
09.11.2005	76	66		
01.02.2006				111
08.02.2006	62	69		
03.05.2006			260	154
17.05.2006	80	40		

7.3 Summary and concluding remarks

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

- Reproducibility of the pesticide analyses was good, total standard deviation being in the range 0.004-0.022 µg/L.
- No differences in reproducibility were observed between pesticides and degradation products.
- Recovery was generally good (70–125%) in external spiked samples. Low recovery of the pesticides or degradation products MCPA, fluroxypyr, pendimethalin, prosulfocarb, CyPM and PPU was observed at single sites.
- Degradation of the rimsulfuron metabolite PPU was observed in the spiked samples, with detection of the secondary degradation product PPU-desamido in amounts corresponding to 14–47% of the added PPU. Findings of PPU at Tylstrup and Jyndevad (section 2.2.3 and 3.2.3) may thus be underestimated.
- PPU was frequently detected in the blank sample matrix used for spiking at Jyndevad, which may have caused erroneous high recoveries of PPU from this site. Analyses of the blank sample matrix will be included in each control sampling set onwards.
- Contamination of samples was not observed during collection, storage and analysis.

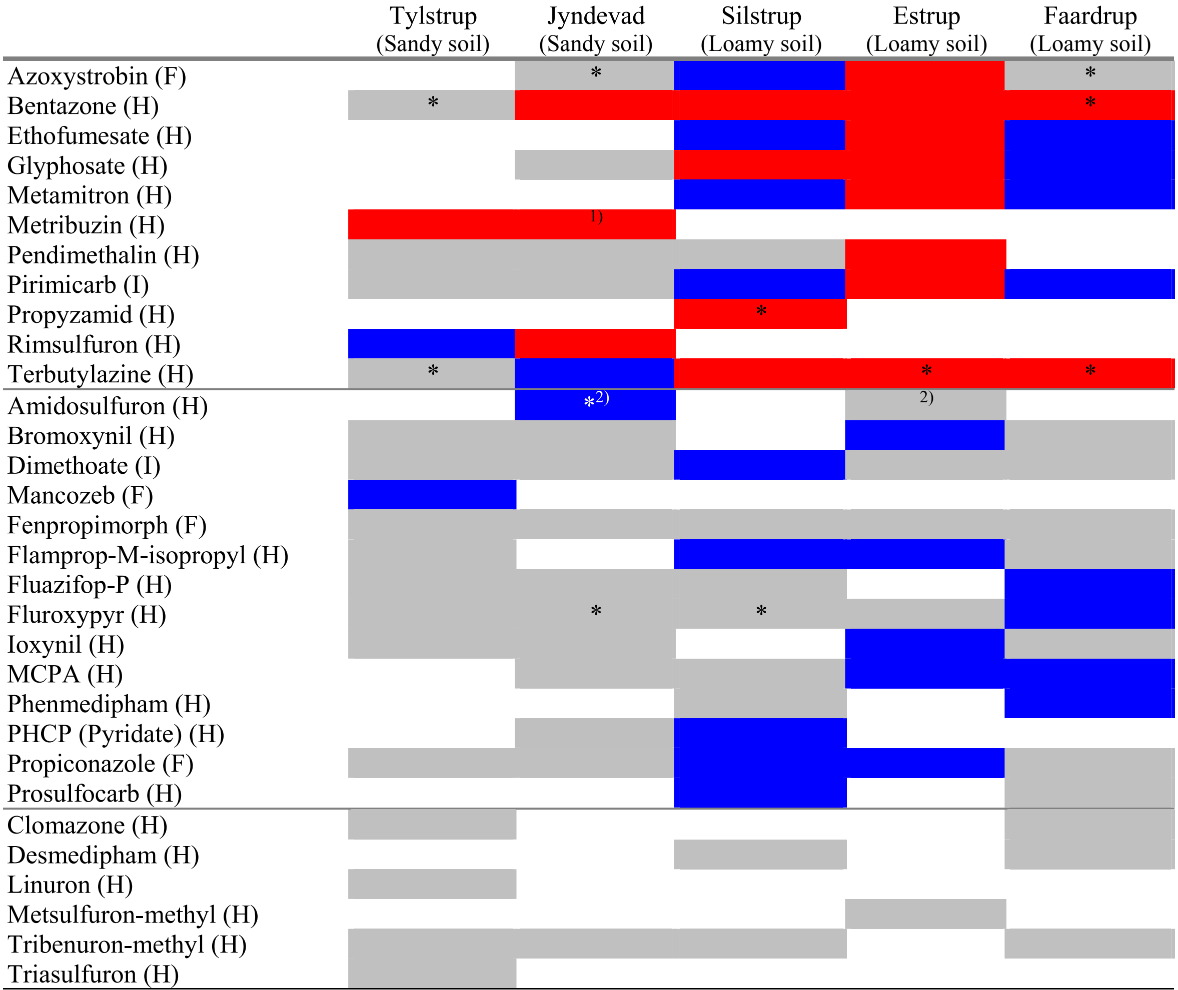
8 Summary of monitoring results

This section summarizes monitoring data from the entire monitoring period, i.e. both data from the three most recent monitoring years (detailed in this report) and data from the previous monitoring years (detailed in previous reports Kjær *et al.,* 2002, 2003, 2004 and 2005c). Pesticide detections in samples from drainage system, suction cups and monitoring wells are detailed in Appendix 6. The monitoring data reveal that the applied pesticides exhibit three different leaching patterns – no leaching, slight leaching and pronounced leaching (see Table 18). Pronounced leaching is here defined as root zone leaching (1 m b.g.s.) exceeding an average concentration of 0.1 µg/L. On sandy and loamy soils, leaching is determined as the weighted average concentration in soil water and drainage water, respectively (See Appendix 2). It should be noted, though, that the present evaluation of the leaching risk of some of these pesticides is still preliminary as their potential leaching period extends beyond the current monitoring period. This applies to those pesticides marked with a single asterisk in Table 18. Eleven of the applied pesticides or their degradation products exhibited pronounced leaching.

- Two degradation products of metribuzin – metribuzin-diketo and metribuzin-desamino-diketo – leached from the root zone (1 m b.g.s.) at average concentrations exceeding 0.1 µg/L at the sandy soil at Tylstrup. Both degradation products appear to be relatively stable and leached for a long period of time. Average concentrations reaching 0.1 µg/L were thus seen as long as three years after application. Evidence was also found that their degradation products might be present in the groundwater several years after application. At both sandy sites (Tylstrup and Jyndevad), previous application of metribuzin has caused marked groundwater contamination with its degradation products (see Kjær *et al.,* 2005b for details).

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

Table 18. Leaching of pesticides or their degradation products at the five PLAP sites. An asterisk indicates pesticides that have been included in the monitoring programme for less than two years. The colours indicate the degree of leaching and the letters H, F and I indicate the type of pesticide: herbicide, fungicide and insecticide respectively. Pesticides applied in spring 2006 are not included in the table.



	Tylstrup (Sandy soil)	Jyndevad (Sandy soil)	Silstrup (Loamy soil)	Estrup (Loamy soil)	Faardrup (Loamy soil)
Azoxystrobin (F)		▨ *	🟦	🟥	▨ *
Bentazone (H)	▨ *	🟥	🟥	🟥	🟥 *
Ethofumesate (H)			🟦	🟥	🟦
Glyphosate (H)		▨	🟥	🟥	🟦
Metamitron (H)			🟦	🟥	🟦
Metribuzin (H)	🟥	🟥 1)			
Pendimethalin (H)	▨	▨	▨	🟥	
Pirimicarb (I)	▨	▨	🟦	🟥	🟦
Propyzamid (H)			🟥 *		
Rimsulfuron (H)	🟦	🟥			
Terbutylazine (H)	▨ *	🟦	🟥	🟥 *	🟥 *
Amidosulfuron (H)		🟦 *2)		▨ 2)	
Bromoxynil (H)	▨	▨		🟦	▨
Dimethoate (I)	▨	▨	🟦	▨	▨
Mancozeb (F)	🟦				
Fenpropimorph (F)	▨	▨	▨	▨	▨
Flamprop-M-isopropyl (H)	▨		🟦	🟦	▨
Fluazifop-P (H)	▨	▨	▨		🟦
Fluroxypyr (H)	▨	▨ *	▨ *	▨	🟦
Ioxynil (H)	▨	▨		🟦	▨
MCPA (H)		▨	▨	🟦	🟦
Phenmedipham (H)			▨		🟦
PHCP (Pyridate) (H)		▨	🟦		
Propiconazole (F)	▨	▨	🟦	🟦	▨
Prosulfocarb (H)			🟦		▨
Clomazone (H)	▨				▨
Desmedipham (H)			▨		▨
Linuron (H)	▨				
Metsulfuron-methyl (H)				▨	
Tribenuron-methyl (H)	▨	▨	▨		▨
Triasulfuron (H)	▨				

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

🟥 Pesticide (or its degradation products) leached through the root zone (1 m b.g.s.) in average concentrations exceeding 0.1 µg/L.

🟦 Pesticide (or its degradation products) was detected in either several (more than three) consecutive samples or in a single sample in concentrations exceeding 0.1 µg/L; average concentration (1 m b.g.s.) below 0.1 µg/L

▨ Pesticide either not detected or only detected in very few samples in concentrations below 0.1 µg/L

Table 19. Number of samples in which the various pesticides were detected at each site with the maximum concentration (µg/L) in parentheses. Degradation products are indicated in italics. The table only encompasses those pesticides/degradation products detected in either several (more than three) consecutive samples or in a single sample in concentrations exceeding 0.1 µg/L. Pesticides applied in spring 2006 are not included.

	Tylstrup	Jyndevad	Silstrup	Estrup	Faardrup
Azoxystrobin		0	6(0.034)	36(0.5)	0
-*CyPM*		0	41(0.34)	60(0.77)	4(0.059)
Bentazone	1(0.012)	25(1.6)	52(6.4)	105(20)	28(43)
- *AIBA*	0	2(0.034)	0	2(0.06)	1(0.057)
Ethofumesate			24(0.227)	35(3.362)	45(12)
Glyphosate		0	71(4.7)	208(31)	8(0.093)
- *AMPA*		3(0.022)	137(0.35)	248(1.6)	17(0.11)
Metamitron			69(0.551)	42(26.369)	35(1.7)
- *metamitron-desamino*			61(0.67)	49(5.549)	63(2.5)
Metribuzin	3(0.024)				
- *metribuzin-desamino-diketo*	312(2.1)	20(1.831)			
- *metribuzin-diketo*	527(0.69)	29(1.372)			
Pendimethalin	0	0	0	37(32)	
Pirimicarb	0	0	17(0.054)	40(0.077)	9(0.056)
- *pirimicarb-desmethyl*	0	1(0.011)	1(0.052)	0	9(0.053)
- *pirimicarb-desmethyl-formamido*	0	0	0	26(0.379)	5(0.076)
Propyzamid			32(1.6)		
- *RH-24644*			17(0.051)		
- *RH-24580*			2(0.016)		
- *RH-24655*			0		
- *PPU*[4]	15(0.11)	44(0.21)			
- *PPU-desamido*[4]	1(0.022)	37(0.092)			
Terbutylazine	0	0	92(1.55)	44(11)	49(10)
- *desethyl-terbutylazine*	2(0.012)	28(0.056)	165(1.08)	45(8.2)	51(8.3)
- *desisopropyl-atrazine*	1(0.024)		35(0.047)*	47(0.44)	38(0.36)
- *2hydroxy- desethyl -terbutylazine*	1(0.016)		29(0.11)*	41(6.3)	10(1)
- *2-hydroxy-terbutylazine*	0		22(0.039)*	41(0.99)	20(0.58)
Amidosulfuron		3(0.11)		0	
Bromoxynil	0	0		3(0.6)	0
Dimethoate	0	0	2(1.417)	0	0
- *ETU*[1]	9(0.038)				
Fenpropimorph	0	2(0.038)	0	1(0.01)	1(0.015)
- *fenpropimorph-acid*	0	0	1(0.019)	0	0
Flamprop-M-isopropyl	0		13(0.109)	20(0.069)	1(0.037)
- *flamprop (free acid)*	0		7(0.096)	13(0.031)	1(0.089)
Fluazifop-P (free acid)[2]	0	0	1(0.072)		17(3.8)
Fluroxypyr	0	0		2(1.4)	1(0.19)
Ioxynil	0	0		20(0.25)	2(0.011)
MCPA		0	0	12(3.894)	2(0.28)
- *4-chlor-2-methylphenol*		0	0	1(0.046)	1(0.24)
Phenmedipham			0		2(0.025)
- *MHPC*			0		3(0.19)
PHCP[3]		0	18(2.69)		
Propiconazole	0	0	6(0.033)	27(0.862)	1(0.035)
Prosulfocarb			6(0.18)		0

1) Degradation product of mancozeb; 2) Degradation product of fluazifop-P-butyl; 3) Degradation product of pyridate; 4) Degradation product of rimsulfuron

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

- The degradation product of terbutylazine – desethylterbutylazine – also leached through the root zone at high average concentrations on loamy soils. The leaching risk at the Estrup and Faardrup sites cannot be fully evaluated until the 2007 monitoring data become available, i.e. when two years of monitoring data have been collated (Table 18). At the three loamy soil sites Silstrup, Estrup and Faardrup, desethylterbutylazine leached from the root zone entering the drainage water at average concentrations exceeding 0.1 µg/L. At the Silstrup and Faardrup sites desethylterbutylazine was frequently detected in the monitoring screen situated beneath the drainage system, concentrations exceeding 0.1 g/l being detected during a 2 and 12 month period, respectively. Leaching at Estrup was confined to the drainage depth, however. Minor leaching of desethylterbutylazine was also seen at the sandy site Jyndevad, where desethylterbutylazine was frequently detected in low concentrations (<0.1 µg/L) in the soil water sampled 1 m b.g.s. Desethylterbutylazine has not been detected in the groundwater monitoring screens located downstream of this site, however (see Kjær *et al.,* 2004 for details).

