The Danish Pesticide Leaching Assessment Programme

Monitoring results May 1999–June 2007

Jeanne Kjær, Annette E. Rosenbom, Preben Olsen, René K. Juhler, Finn Plauborg, Ruth Grant, Per Nygaard, Lasse Gudmundsson and Walter Brüsch.

Geological Survey of Denmark and Greenland
Ministry of Climate and Energy

Faculty of Agricultural Sciences
University of Aarhus

National Environmental Research Institute
University of Aarhus

Editor: Jeanne Kjær
Cover photo: Lasse Gudmundsson
Cover: Henrik Klinge Pedersen
Layout and graphic production: Authors
Printed: July 2008
Price: DKK 200

ISBN 978-87-7871-220-2

Available from

Geological Survey of Denmark and Greenland
Øster Voldgade 10, DK-1350 Copenhagen K, Denmark
Phone: +45 38 14 20 00. Fax: +45 38 14 20 50
E-mail: geus@geus.dk
Homepage: www.geus.dk

The report is also available at www.pesticidvarsling.dk

Table of contents

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), Lis Wollesen de Jonge (DJF), Preben Olsen (DJF), Ruth Grant (NERI), Christian Ammitsøe (Danish Environmental Protection Agency) and Steen Marcher (Danish Environmental Protection Agency).

This report presents the results for the period May 1999–June 2007. Results covering part of the period (May 1999–June 2006) have been reported previously (Kjær *et al.*, 2002, Kjær *et al.*, 2003, Kjær *et al.*, 2004, Kjær *et al.*, 2005c and Kjær *et al.*, 2007). The present report should therefore be seen as a continuation of previous reports with the main focus on the leaching risk of pesticides applied during 2005.

The report was prepared jointly by Jeanne Kjær, Walter Brüsch, René K. Juhler, Annette E. 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: Walter Brüsch and Preben Olsen.
- Soil water dynamics and water balances: Annette E. Rosenbom, Finn Plauborg and Ruth Grant .
- Pesticide analysis quality assurance: René K. Juhler.

Jeanne Kjær
June 2008

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 groundwater in unacceptable concentrations. The programme presently evaluates the leaching risk of 36 pesticides applied at five agricultural sites ranging in size from 1.1 to 2.4 ha. The results so far show that:

- Of the 36 pesticides applied, eight (clopyralid, desmedipham, linuron, florasulam metsulfuron-methyl, thiamethoxam, triazinamin-methyl and triasulfuron) did not leach during the current monitoring period.

- The monitoring data indicate pronounced leaching of 10 of the applied pesticides and three of their degradation products. Thus ethofumesate, bentazone, propyzamide, 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 metribuzine, terbutylazine, pirimicarb and rimsulfuron, leached through the root zone to 1 m below ground surface (hereafter m b.g.s.) in average concentrations exceeding 0.1 µg/l. Except for the degradation products of metribuzine, rimsulfuron and terbutylazine, leaching was mainly confined to the depth of 1 m, where pesticides were frequently detected in the samples from suction cups and drainage systems.

- The monitoring data also indicate leaching of an additional 18 pesticides, in low concentrations, however. Thus, although the concentrations exceeded 0.1 µg/l in several samples, the average leaching concentrations at 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).

Pesticides were always applied in 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 covers the period May 1999–June 2007 and presents the monitoring results from the five agricultural sites presently monitored. The main focus is on evaluating the leaching risk of the pesticides applied during 2005.

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. 36 stoffers udvaskningsrisiko undersøges således på fem marker af en størrelse på mellem 1,1 og 2,4 ha. De hidtidige resultater viser, at:

- Af de 36 pesticider, der er blevet udbragt, blev de otte (clopyralid desmedipham, linuron, florasulam metsulfuron-methyl, thiamethoxam, triazinamin-methyl og triasulfuron) ikke fundet udvasket i løbet af perioden 1999–2007.

- 10 af de udbragte stoffer eller nedbrydningsprodukter heraf gav anledning til en markant udvaskning. Ethofumesat, bentazon, propyzamid, glyphosat, dettes nedbrydningsprodukt AMPA, metamitron, dettes nedbrydningsprodukt metamitron-desamino, azoxystrobin, dettes nedbrydningsprodukt CyPM, samt nedbrydningsprodukter fra henholdsvis metribuzin, terbutylazin, pirimicarb og rimsulfuron blev udvasket fra rodzonen (1 meter under terræn, herefter m.u.t.) i gennemsnitskoncentrationer over 0,1 µg/l. På nær gældende metribuzins, rimsulfurons and terbutylazins nedbrydningsprodukter var udvaskningen primært begrænset til 1 m u.t., hvor stofferne hyppigt blev fundet i prøver udtaget i sugeceller og dræn.

- Andre 18 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 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 2007 primært med fokus på pesticider udbragt i 2005. 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 groundwater during the past decade and are now present in much of the Danish groundwater. Under the Danish National Groundwater Monitoring Programme (GRUMO) they have so far been detected in 45% of all screens monitored (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 groundwater is largely based on data from modelling, laboratory or lysimeter studies. However, these types of data may not adequately describe 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 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 on 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, 36 pesticides and several of their degradation products are included in the PLAP. All the compounds analysed are listed in Appendix 1.