- The degradation product of rimsulfuron – PPU – leached from the root zone (1 m b.g.s.) in average concentrations reaching 0.10–0.13 µg/L at the sandy soil site at Jyndevad. PPU appeared to be relatively stable and leached for a long period of time. Average concentrations reaching 0.1 µg/L were thus seen as much as three years after application. With an overall transport time of about 4 years PPU also reached the downstream monitoring screens, although in concentrations below 0.1 µg/L. The concentration in both suction cups and monitoring wells was still elevated towards the end of the current monitoring period, thus indicating that leaching of the PPU has not yet ceased. Minor leaching of PPU was also seen at the sandy site Tylstrup, where PPU was detected in low concentrations (0.021 - 0.11 µg/L) in the soil water sampled 1 and 2 m b.g.s., but only in one groundwater sample from a monitoring well (Appendix 6). It should be noted that the concentration of PPU is likely to be underestimated by 14-47%. Results from the field-spiked samples thus indicate that PPU is unstable and may have further degraded to PPU-desamido during subsequent storage and transport.

- Ethofumesate, metamitron and its degradation product metamitron-desamino also leached through the root zone at high average concentrations in one loamy soil. At the loamy site Estrup these compounds leached from the root zone into the drainage water at average concentrations exceeding 0.1 µg/L. Leaching has hitherto been confined to the depth of the drainage system, and the compounds have not been detected in deeper monitoring screens. These compounds also leached from the root zone at the Silstrup and Faardrup sites, reaching both drainage system and groundwater monitoring screens. Average concentrations in drainage water were not as high as at the Estrup site, although concentrations exceeding 0.1 µg/L were observed in both drainage water and groundwater monitoring screens during a 1–4-month period (see Kjær *et al.,* 2002 and Kjær *et al.,* 2004 for details).

- Pirimicarb-desmethyl-formamido (degradation product of pirimicarb) also leached through the root zone at high average concentrations in one loamy soil. At the loamy site Estrup this compound leached from the root zone into the drainage water at average concentrations exceeding 0.1 µg/L. Leaching has hitherto been confined to the depth of the drainage system, and pirimicarb-desmethyl-formamido has not been detected in deeper monitoring screens. Similar high leaching of pirimicarb-desmethyl-formamido has not been observed with any of the previous applications of pirimicarb at the five PLAP sites (Table 18 and Kjær *et al.*, 2004).

- Bentazone leached through the root zone at high average concentrations at the loamy sites. At the Silstrup, Estrup and Faardrup sites bentazone thus leached into the drainage water at average concentrations exceeding 0.1 µg/L. Moreover, bentazone was frequently detected in the monitoring screen situated beneath the drainage system at the Silstrup and Faardrup sites. Apart from a few samples, however, the concentrations detected were all below 0.1 µg/L. At the Estrup site leaching was confined to the depth of the drainage system, and bentazone has rarely been detected in deeper monitoring screens (Appendix 6). On sandy soil bentazone leached at the Jyndevad site but not at the Tylstrup site. At the Jyndevad site, moreover, high concentrations (exceeding 0.1 µg/L) were detected in the soil water samples from suction cups 1 m b.g.s. four months following application. Thereafter leaching decreased and bentazone has not subsequently been detected in the monitoring wells. The leaching risk at the Faardrup and Tylstrup sites cannot be fully evaluated until the 2007 monitoring data become available, i.e. when two years of monitoring data have been collated (Table 18).

- Propyzamid leached from the root zone at the loamy Silstrup site, entering the drainage water at average concentrations exceeding 0.1 µg/L. Propyzamid was also detected in the monitoring screen situated beneath the drainage system. Apart from a few samples the concentrations in the screen were always below 0.1 µg/L, however (Appendix 6). The leaching risk at the Silstrup site cannot be fully evaluated until the 2007 monitoring data become available, i.e. when two years of monitoring data have been collated.

- When applied in late autumn on loamy soil (Estrup site), pendimethalin leached from the root zone and entered the drainage water at average concentrations exceeding 0.1 µg/L. The leaching risk at the Estrup site cannot be fully evaluated until the 2007 monitoring data become available, i.e. when two years of monitoring data have been collated. The preliminary results indicate that leaching at the Estrup site is confined to the depth of the drainage system as pendimethalin is not detected in deeper monitoring screens. Similar high leaching has not been observed with any of the previous three applications made at PLAP sites. Two of these applications were made during spring on sandy soil (Jyndevad site) and loamy soil (Silstrup site) soil, and the third was made during autumn on sandy soil (Tylstrup site). Although the autumn application was followed by much more percolation at the Tylstrup site (109 mm) than at the Estrup site (68 mm), no leaching occurred at the sandy Tylstrup site.

- Azoxystrobin, and in particularly its degradation product CyPM, leached through the root zone at high average concentrations at the loamy sites Silstrup and Estrup. CyPM leached into the drainage water at average concentrations exceeding 0.1 µg/L at both the Silstrup and Estrup sites while azoxystrobin only leached in concentrations exceeding 0.1 µg/L at the Estrup site. Leaching of azoxystrobin and CyPM has hitherto been confined to the depth of the drainage system, and they have rarely been detected in monitoring screens situated below drainage depth. No similar high leaching was detected at either the loamy Faardrup site or the sandy Jyndevad site (Appendix 6).

The monitoring data also indicate leaching of a further 14 pesticides, but not in such high concentrations. Although the concentration exceeded 0.1 µg/L in several samples, the average leaching concentration (1 m b.g.s.) did not. This is summarized in Table 19, which shows the number of samples in which the various pesticides were detected at each site and the maximum concentration. Apart from slight leaching of ETU(Kjær *et al.*, 2002) and amidosulfuron, leaching within this group of pesticides was only observed at the loamy soil sites, where leaching was associated with pronounced macropore transport resulting in very rapid movement of pesticides through the unsaturated zone. It should be noted that the findings regarding amidosulfuron are of very limited use since its degradation products – with which the leaching risk is mainly associated – are not included, as methods for their analysis are not yet available.

Six of the 31 pesticides applied – about 19% – did not leach during the monitoring period. This group includes the three different sulfonylureas – metsulfuronmethyl, triasulfuron and tribenuron methyl – that were applied at several sites. For example, tribenuron methyl was applied at four different sites under different hydrological conditions with percolation (1 m b.g.s.) during the first month after application ranging from 0 to 114 mm. The monitoring results provide no evidence of leaching of any of the applied compounds or their degradation products, including triazinamin and triazinamin-methyl. It should be noted, though, that the leaching risk associated with the late autumn application of tribenuron methyl has not yet been evaluated for the loamy soils.

The difference between the five field sites is further illustrated in Figure 47, which shows the percentage of analysed samples containing one or more pesticides. At the sandy site Tylstrup the predominant pesticides detected were the degradation products of metribuzin (Figure 47A). Excluding these degradation products from the analysis (Tylstrup-II and Jyndevad-II) revealed that very few samples from Tylstrup contained other pesticides (Figure 47B). At Jyndevad the percentage of samples containing pesticides/degradation products was higher due to the incipient leaching of desethylterbutylazine (degradation product of terbutylazine), PPU and PPU-desamido (degradation products of rimsulfuron).

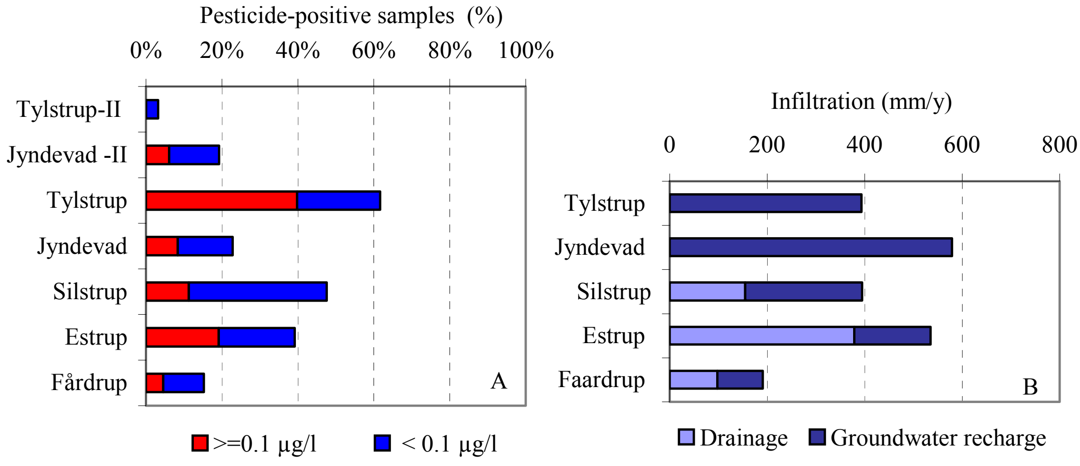


Figure 47. A: Percentage of all analysed samples containing one or more pesticides. In Tylstrup-II and Jyndevad-II, metribuzin-diketo and metribuzin-desamino-diketo have been excluded from the analyses. B: Infiltration apportioned as estimated groundwater recharge and measured drainage runoff (loamy soils).

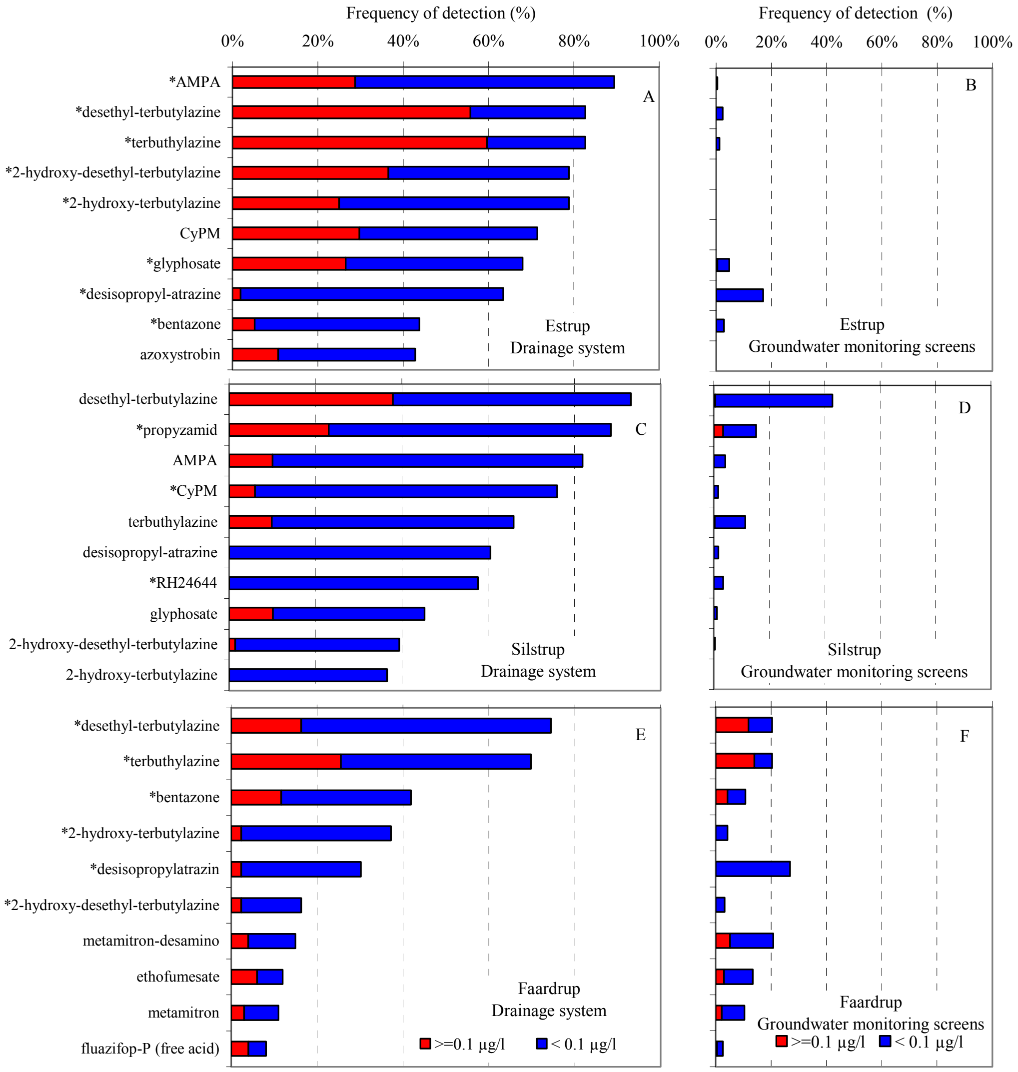


Figure 48. Frequency of detection in samples from the drainage system (left) and groundwater monitoring screens located deeper than the drainage system (right) at the loamy soil sites Silstrup (A, B), Estrup (C, D) and Faardrup (E, F). Frequency is estimated for the entire monitoring period and the time that the different pesticides have been included in the programme and the number of analysed samples thus varies considerably among the different pesticides. The figure only includes the ten most frequently detected pesticides. Pesticides monitored for less than two years are indicated by an asterisk and pesticides monitored for less than one year are not included.

Comparing the loamy sites, the number of samples containing pesticides/degradation products was markedly higher at Silstrup and Estrup than at Faardrup. This is largely attributable to the differences in the hydrological conditions, precipitation and subsequent infiltration being markedly higher at Silstrup and Estrup than at Faardrup (Figure 47B). Moreover, the amount of percolation occurring within the first month after application was generally higher at Silstrup and Estrup than at Faardrup (Table 8, Table 10 and Table 12).

At the loamy sites, several pesticides were frequently detected in the drainage system, whereas the amount of pesticide reaching the monitoring screens situated beneath the drainage system was limited and varied considerably among the three sites (Figure 48). These differences should be seen in relation to the different sampling procedures applied.

The drainage system provides frequent, integrated water samples that continuously capture water infiltrating during the drainage runoff season. On the other hand, the monitoring screens situated beneath the drainage systems were sampled less frequently (monthly basis from a limited number of the monitoring screens; Appendix 2).

Nevertheless, evidence of pesticide leaching was frequently found in selected monitoring screens at the Faardrup site (Kjær *et al.,* 2003) and in particular at the Silstrup site, where the highest concentrations were detected. On the other hand, pesticide leaching at the Estrup site has hitherto mainly been confined to the depth of the drainage system. Apart from 21 samples containing glyphosate, pesticides have only sporadically been detected in monitoring screens located deeper than the drainage system(Appendix 6 and Appendix 8). Again, these differences are largely attributable to the hydrological conditions. Compared to the Silstrup and Faardrup sites the C horizon (situated beneath the drainage depth) at the Estrup site was less permeable with a lower degree of preferential flow occurring through macropores (Section 5.2.3). Water and solute transport may therefore be slower at Estrup, thereby allowing dispersion, dilution, sorption and degradation to reduce the deeper transport.

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Appendix 1. Chemical abstracts nomenclature for the pesticides encompassed by the PLAP

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

Parameter	Systematic chemical nomenclature
AIBA*	2-amino-N-isopropyl-benzamid
AMPA	Amino-methylphosphonic acid
Amidosulfuron	N-[[[[(4,6-dimethoxy-2-pyrimidinyl)amino]carbonyl]-amino]sulfonyl]-N-methylmethanesulfonamide
Azoxystrobin	Methyl (E)-2-{2-[(6-(2-cyanophenoxy)-4-pyrimidin-4-yloxy]phenyl}-3-methoxyacrylate
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
CyPM*	E-2-(2-[6-cyanophenoxy)-pyrimidin-4-yloxy]-phenyl) – 3-methoxyacrylic acid
Desethyl-terbutylazine *	6-chloro-N-(1,1-dimethylethyl)-1,3,5,triazine-2,4-diamine
Desisopropyl-atrazine *	6-chloro-N-ethyl-1,3,5,triazine-2,4-diamine
Desmedipham	Ethyl 3-(phenylcarbamoyloxy)phenylcarbamate
Dimethoate	O,O-dimethyl S-methylcarbamoylmethyl-phosphorodithioate
EHPC*	Ethyl 3-hydroxy-phenylcarbamate
Ethofumesate	(±)-2-ethoxy-2,3-dihydro-3,3-dimethylbenzofuran-5-yl-methanesulfonate
ETU*	Ethylenethiourea
Fenpropimorph	Cis-4-[3-[4-(1,1-dimethylethyl)-phenyl]-2-methylpropyl]-2,6-dimethylmorpholine
Fenpropimorphic acid*	Cis-4-[3-[4-(2-carboxypropyl)-phenyl]-2-methylpropyl]-2,6-dimethylmorpholine
Flamprop (free acid)*	N-benzoyl-N-(3-chloro-4-flourophenyl)-D-alanine
Flamprop-M-isopropyl	Isopropyl N-benzoyl-N-(3-chloro-4-flourophenyl)-D-alaninate
Fluazifop-P-butyl	Butyl (R)-2-[4-(5-trifuoromethyl-2-pyridyloxy)phenoxy]propionate
Fluazifop-P (free acid)*	(R)-2-[4-(5-trifluoromethyl-2-pyridyloxy)phenoxy]propanoic acid
Fluroxypyr	(4-amino-3,5-dichloro-6-fluro-2-pyridinyl)oxy]acetic acid
Glyphosate	N-(phosphonomethyl)glycine
2-hydroxy-terbutylazine*	6-hydroxy-N-(1,1-dimethylethyl)-N´-ethyl-1,3,5,triazine-2,4-diamine
2-hydroxy-desethyl-terbutylazine*	6-hydroxy-N-(1,1-dimethylethyl)-1,3,5,triazine-2,4-diamine
Ioxynil	4-hydroxy-3,5-diiodobenzonitrile
Linuron	3-(3,4-dichlorophenyl)-1-methoxy-1-methylurea
MCPA	(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-triazine-5-one
Metribuzin	4-amino-6-tert-butyl-4,5-dihydro-3-methylthio-1,2,4-triazine-5-one
Metribuzin-desamino-diketo*	6-tert-butyl-4,5-dihydro-3-methylthio-1,2,4-triazine-3,5-dione

* Degradation product

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

Parameter	Systematic chemical nomenclature
Metribuzin-desamino	6-(1,1-dimethylethyl)-3-(methylthio)-1,2,4-triazin-5(4H)-one
Metribuzin-diketo*	4-amino-6-tert-butyl-4,5-dihydro-1,2,4-triazine-3,5-dione
Metsulfuron-methyl	Methyl2-[[[[(4-methoxy-6-methyl-1,3,5-triazine-2-yl)amino]=carbonyl]amino]-sulfonyl]benzoic acid
MHPC*	Methyl-N-(3-hydoxyphenyl)-carbamate
Pendimethalin	N-(1-ethyl)-2,6-dinitro-3,4-xynile
Phenmedipham	3-[(methoxycarbonyl)amino]phenyl (3-methylphenyl)carbamate
PHCP*	3-phenyl-4-hydroxy-6-chloropyridazine
Pirimicarb	2-(dimethylamino)-5,6-dimethyl-4-pyrimidinyldimethylcarbamate
Pirimicarb-desmethyl*	2-(dimethylamino)-5,6-dimethyl-4-pyrimidinylmethylcarbamate
Pirimicarb-desmethyl-formamido*	2-methylformamido-5,6-dimethylpyrimidine-4-yl dimethylcarbamate
PPU*	N-(4,6-dimethoxy-2-pyrimidinyl-N-((3-ethylsulfonyl)-2-pyridinyl)urea (IN70941)
PPU-desamido*	N-((3-(ethylsulfonyl)-2-pyridyl)-4,6 dimethoxy-2 pyrimidinamine (IN70942)
Propanamide-clomazone*	(N-[2- chlorophenol)methyl] -3-hydroxy-2,2- dimethyl propanamide
Propiconazole	1-[[2-(2,4-dichlorophenyl)-4-propyl-1,3-dioxolan-2-yl]methyl]-1H-1,2,4-triazole
Propyzamid	3,5-dichloro-N-(1,1-dimethylprop-2-ynyl)benzamide
Prosulfocarb	N-[[3-(4-methoxy-6-methyl-1,3,5-triazin-2-yl)-3-[2-(3,3,3,-trifluro=propyl)phenylsulfonyl]urea
Rimsulfuron	N-[[(4,6-dimethoxy-2-pyrimidinyl)amino]carbonyl]-3-(ethylsulfonyl)-2-pyridinesulfonamide
RH-24580*	N-(1,1-dimethylacetonyl)-3,5-dichlorobenzamide
RH-24644*	2-(3,5-dichlorophenyl)-4,4-dimethyl-5-methylene-oxalzoline
RH-24655*	3,5-dichloro-N-(1,1-dimethylpropenyl)benzamide
Terbutylazine	6-chloro-N-(1,1-dimethylethyl)-N-ethyl-1,3,5,triazine-2,4-diamine
Triasulfuron	1-[2-(2-chloroethoxy)phenylsulfonyl]-2-(4-methoxy-6-methyl-1,3,5-triazine-2-yl)-urea
Triazinamin	4-methoxy-6-methyl-1,3,5-triazine-2-amin
Triazinamin-methyl*	1,3,5-triazine-2-2-amine 4-methoxy-N, 6-dimethyl

* Degradation product

From each of the PLAP sites, samples were collected of groundwater, drainage water and soil water in the unsaturated zone. A full description of the monitoring design and sampling procedure is provided in Lindhardt *et al.* (2001) and Kjaer *et al.* 2003 respectively.

Until March 2002, pesticide analysis was performed monthly on water samples from the suction cups located both 1 m b.g.s. and 2 m b.g.s., from two screens of the horizontal monitoring wells and from two of the downstream vertical monitoring wells. In addition, more intensive monitoring encompassing all four groups of suction cups, six screens of the horizontal monitoring wells and five monitoring wells was performed every fourth month (Kjær *et al.*, 2002). At the loamy sites, the pesticide analysis was also performed on drainage water samples. The monitoring programme was revised in March 2002 and the number of pesticide analyses was reduced. At the loamy sites, pesticide analysis of water sampled from the suction cups was ceased, and the monthly monitoring was restricted to just one monitoring well. At Jyndevad, pesticide analysis of the suction cups located 2 m b.g.s. was ceased and the interval for the intensive monitoring encompassing the larger number of monitoring screens was extended to six months except for the suction cups 2 m b.g.s. at Tylstrup, where the four-month interval was retained (Kjær *et al.*, 2003).

Until July 2004, pesticide analyses were performed weekly on water sampled time proportionally from the drainage system. Moreover, during storm event additional samples (sampled flow proportional during 1 – 2 days) were also analysed for pesticides. In June 2004 the drainage monitoring programme was revised. From July 2004 and onwards pesticide analysis were done weekly on water sampled flowproportional from the drainage water system. See Kjaer *et al.* 2003 for further details on the methods of flowproportional sampling. The weighted average concentration of pesticides in the drainage water was calculated according to the following equation:

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

$$M_i = C_i \cdot V_i$$

where:
n = Number of weeks within the period of continuous drainage runoff
V_i = Weekly accumulated drainage runoff (mm/week)
C_i = Pesticide concentration collected by means of the flow-proportional sampler (µg/L)

Until July 2004 where both time and flowproportional sampling was applied the numbers were:

$$M_i = Ct_i \cdot V_i \quad \textit{If no flow event occurs within the i'te week}$$

$$M_i = Cf_i \cdot Vf_i \quad \textit{If a flow event occurs within the i'te week and if } Cf_i \cdot Vf_i > Ct_i \cdot V_i$$

where:
n = Number of weeks within the period of continuous drainage runoff
V_i = Weekly accumulated drainage runoff (mm/week)
Vf_i = Drainage runoff accumulated during a “flow event” (mm/storm event)

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

At the sandy soils the weighted average concentration of pesticides being leached to the suction cups situated 1 m b.g.s. was estimated using the measured pesticide concentration and estimated percolation on a monthly basis. Pesticide concentrations measured in suction cups S1 and S2 were assumed to be representative for each sample period. Moreover, accumulated percolation rates deriving from the MACRO model were assumed to be representative for both suction cup S1 and suction cup S2. For each of the measured concentrations, the corresponding percolation (Perc.) was estimated according to the equation:

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

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.

Table A3.1 Management practice at Tylstrup during the 2003 to 2005 growing seasons. The active ingredients of the various pesticides are indicated in parentheses.

Date	Management practice
27.07.02	Winter rape harvested (seed yield 25.9 hkg/ha; 91% dry matter)
12.08.02	Disk harrowed – 6 cm depth
19.09.02	Winter wheat sown – cultivare Solist
09.10.02	Herbicide – 3.0 l/ha Boxer EC (prosulfocarb) + 1.0 l/ha Oxitril (ioxynil + bromoxynil)
17.03.03	Tracer application – 30 kg/ha potassium bromide
17.03.03	Fertilization – 61.1 kg N/ha, 8.7 kg P/ha and 29.1 kg K/ha
08.05.03	Herbicide – 0.8 l/ha Starane 180 (fluroxypyr)
13.05.03	Fertilization – 76.4 kg N/ha, 10.9 kg P/ha and 36.4 kg K/ha
15.05.03	Herbicide – 3.0 l/ha Barnon Plus (flamprop-m-isopropyl)
28.05.03	Fungicide – 0.25 l/ha Tilt 250 EC (propiconazole)
17.06.03	Fungicide – 0.25 l/ha Tilt 250 EC (propiconazole)
24.06.03	Irrigation – 23 mm/ha
08.07.03	Insecticide – 0.6 l/ha Perfekthion 500 S (dimethoate)
20.08.03	Winter wheat harvested (grain yield 54.5 hkg/ha, 85% dry matter. Straw yield 35.0 hkg/ha, 100% dry matter)
17.09.03	Stubble harrowed – 10 cm depth
29.10.03	Ploughed – 20 cm depth
22.04.03	Fertilization – 183.8 kg N/ha
24.04.04	Fertilization – 23.4 kg P/ha, 154.3 kg K/ha
27.04.04	Seed bed preparation – 12-15 cm depth
29.04.04	Potatoes planted – cultivare Kuras
30.04.04	Ridging
13.05.04	Herbicide – 2.0 l/ha Fenix (aclonifen)
27.05.04	Herbicide – 0.75 l/ha Fusilade X-tra (fluazifop-P-butyl)
03.06.04	Herbicide – 30 g/ha Titus (rimsulfuron)
17.06.04	Herbicide – 0.75 l/ha Fusilade X-tra (fluazifop-P-butyl)
22.06.04-07.07.04	Three Fungicide applications – each comprising 0.3 l/ha Shirlan (fluazinam)
07.07.04	Insecticide – 0.2 l/ha IT-Cypermethrin (pyrethroid)
14.07.04-16.09.04	Nine Fungicide applications – each comprising 0.3 l/ha Shirlan (fluazinam)
09.08.04	Irrigation – 28 mm/ha
16.08.04	Irrigation – 29 mm/ha
05.10.04	Potatoes harvested (Tuber yield 119.9hkg/ha, 100% dry matter, 512 hkg/ha)
01.04.05	Rotary cultivated – 8 cm depth
05.04.05	Liming – 4.8 t/ha
07.04.05	Ploughed – 20 cm depth
20.04.05	Seed bed preparation – 4 cm depth
26.04.05	Fertilization – 130.4 kg N/ha, 16.5 kg P/ha, 60.8 kg K/ha and 119.0 kg K/ha
26.04.05	Seed bed preparation – 7 cm depth
28.04.05	Fertilization – 30.5 kg N/ha, 15.3 kg P/ha
28.04.05	Maize Sown – cultivare Vernal
18.05.05	Herbicide – 1.36 l/ha Inter-Terbutylazin (terbutylazine)
08.06.05	Herbicide – 2.5 l/ha Laddok TE (bentazone + terbutylazine)
13.07.05	Irrigation – 38 mm/ha
10.10.05	Maize harvested (harvest yield 137.75 hkg/ha, 100% dry matter, Left on field 18.9 hkg/ha in stubble)

Table A3.2 Management practice at Jyndevad during the 2003 to 2005 growing seasons. The active ingredients of the various pesticides are indicated in parentheses.

Date	Management practice
24.09.02	Potatoes harvested (tuber yield 515.8 hkg/ha; 23.0% dry matter)
01.10.02	Stubble harrowed – 12 cm depth
12.03.03	Tracer application – 30.0 kg/ha potassium bromide
07.04.03	Ploughed – 20 cm depth (furrow packed)
08.04.03	Fertilization – 128 kg N/ha, 19 kg P/ha and 64 kg K/ha
09.04.03	Spring barley sown – cultivare Otira
06.05.03	Herbicide – 0.020 kg/ha Ally (metsulfuron-methyl)
03.06.03	Herbicide – 2.0 l/ha Metaxon (MCPA)
06.06.03	Fungicide – 0.25 l/ha Tilt 250 EC (propiconazole)
07.06.03	Irrigation – 26 mm/ha
25.06.03	Insecticide – 0.6 l/ha Perfekthion 500 S (dimethoate)
25.06.03	Fungicide – 0.25 l/ha Tilt 250 EC (propiconazole)
04.08.03	Spring barley harvested (seed yield 73.3 hkg/ha; 85% dry matter. Straw yield 26.5 hkg/ha; 100% dry matter)
09.12.03	Ploughed – 20 cm depth
25.03.04	Fertilization – 18 kg P/ha, and 92 kg K/ha
29.03.04	Peas sown – cultivare Algarve
05.05.04	Herbicide – 1.0 l/ha Basagran (bentazone)
05.05.04	Herbicide – 1.5 l/ha Stomp (pendimethalin)
01.06.04	Irrigation – 27 mm/ha
03.06.04	Herbicide – 1.0 l/ha Fusilade X-tra (fluazifop-P-butyl)
03.06.04	Herbicide – 0.25 kg/ha Pirimor (pirimicarb)
09.08.04	Peas harvested (seed yield 42.9 hkg/ha; 86% dry matter. Straw yield 24.0 hkg/ha; 100% dry matter)
24.09.04	Winter wheat sown – cultivare Biscay
19.10.04	Herbicide – 1.0 l/ha Oxitril CM (ioxynil + bromoxynil)
30.03.05	Fertilization – 12 kg P/ha, and 63 kg K/ha
31.03.05	Fertilization – 89 kg N/ha
15.04.05	Herbicide – 20 g/ha Gratil 75 WG (amidosulfuron)
26.04.05	Fertilization – 58 kg N/ha
03.05.05	Herbicide – 1.0 l/ha Starane (fluroxypyr)
18.05.05	Herbicide – 1.0 l/ha Amistar (azoxystrobin)
31.05.05	Irrigation – 33 mm/ha
10.06.05	Fungicide – 0.5 l/ha Bumper (propiconazole)
23.06.05	Irrigation – 27 mm/ha
30.06.05	Irrigation – 27 mm/ha
13.07.05	Irrigation – 30 mm/ha
19.08.05	Winter wheat harvested (grain yield 57.5 hkg/ha, 85% dry matter. Straw yield 34.0 hkg/ha, 100% dry matter)

Table A3.3 Management practice at Silstrup during the 2003 to 2005 growing seasons. The active ingredients of the various pesticides are indicated in parentheses.

Date	Management practice
23.09.02	Maize harvested (total yield 134.3 hkg/ha; 100% dry matter. Left on field 27.5 hkg/ha in stubble)
08.10.02	Stubble harrowed – 5 cm depth
11.11.02	Ploughed – 24 cm depth
07.04.03	Fertilization – 8.7 kg P/ha and 45.4 kg K/ha
07.04.03	Seedbed preparation – 3 cm depth
14.04.03	Peas sowing – cultivare Attica
17.05.03	Herbicide – 1.0 l/ha Basagran 480 (bentazone) + 1.5 l/ha Stomp SC (pendimethalin)
10.08.03	Peas harvested (seed yield 39.8 hkg/ha; 86% dry matter. Straw yield 30.0 hkg/ha; 100% dry matter)
15.09.03	Herbicide – 4.0 l/ha Roundup Bio (glyphosate)
26.09.03	Ploughed
26.09.03	Winter wheat sown – cultivare Deben
29.10.03	Herbicide – 4.0 l/ha Boxer EC (prosulfocarb)
31.03.04	Fertilization – 67.0 kg N/ha, 8.5 kg P/ha and 37.4 K kg/ha
10.05.04	Fertilization – 100.1 N, 12.6 P and 55.9 K kg/ha
12.05.04	Herbicide – 2.0 l/ha Metaxon (MCPA)
14.06.04	Fungicide – 1.0 l/ha Amistar (azoxystrobin)
20.07.04	Insecticide – 0.25 kg/ha Pirimor G (pirimicarb)
23.08.04	Winter wheat harvested (grain yield 97.6 hkg/ha 85% dry matter, straw yield 40.8 hkg/ha 100% dry matter)
11.11.04	Ploughed – 24 cm depth
19.04.05	Seedbed preparation – 4 cm depth
23.04.05	Pig slurry application – 30.2 t/ha: 168.5 Total-N (97.5 NH4-N), 54.4 kg P/ha, 68.0 kg K/ha
24.04.05	Spring barley sown – cultivare Cabaret
25.04.05	Fertilization – 20.4 kg N/ha, 2.6 kg P/ha and 9.5 K kg/ha
27.07.05	Herbicide – 0.7 l/ha Starane (fluroxypyr)
30.06.05	Fungicide – 1.0 l/ha Amistar (azoxystrobin)
14.07.05	Insecticide – 0.25 kg/ha Pirimor G (pirimicarb)
22.08.05	Spring barley harvested (seed yield 71.4 hkg/ha; 85% dry matter. Straw yield 29.5 hkg/ha; 100% dry matter)
29.08.05	Pig slurry application – 15.8 t/ha: 69.2 Total-N, 10.1 kg P/ha, 36.3 kg K/ha
29.08.05	Ploughed – 23 cm depth
30.08.05	Harrowed and packed – 2 cm depth
31.08.05	Harrowed across – 3 cm depth
01.09.05	Winter rape sown – cultivare Calypso
03.09.05	Herbicide – 0.33 l/ha Command CS (Clomazone)
17.11.05	Herbicide – 1.0 l/ha Kerb 500 SC (Propyzamid)

Table A3.4 Management practice at Estrup during the 2003 to 2005 growing seasons. The active ingredients of the various pesticides are indicated in parentheses.

Date	Management practice
09.08.02	Winter wheat harvested (grain yield 69.4 hkg/ha; 85% dry matter)
19.08.02	Straw removed (straw yield 41.4 hkg/ha; 100% dry matter)
02.09.02	Herbicide – 4.0 l/ha Roundup Bio
14.04.03	Cattle slurry – 60.8 tonnes/ha: 265.7 kg Total-N/ha, 60.2 kg P/ha, 266.3 kg K/ha and 169.0 kg NH_4-N/ha
15.04.03	Ploughed – 20 cm depth
16.04.03	Seedbed preparation – 5 cm depth
16.04.03	Fodder beet sown – cultivare Magnum,
08.05.03, 22.05.03 & 16.06.03	Herbicide – 1.0 l/ha Goltix SC700 + 1.0 l/ha Betanal Optima (metamitron, phenmedipham, desmedipham and ethofumesate)
28.07.03	Insecticide – 0.3 kg/ha Pirimor G (pirimicarb)
22.10.03	Fodder beet harvested (root yield 18.95 t/ha and top yield 3.42 t/ha, 100% dry matter)
26.10.03	Ploughed – depth 20 cm
07.04.04	Seedbed preparation – 10 cm depth
13.04.04	Fertilization – 105.0 kg N/ha, 15.0 kg P/ha and 50.0 K kg/ha
14.04.04	Spring barley sown – cultivare Prestige
11.05.04	Herbicide – 0.7 l/ha Starane (fluroxypyr)
22.06.04	Fungicide – 1.0 l/ha Amistar (azoxystrobin)
29.08.04	Spring barley harvested (seed yield 51.3 hkg/ha; 85% dry matter)
07.09.04	Straw removed (Straw yield 11.9 hkg/ha; 100% dry matter)
18.04.05	Sow slurry application – 53.0 t/ha: 134.1 Total-N (110.2 NH4-N), 84.8 kg P/ha, 28.1 kg K/ha
18.04.05	Ploughed – depth 20 cm
27.04.05	Fertilization – 75.0 K kg/ha
28.04.05	Fertilization – 24.0 N kg/ha
13.05.05	Rotor harrowed – 5 cm depth
13.05.05	Maize Sown – cultivare Tassilo
13.05.05	Fertilization – 30.0 N kg/ha and 15.0 P kg/ha
26.05.05	Herbicide – 1.25 l/ha Inter-Terbutylazin (terbutylazine)
08.06.05	Herbicide – 2.5 l/ha Laddok TE (Bentazone + terbutylazine)
13.10.05	Maize harvested (harvest yield 143.4 hkg/ha, 100% dry matter)
09.11.05	Tracer application – 30 kg/ha potassium bromide
09.11.05	Herbicide – 4.0 l/ha Roundup Bio (glyphosate) and 3.6 l/ha Stomp (pendimethalin)

Table A3.5 Management practice at Faardrup during the 2003 to 2005 growing seasons. The active ingredients of the various pesticides are indicated in parentheses.

Date	Management practice
09.08.02	Spring barley harvested (grain yield 65.6 hkg; 85% dry matter. Straw yield 60.2 hkg/ha; 100% dry matter)
19.08.02	Ploughed – 25 cm depth
20.08.03	Fertilization – 30 N kg/ha
22.08.03	Winter rape sown – cultivare Canberra
23.08.03	Herbicide – 0.33 l/ha Command CS (clomazone)
25.09.02	Herbicide – 1.0 l/ha Matrigon (clopyralid)
24.03.03	Fertilization – 145 kg N/ha, 20 kg P/ha and 53 kg K/ha
24.04.03	Insecticide – 0.5 l/ha Fastac-50 (alpha-cypermethin)
28.07.03	Winter rape harvested (seed yield 28.7 hkg/ha; 9% dry matter. Straw yield 38.9 hkg/ha; 100% dry matter).
12.08.03	Rotary cultivated. Depth 5 cm
19.09.03	Ploughed and packed. Depth 25 cm
19.09.03	Winter wheat sown – cultivare Galicia
17.10.03	Herbicide – 4.0 l/ha Boxer (prosulfocarb)
29.03.04	Fertilization – 70.4 kg N/ha, 9.6 kg P/ha and 25.6 kg K/ha
30.04.04	Fertilization – 83.6 kg N/ha, 11.4 kg P/ha and 30.4 kg K/ha
03.06.04	Herbicide – 2.0 l/ha Metaxon (MCPA)
03.06.04	Fungicide – 1.0 l/ha Amistar (azoxystrobin)
07.09.04	Winter wheat harvested (grain yield 89.3 hkg/ha 85% dry matter. Straw yield 69.3 hkg/ha 100% dry matter)
25.11.04	Ploughed – 25 cm depth
14.04.05	Seedbed preparation – 10 cm depth
18.04.05	Fertilization – 128.7 kg N/ha, 17.5 kg P/ha and 46.8 kg K/ha
25.04.05	Seedbed preparation – 10 cm depth
26.04.05	Maize Sown – cultivare Nescio
18.04.05	Fertilization – 19.7 kg N/ha and 36.8 kg P/ha
17.05.05	Herbicide – 1.25 l/ha Inter-Terbutylazin (terbutylazine)
27.05.05	Herbicide – 2.5 l/ha Laddok TE (Bentazone + terbutylazine)
28.09.05	Maize harvested (harvest yield 160.3 hkg/ha, 100% dry matter, Total N-yield 202.0 kg N/ha.)
30.11.05	Ploughed – 25 cm depth

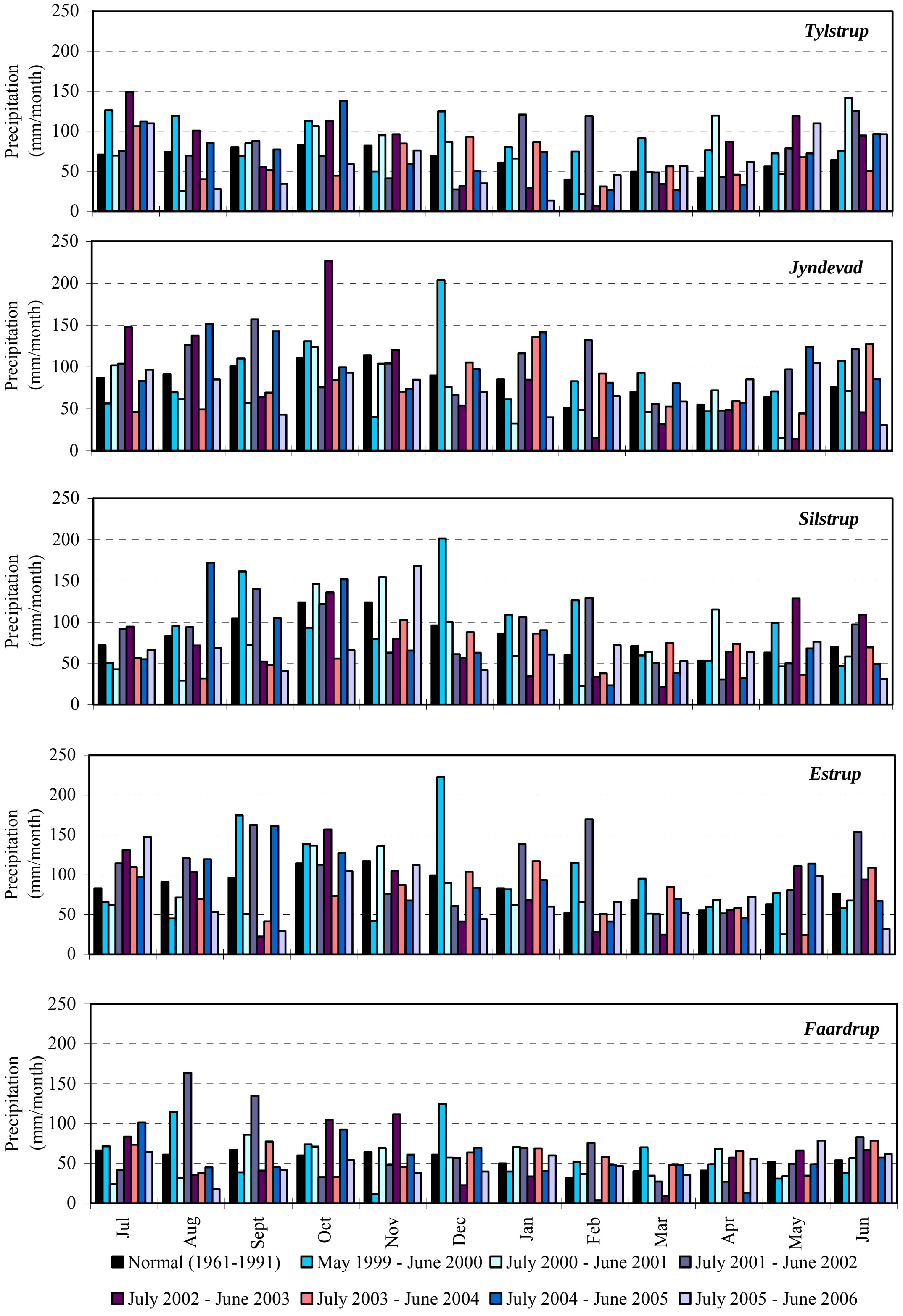

Figure A4.1. Monthly precipitation at all localities for the monitoring period July 2000–June 2006. Normal values (1961–1990) are included for comparison.

Table A5.1. Titus application on the Jyndevad test site and neighbouring upstream fields. The positions of the various fields are indicated in the figure below. The direction of groundwater flow is indicated by a red arrow.

Field-ID	Year of application	Dosage (kg Sencor/ha)
Jyndevad PLAP site	2002	0.03
F2	2004	0.03
F5	2004	0.03
D2	2004	0.03
S4	2004	0.02
N-E	2005	0.033
S1	2005	0.02
S2	2006	0.02

Appendix 6. Pesticide detections in samples from drainage system, suction cups and monitoring screens

Table 6.1 Number of samples where pesticides were either not detected (n.d.), detected in concentration below 0.1 µg/L (det<0.1 µg/L) or detected in concentration above 0.1 µg/L (det>=0.1µg/L) at Tylstrup. Numbers are accumulated for the entire monitoring period, and pesticides monitored for less than one year is not included.

	Vertical screens			Suction cups		
	n.d.	det.<0.1 µg/L	det.>=0.1 µg/L	n.d.	det.<0.1 µg/L	det.>=0.1 µg/L
AIBA	102			40		
2-hydroxy-desethyl-terbutylazine	102			39	1	
2-hydroxy-terbutylazine	102			40		
bentazone	102			39	1	
bromoxynil	192			72		
clomazone	224			82		
desethylterbutylazine	102			38	2	
desisopropylatrazine	102			39	1	
dimethoate	176			63		
epoxiconazole	18			8		
ETU	198	2		37	7	
fenpropimorph	307			89		
fenpropimorph-acid	276			73		
flamprop (free acid)	176			63		
flamprop-M-isopropyl	176			63		
fluazifop-P (free acid)	178			63		
fluroxypyr	194			68		
propanamid-clomazone	208			74		
PPU	177	1		51	13	1
PPU-desamido	178			64	1	
ioxynil	198			72		
linuron	270			67		
metribuzin	386	1		89	2	
metribuzin-desamino	365			85		
metribuzin-desamino-diketo	289	231	5	109	27	51
metribuzin-diketo	71	136	317	41	82	63
pendimethalin	242			70		
pirimicarb	295			82		
pirimicarb-desmethyl	295			81		
pirimicarb-desmethyl-formamido	167			52		
propiconazole	307			89		
terbutylazine	102			40		
triasulfuron	295			82		
triazinamin	285			75		
triazinamin-methyl	259			71		

Table A6.2 Number of samples where pesticides were either not detected (n.d), detected in concentration below 0.1 µg/L (det<0.1 µg/L) or detected in concentration above 0.1 µg/L (det>=0.1µg/L) at Jyndevad. Numbers are accumulated for the entire monitoring period, and pesticides monitored for less than one year is not included.

	Vertical screens			**Suction cups**		
	n.d.	det.<0.1 µg/L	det.>=0.1 µg/L	n.d.	det.<0.1 µg/L	det.>=0.1 µg/L
AIBA	178			45	2	
4-chlor-2-methylphenol	189			52		
amidosulfuron	88			20	2	1
AMPA	221	2		68	1	
azoxystrobin	106			29		
bentazone	190			26	22	3
bromoxynil	151			41		
CyPM	106			29		
desethylterbutylazine	405	24		108	18	
desmethyl-amidosulfuron	88			23		
dimethoate	169			48		
epoxiconazole	18			6		
fenpropimorph	246	1		76	1	
fenpropimorph-acid	259			79		
flamprop (free acid)	12			4		
flamprop-M-isopropyl	12			4		
florasulam	18			6		
florasulam-desmethyl				1		
fluazifop-P (free acid)	190			51		
fluroxypyr	106			29		
glyphosate	223			69		
PPU	317	29		5	41	49
PPU-desamido	344	2		34	57	4
ioxynil	151			41		
MCPA	189			52		
metribuzin	26			6		
metribuzin-desamino	26			4		
metribuzin-desamino-diketo	6	7	13	6		
metribuzin-diketo		7	19	3	3	
pendimethalin	190			51		
PHCP	184			59		
pirimicarb	184			49		
pirimicarb-desmethyl	184			48	1	
pirimicarb-desmethyl-formamido	184			49		
propiconazole	236			75		
pyridate	116			39		
terbutylazine	239			75		
triazinamin-methyl	247			77		

Table A6.3 Number of samples where pesticides were either not detected (n.d), detected in concentration below 0.1 µg/L (det<0.1 µg/L) or detected in concentration above 0.1 µg/L (det>=0.1µg/L) at Silstrup. Numbers are accumulated for the entire monitoring periode, and pesticides monitored for less than one year is not included.

	Drainage			**Horizontal screens**			**Vertical screens**			**Suction cups**		
	n.d.	det <0.1 µg/L	det >=0.1 µg/L	n.d.	det <0.1 µg/L	det >=0.1 µg/L	n.d.	det <0.1 µg/L	det >=0.1 µg/L	n.d.	det <0.1 µg/L	det >=0.1 µg/L
AIBA	64			75			131					
2-hydroxy-desethyl-terbutylazine	43	27	1	85			151	1				
2-hydroxy-terbutylazine	45	26		85			152					
3-aminophenol	53			70			170			36		
4-chlor-2-methylphenol	51			67			124					
AMPA	27	107	15	123	5		227	10		8		
azoxystrobin	44	6		66			121					
bentazone	58	26	5	95	5	1	169	12	3			
clopyralid	6			6			9					
CyPM	12	35	3	66			118	3				
desethylterbutylazine	8	64	44	102	32		113	127	2			
desisopropylatrazine	28	43		85			148	4				
desmedipham	101			107	1		240			58		
dimethoate	81		1	73	1		147			27		
EHPC	68			62			118			20		
ethofumesate	86	14	1	107	1		237	3		54	3	2
fenpropimorph	82			74			148			27		
fenpropimorph-acid	81	1		74			147			27		
flamprop (free acid)	73	7		74			148			26		
flamprop-M-isopropyl	70	11	1	73	1		148			27		
fluazifop-P (free acid)	74			81	1		189			56		
fluroxypyr	27			37			67					
glyphosate	81	52	15	128			233	4		8		
MCPA	51			67			123					
metamitron	76	21	4	99	9		223	15	2	40	9	9
metamitron-desamino	75	23	3	102	3	3	230	9	1	40	15	4
MHPC	100			106			234			55		
pendimethalin	64			74			131					
PHCP	62		4	66	2		109	8	4			
phenmedipham	101			108			240			59		
pirimicarb	137	14		173			358	3		59		
pirimicarb-desmethyl	150	1		173			361			59		
pirimicarb-desmethyl-formamido	118			123			233			20		
propiconazole	76	6		74			148			27		
propyzamid	3	17	6	18	2	1	32	5	1			
prosulfocarb	69	4	1	79	1		147					
RH24580	24	2		21			38					
RH24644	11	15		20	1		37	1				
RH24655	26			21			38					
terbutylazine	31	51	9	108	5		173	30	1			
triazinamin-methyl	82			74			148			27		

Table A6.4 Number of samples where pesticides were either not detected (n.d), detected in concentration below 0.1 µg/L (det<0.1 µg/L) or detected in concentration above 0.1 µg/L (det>=0.1µg/L) at Estrup. Numbers are accumulated for the entire monitoring periode, and pesticides monitored for less than one year is not included.

	Drainage			**Horizontal screens**			**Vertical screens**			**Suction cups**		
	n.d.	det <0.1 µg/L	det >=0.1 µg/L	n.d.	det <0.1 µg/L	det >=0.1 µg/L	n.d.	det <0.1 µg/L	det >=0.1 µg/L	n.d.	det <0.1 µg/L	det >=0.1 µg/L
AIBA	199	1		63	1		215			5		
2-hydroxy-desethyl-terbutylazine	11	22	19	18			64					
2-hydroxy-terbutylazine	11	28	13	18			64					
4-chlor-2-methylphenol	101	1		34			112					
amidosulfuron	98			34			109					
AMPA	29	167	79	95			351	2		23		
azoxystrobin	48	27	9	32			115					
bentazone	118	81	11	63	8		243	1		3	2	2
bromoxynil	135	1	2	41			125			3		
clopyralid	1											
CyPM	24	35	25	32			115					
desethylterbutylazine	9	14	29	16	2		64					
desisopropylatrazine	19	32	1	18			50	14				
dimethoate	88			42			160			23		
ethofumesate	91	27	8	46			158					
fenpropimorph	82	1		39			152			23		
fenpropimorph-acid	82			34			125			17		
flamprop (free acid)	118	13		55			210			23		
flamprop-M-isopropyl	111	20		55			210			23		
florasulam	13			3			9					
florasulam-desmethyl	4			1			3					
fluroxypyr	87	1	2	34			120	1				
glyphosate	88	114	73	92	1		331	18	2	23		
ioxynil	118	14	6	41			125			3		
MCPA	91	9	2	34			111	1				
metamitron	81	27	15	46			158					
metamitron-desamino	76	38	11	46			157					
metsulfuron methyl	130			55			210			22	1	
pendimethalin	119	10	27	51			183			7		
pirimicarb	159	39		67			225	1		6		
pirimicarb-desmethyl	191			66			223			6		
pirimicarb-desmethyl-formamido	198	13	13	76			261			5		
propiconazole	192	22	3	86			311	2		23		
terbutylazine	9	12	31	18			63	1				
triazinamin	125			52			197	1		22		
triazinamin-methyl	1											

Table A6.5 Number of samples where pesticides were either not detected (n.d), detected in concentration below 0.1 µg/L (det<0.1 µg/L) or detected in concentration above 0.1 µg/L (det>=0.1µg/L) at Fårdrup. Numbers are accumulated for the entire monitoring periode, and pesticides monitored for less than one year is not included.

	Drainage			**Horizontal screens**			**Vertical screens**			**Suction cups**		
	n.d.	det <0.1 µg/L	det >=0.1 µg/L	n.d.	det <0.1 µg/L	det >=0.1 µg/L	n.d.	det <0.1 µg/L	det >=0.1 µg/L	n.d.	det <0.1 µg/L	det >=0.1 µg/L
AIBA	42	1		29			64					
2-hydroxy-desethyl-terbutylazine	36	6	1	29			61	3				
2-hydroxy-terbutylazine	27	15	1	29			60	4				
4-chlor-2-methylphenol	144		1	109			254					
AMPA	131	9	1	110			282	2		57	5	
azoxystrobin	73			53			110					
bentazone	25	13	5	26	2	1	57	4	3			
bromoxynil	101			81			226			73		
clomazone	84		1	69			166					
CyPM	69	4		53			110					
desethylterbutylazine	11	25	7	23	6		51	2	11			
desisopropylatrazine	30	12	1	16	13		52	12				
desmedipham	99			66			165			29		
dimethoate	77			58			148					
EHPC	83			52			123			16		
epoxiconazole	12			6			13					
ethofumesate	88	6	6	66			134	24	7	27	2	
fenpropimorph	70			58	1		157			54		
fenpropimorph-acid	70			59			157			54		
flamprop (free acid)	76	1		58			148					
flamprop-M-isopropyl	70	1		56			142					
fluazifop-P (free acid)	91	4	4	66			159	5	1	26	3	
fluazifop-P-butyl	99			66			165			29		
fluroxypyr	86		1	68	1		176			55		
propanamid-clomazone	84		1	69			166					
glyphosate	137	4		109	1		282	2		61	1	
ioxynil	99	1		81			225	1		73		
MCPA	143	1	1	109			255					
metamitron	89	8	3	66			141	19	5	29		
metamitron-desamino	85	11	4	66			117	36	12	29		
MHPC	97	1	1	66			163	1		29		
phenmedipham	99			66			163	2		29		
pirimicarb	113	7		90			244	2		52		
pirimicarb-desmethyl	94	6		66			162	3		29		
pirimicarb-desmethyl-formamido	97	3		66			163	2		29		
propiconazole	147			116			304	1		54		
prosulfocarb	80			61			126					
terbutylazine	13	19	11	23	5	1	51	1	12			
triazinamin-methyl	77			57			147					

Table A7.1 Detection of AMPA, glyphosate and bentazone in groundwater monitoring screens at Silstrup during the period from date of first application until 01.10.05 (AMPA & Glyphosate) and 01.07.06 (bentazone) (µg/L). The location of the monitoring installations is indicated in Figure 15. The pesticides were not found in water sampled from H2 (monitored monthly) and M4, M9, M12 and M13 (monitored half-yearly).

Monitoring well	H1.1^{2}	H1.2^{1}	H1.3^{2}	M5^{1}				M6^{2}			M12^{2}	M13^{2}
Screen depth (m b.g.s.)	3.5	3.5	3.5	1.5–2.5	2.5–3.5	3.5–4.5	4.5–5.5	2.5–3.5	3.5–4.5	1.5–2.5	1.5–2.5	2.5–3.5
AMPA												
06.11.01		<		0.011	0.08	<						
04.12.01		<		<	0.01	<						
08.01.02		0.014		0.012	<	<						
05.02.02		<		<	<	<						
05.03.02		0.01		0.014	<	<						
03.07.02		0.033	0.021									
14.01.03		<	0.011	0.019	<	<					0.012	<
04.02.03		<		0.01	<	<						
03.02.04		<	<	0.021	<	<						
31.03.05		<	<	0.01		<						
Glyphosate												
09.10.01		<	<	<	<	<						
06.11.01		<		0.014	0.031	<						
04.12.01		<	<	<	0.012	<						
03.07.02		<	<	<	<	<					<	0.014
Bentazone												
03.06.03		<		0.056	0.038	<						
01.07.03		0.44		0.37	0.23	0.1						
05.08.03	0.035	0.081	<		0.048	0.099						
02.09.03		0.035			0.01	0.041	0.036					
07.10.03		0.025			<	0.026	0.02					
04.11.03		0.015			<	0.014	<					
06.07.04								<	0.027	<		
06.01.05								<	0.024			

<: Concentration below the detection limit of 0.01 µg/L, ^{1} Monitored monthly, ^{2} Monitored half-yearly

Table A7.2 Detection of desethylterbutylazine in groundwater monitoring screens at Silstrup during the period from 19.05.02 (date of first application) until 01.07.06 (µg/L). The location of the monitoring installations is indicated in Figure 15. Desethylterbutylazine was not found in water sampled from H2 (monitored monthly) and M4, M9, M12 and M13 (monitored half-yearly).

Monitoring well	H1.1^2	H1.2^1	H1.3^2	M5^1				M6^2	M9^2
Screen depth (m b.g.s.)	3.5	3.5	3.5	1.5–2.5	2.5–3.5	3.5–4.5	4.5–5.5	3.5-4.5	1.5–2.5
28.05.02		<		<	<	<			
03.07.02	0.02	0.018	0.016	0.143	0.051	0.011			0.022
05.08.02		0.028		0.131	0.07	0.038			
03.09.02		0.015			0.05	0.045			
02.10.02		<			0.037	0.045	0.011		
29.10.02		0.026		0.062	0.046	0.043			
03.12.02		0.014		0.046	0.04	0.042			
14.01.03	0.012	0.011	0.013	0.075	0.042	0.045			0.019
04.02.03		0.029		0.064	0.048	0.043			
12.03.03		0.014		0.052	0.054	0.044			
01.04.03		0.017		0.067	0.047	0.047			
05.05.03		0.011		0.056	<	0.049			
03.06.03		0.015		0.066	<	0.051			
01.07.03		0.017		0.068	0.048	0.046			
05.08.03	0.012	0.01	0.011		0.044	0.049			0.021
02.09.03		<			0.038	0.048	0.031		
07.10.03		<			0.049	0.056	0.028		
04.11.03		<			0.034	0.043	0.017		
02.12.03		0.012		0.034	0.027	0.044			
07.01.04	0.013	0.011	0.014	0.032	0.026	0.032			0.01
03.02.04		0.011		0.015	0.033	0.026			
02.03.04		0.011		0.029	0.025	0.024			
30.03.04		0.011		0.032	0.024	0.02			
04.05.04		0.011		0.035	0.025	0.026			
02.06.04		0.012		0.045	0.028	0.032			
06.07.04					0.027	0.033	0.02		
03.08.04		0.013				<	<		
02.09.04					0.014	0.02	0.015		
07.10.04				0.021	0.011	0.023			
04.11.04		0.023		0.039	0.034	0.045			
01.12.04		0.01		<	<	0.012			
06.01.05				0.014	0.014	0.016			
08.02.05				0.025	0.021	0.026			
03.03.05		0.012		0.031	0.026	0.033			
31.03.05				0.017	0.018	0.021			
28.04.05				0.02	0.026	0.022			
02.06.05				0.019	0.019	0.019			
30.06.05				0.017	0.02	0.019		0.013	
04.08.05					0.02	0.021	0.019		
01.09.05					0.019	0.018	0.012		
06.10.05						0.016	<		
03.11.05					0.01	0.014	<		
01.12.05				0.015	0.01	0.017			
05.01.06				0.011	0.011	0.016			
02.02.06				<	0.012	0.015			
02.03.06				<	<	0.012			
06.04.06				<	<	0.012			
04.05.06				<	<	0.012			
01.06.06				0.01	<	0.013			

<: Concentration below the detection limit of 0.01 µg/L, ^{1} Monitored monthly, ^{2} Monitored half-yearly

Table A7.3 Detection of terbutylazine in groundwater monitoring screens at Silstrup during the period from 19.05.02 (date of first application) until 01.04.06 (µg/L). The location of the monitoring installations is indicated in Figure 15. Terbutylazine was not found in water sampled from H2 (monitored monthly) and M4, M6, M9, M12 and M13 (monitored half-yearly).

Monitoring well	H1.1^2	H1.2^1	H1.3^2	M5^1				M9^2
Screen depth (m b.g.s.)	3.5	3.5	3.5	1.5–2.5	2.5–3.5	3.5–4.5	4.5–5.5	1.5–2.5
28.05.02		<		<	<	<		
03.07.02	0.014	0.011	0.012	0.124	0.03			0.012
05.08.02		0.011		0.082	0.033			
03.09.02		<			0.022	0.01		
02.10.02		<			0.013	0.011	<	
29.10.02		<		0.025	0.014	<		
03.12.02		<		0.016	0.012	0.011		
14.01.03	<	<	<	0.025	0.011	0.01		<
04.02.03		0.012		0.022	0.014	0.01		
12.03.03		<		0.016	0.013	0.01		
01.04.03		<		0.019	0.01	0.01		
05.05.03		<		0.013	<	<		
03.06.03		<		0.02	0.012	0.012		
01.07.03		<		0.014	<	<		
05.08.03	<	<	<		<	<		<
02.09.03		<			<	<	<	
07.10.03		<			<	<	<	
04.11.03		<			<			
02.12.03		<		<	<	<		
07.01.04	<	<	<	<	<	<		<
03.02.04		<		<	<	<		
02.03.04		<		<	<	<		
30.03.04		<		<	<	<		
04.05.04		<		<	<	<		
02.06.04		<		<	<	<		
06.07.04	<	<	<	<	<	<		
03.08.04		<			<	<		
02.09.04		<		<	<	<		
07.10.04		<		<	<			
04.11.04		<		<	<			
01.12.04		<		<	<			
06.01.05	<	<	<	<	<		<	<
08.02.05		<		<	<			
03.03.05		<		<	<			
31.03.05		<		<	<			
28.04.05		<		<	<			
02.06.05		<		<	<			
30.06.05	<	<	<	<	<		<	<
01.09.05		<		<	<	<		
02.02.06		<		<	<			

<: Concentration below the detection limit of 0.01 µg/L, ^{1} Monitored monthly, ^{2} Monitored half-yearly

Appendix 8. Pesticide detection in monitoring screens at Estrup

Table A8.1 Detection of pesticides in groundwater monitoring screens at Estrup during the period from date of pesticide application until 10.11.06 (µg/L). The location of the monitoring installations is indicated in Figure 26.

Monitoring well		H1.1[1]	H1.2[1]	H1.2[2]	H1.3[1]	M1[2]			M3[2]			M4[3]			M5[1]				M6[2]			
Screen depth (m b.g.s.)		3.5	3.5	3.5	3.5	1.5-2.5	3.5-4.5	4.5-5.5	1.5-2.5	2.5-3.5	3.5-4.5	1.5-.25	2.5-.3.5	3.5-.45	1.5-2.5	2.5-3.5	3.5-4.5	4.5-5.5	1.5-2.5	2.5-3.5	3.5-4.5	4.5-5.5
AIBA	18.09.02		0.026																			
AMPA	07.07.05							0.01													0.057	
Bentazone	11.08.05		0.01									<	0.014	<								
	08.09.05		0.015																			
	10.11.05		0.011																			
	12.01.06	<	<		0.015																	
	09.02.06			0.012																		
	07.03.06			0.014																		
	06.04.06			0.011																		
	10.05.06			0.01																		
desethylterbutylazine	12.01.06	0.016	<		0.01																	
desisopropylatrazine	07.04.05											0.021	<	<								
	12.05.05											0.019	<	<								
	07.07.05											0.024		<								
	11.08.05											0.034	0.011	<								
	10.11.05											0.028	0.011	<								
	08.12.05											0.018	<	<								
	12.01.06											0.017	<	<								
	09.02.06											0.015	<	<								
	07.03.06											0.014	<	<								
	06.04.06											0.014	<	<								
	10.05.06											<		0.019								
	08.06.06											0.019		<								
fluroxypyr	10.11.06											<	<	0.058								
Glyphosate	20.03.02														<	<	0.033					
	16.04.02															<	0.014	0.036				
	18.12.02															<	0.014	0.013				
	22.01.03																			0.015		
	19.02.03															<	0.011	<				
	13.01.04								0.017	<	<	<	<	<	<	<	<					
	07.07.05						0.024	0.67	<	<	0.023	<		<						<	0.59	
	10.11.05		0.015																			
	12.01.06					<	<	<	0.01	0.04	<	0.018	<	<	0.017	0.018	0.011		<	<	0.017	
	09.02.06											<	<	0.023								
MCPA	14.05.02															0.019	<	<	<	<	<	
Pirimicarb	22.01.03					<	0.015	<	<	<	<	<	<	<	<	<	<					
Propiconazol	22.01.03					0.017	0.022	<	<	<	<	<	<	<	<	<	<		<	<	<	
Terbutylazine	07.07.05						0.022	<	<	<	<	<		<		<	<	<		<	<	<
Triazinamin	16.04.02															0.042	<	<				

[1] Monitored monthly; [2] Monitored half-yearly [3]Monitored half-yearly until July 2003 and monthly from July 2003; [3]Monitored monthly until July 2003 and half-yearly from thereon

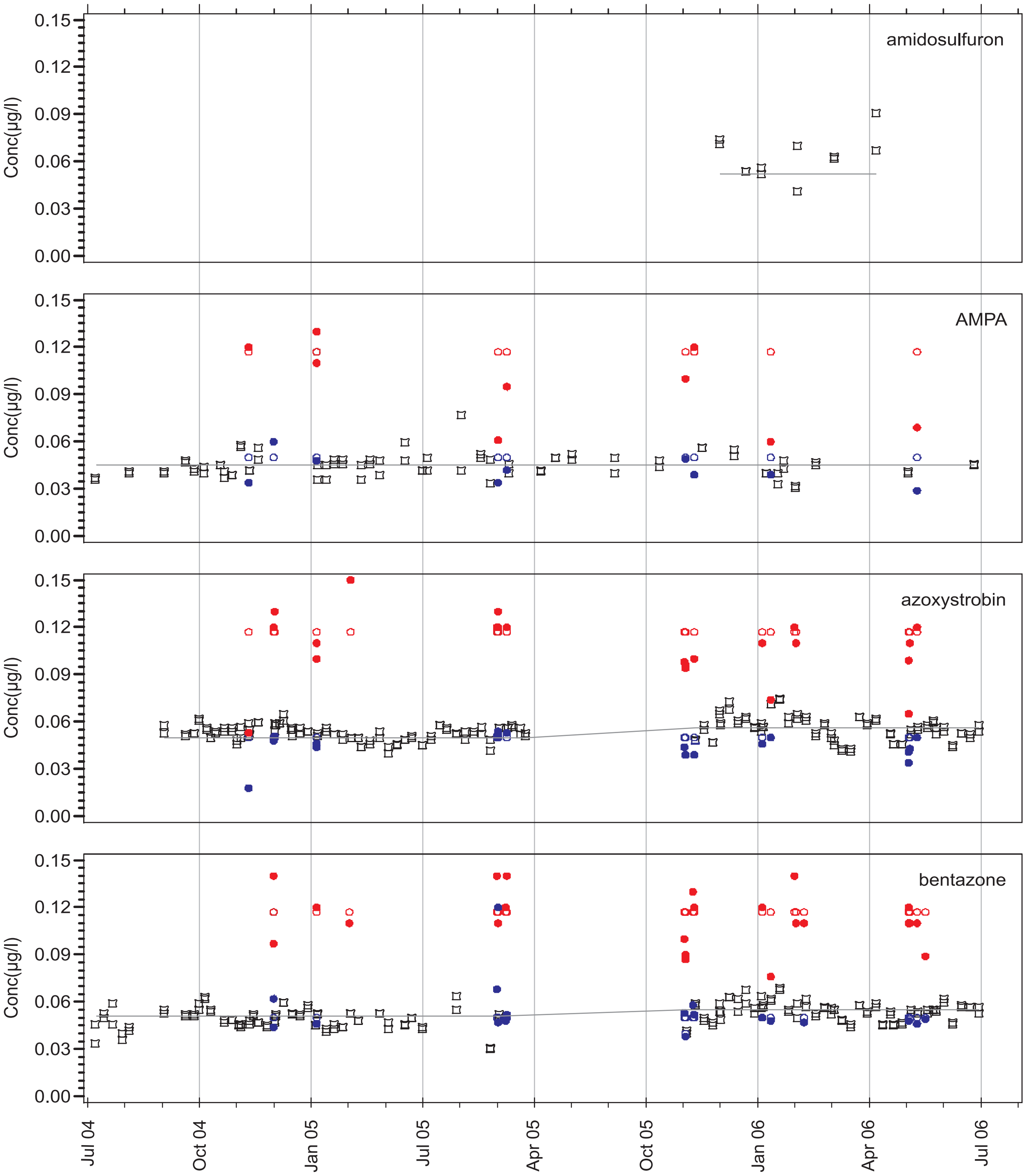

Figure A9.1 Quality control data for pesticide analysis by laboratory 1. Internal laboratory control samples are indicated by square symbols and the nominal level is indicated by the solid grey line (⌑ IQ measured, — IQ nominal concentration). External control samples are indicated by circles. Open circles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

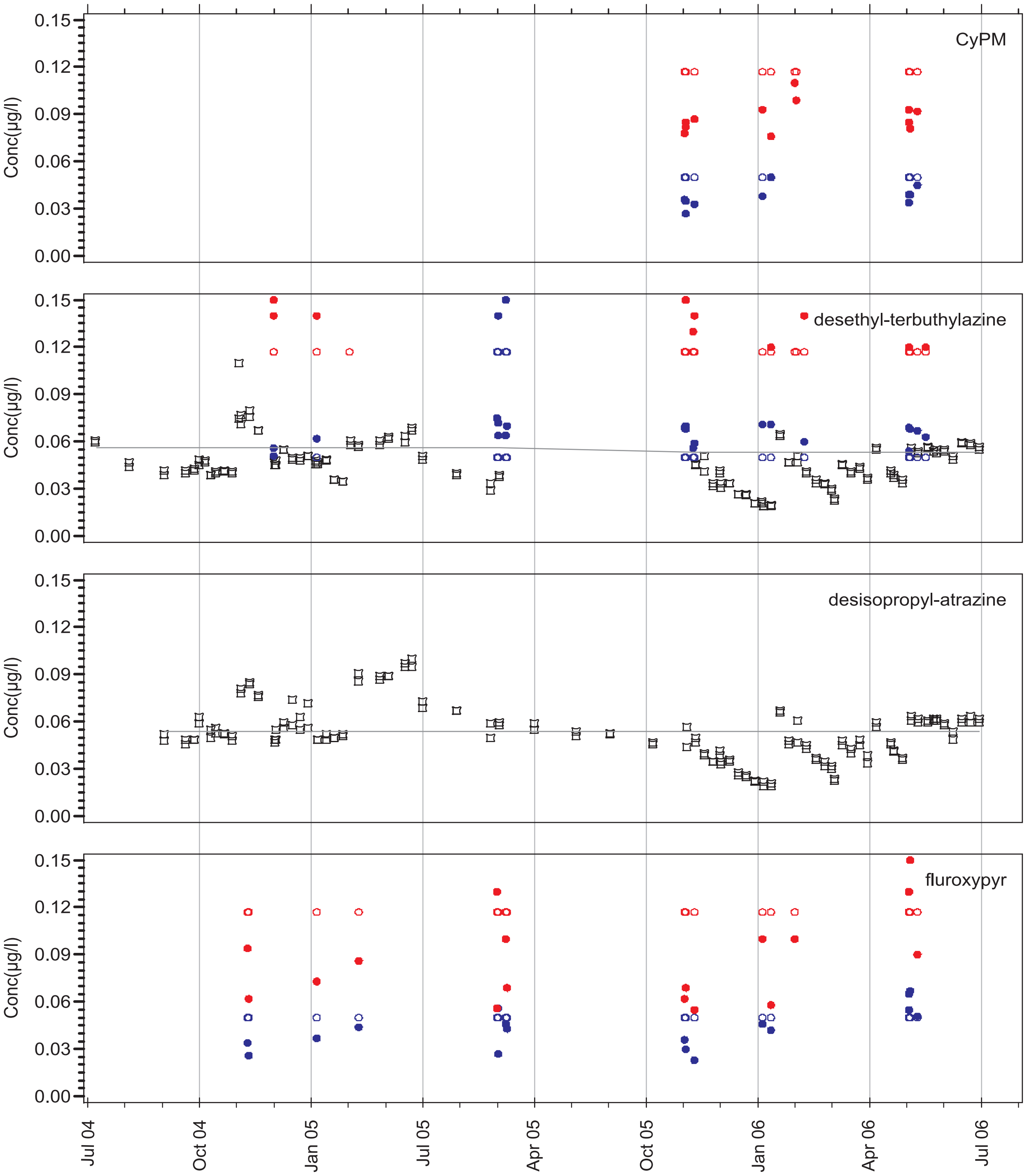

Figure A9.1 (Continued) Quality control data for pesticide analysis by laboratory 1. Internal laboratory control samples are indicated by square symbols and the nominal level is indicated by the solid grey line (⌑ IQ measured, — IQ nominal concentration). External control samples are indicated by circles.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

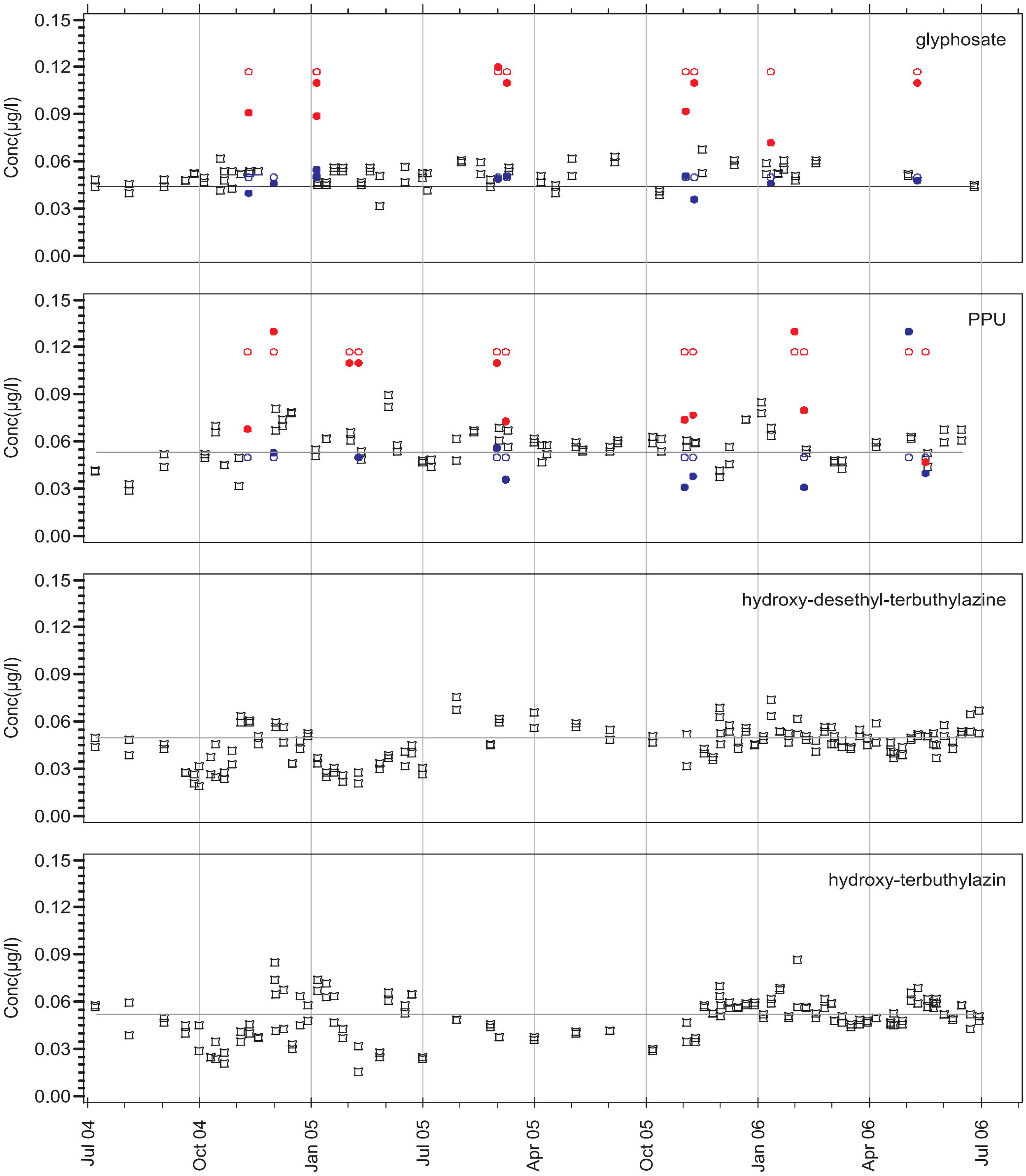

Figure A9.1 (Continued) Quality control data for pesticide analysis by laboratory 1. Internal laboratory control samples are indicated by square symbols and the nominal level is indicated by the solid grey line (⌑ IQ measured, — IQ nominal concentration). External control samples are indicated by circles.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

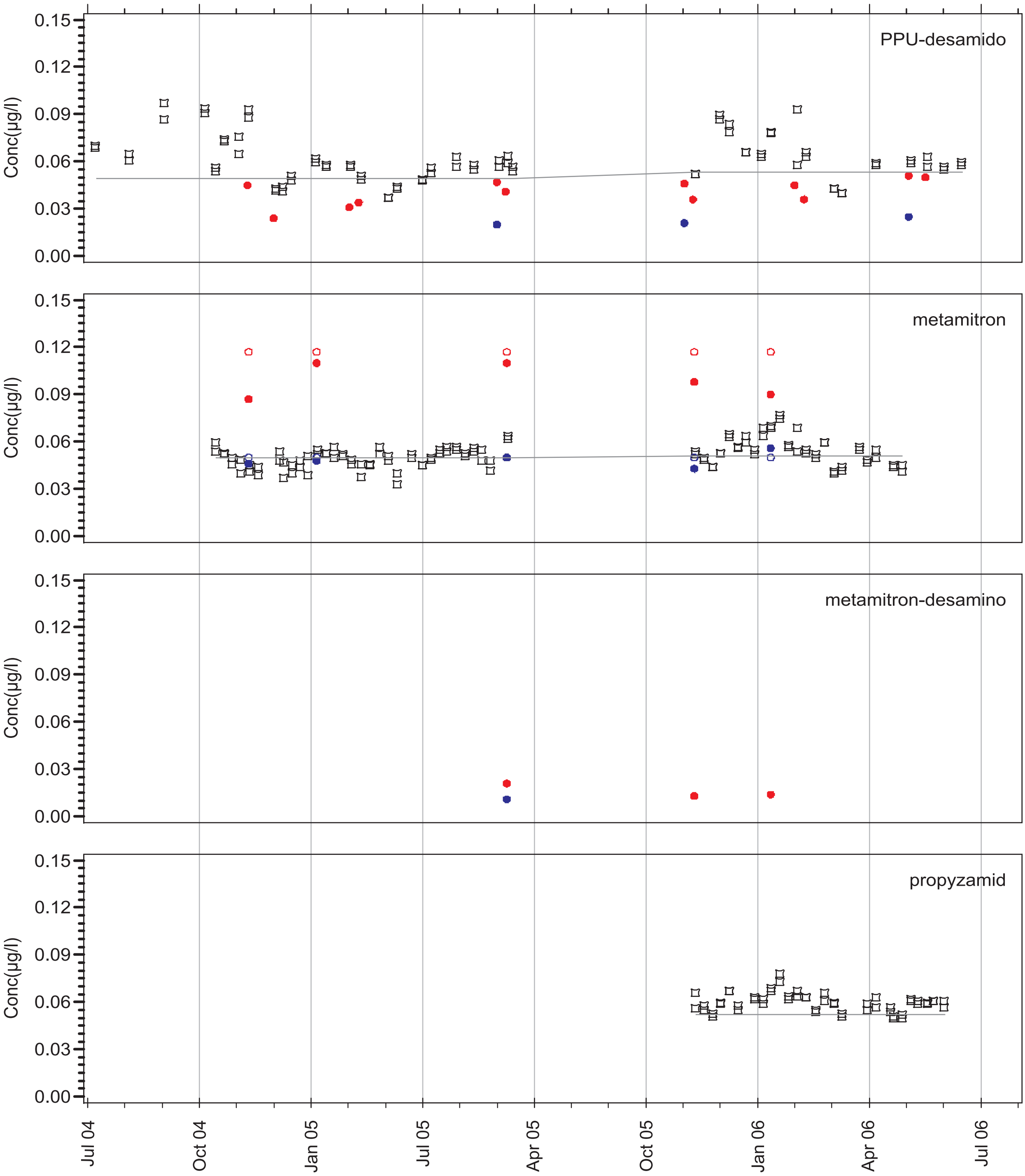

Figure A9.1 (Continued) Quality control data for pesticide analysis by laboratory 1. Internal laboratory control samples are indicated by square symbols and the nominal level is indicated by the solid grey line (⌑ IQ measured, — IQ nominal concentration). External control samples are indicated by circles.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

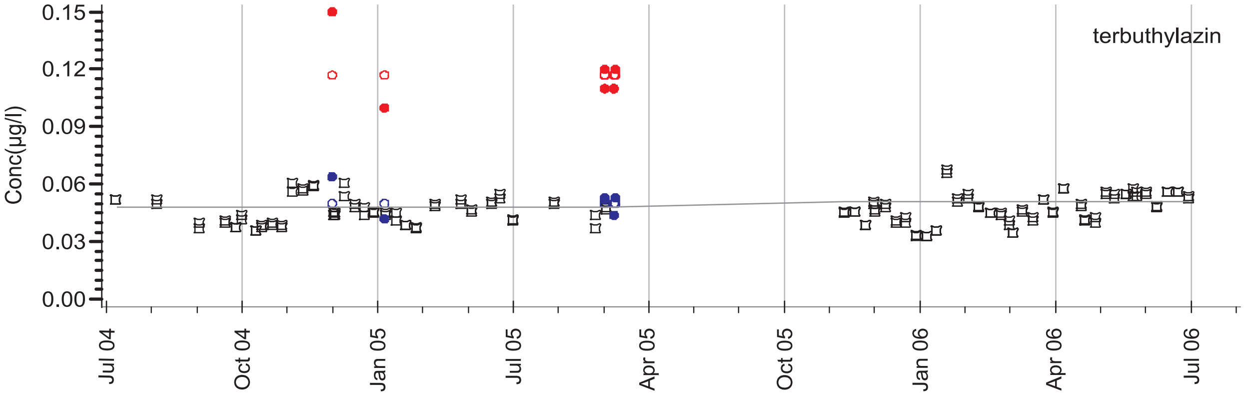

Figure A9.1 (Continued) Quality control data for pesticide analysis by laboratory 1. Internal laboratory control samples are indicated by square symbols and the nominal level is indicated by the solid grey line (⌑ IQ measured, — IQ nominal concentration). External control samples are indicated by circles.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