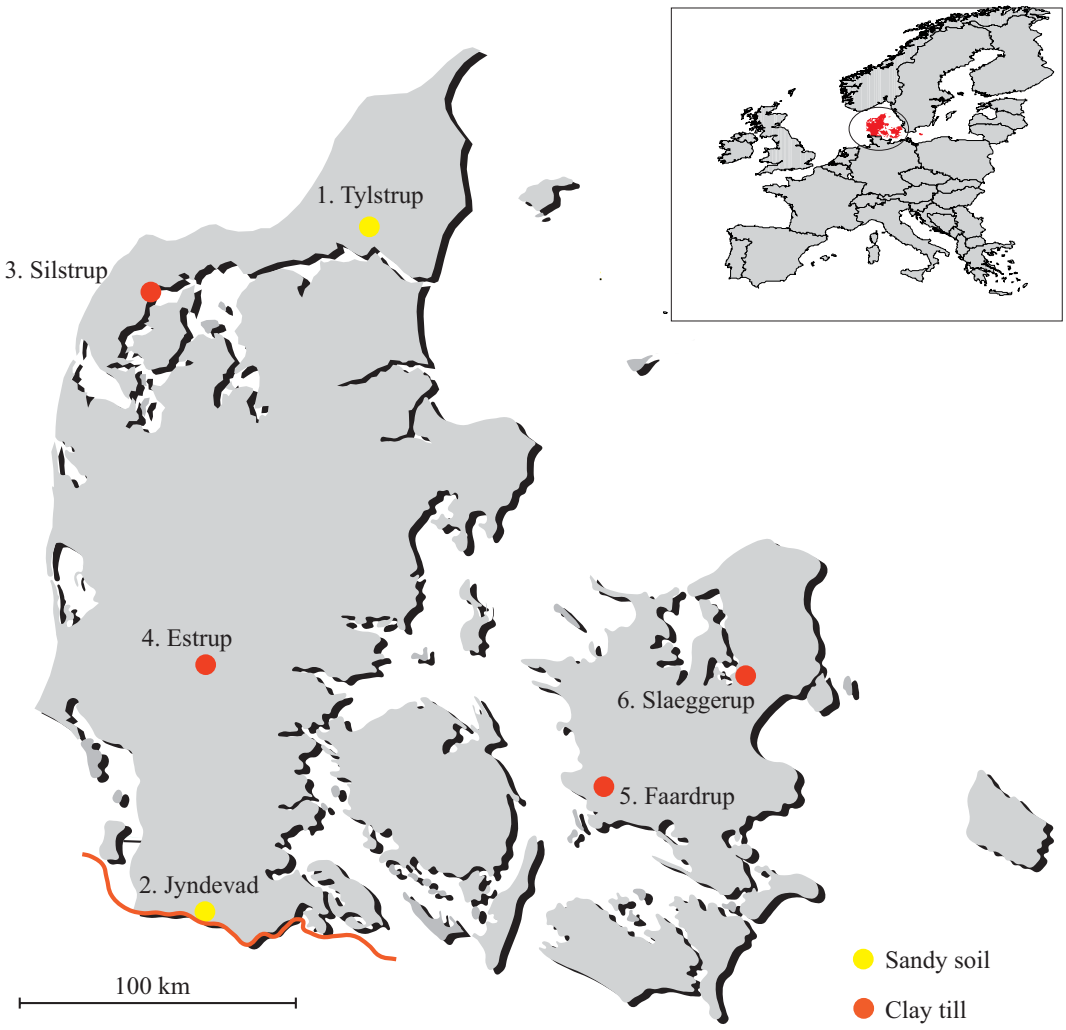

Figure 1. Location of the PLAP sites Tylstrup, Jyndevad, Silstrup, Estrup and Faardrup. Monitoring at Slaeggerup was terminated on 1 July 2003.

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 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 dose 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 to 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)	$2.0 \cdot 10^{-5}$	$1.3 \cdot 10^{-4}$	$3.4 \cdot 10^{-6}$	$8.0 \cdot 10^{-8}$	$7.2 \cdot 10^{-6}$
Topsoil characteristics					
– DK classification	JB2	JB1	JB7	JB5/6	JB5/6
– Classification	Loamy sand	Sand	Sandy clay loam/ sandy loam	Sandy loam	Sandy loam
– Clay content (%)	6	5	18–26	10–20	14–15
– Silt content (%)	13	4	27	20–27	25
– Sand content (%)	78	88	8	50–65	57
– pH	4–4.5	5.6–6.2	6.7–7	6.5–7.8	6.4–6.6
– TOC (%)	2.0	1.8	2.2	1.7–7.3	1.4

[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). The present report presents the results of the monitoring period May 1999–June 2007. The main focus of this report is on the leaching risk of pesticides applied during 2005. For a detailed description of the earlier part of the monitoring period (May 1999–June 2006), see Kjær et al., (2002), Kjær et al. (2003), Kjær et al. (2004), Kjær et al. (2005c) and Kjær et al. (2007).

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 length of time.

Hydrological modelling of the unsaturated zone at each PLAP site supports the monitoring data. The MACRO model (version 5.1), see Larsbo *et al.* (2005), was used to describe the soil water dynamics at each site during the full monitoring period May 1999–June 2007. The five site models have been calibrated for the monitoring period May 1999-June 2004 and validated for the monitoring period July 2004-June 2007.

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 windbreaks 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). The overall direction of groundwater flow is towards the west (Figure 2). During the monitoring period the groundwater table was 2.6–4.5 m b.g.s. (Figure 3). 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).

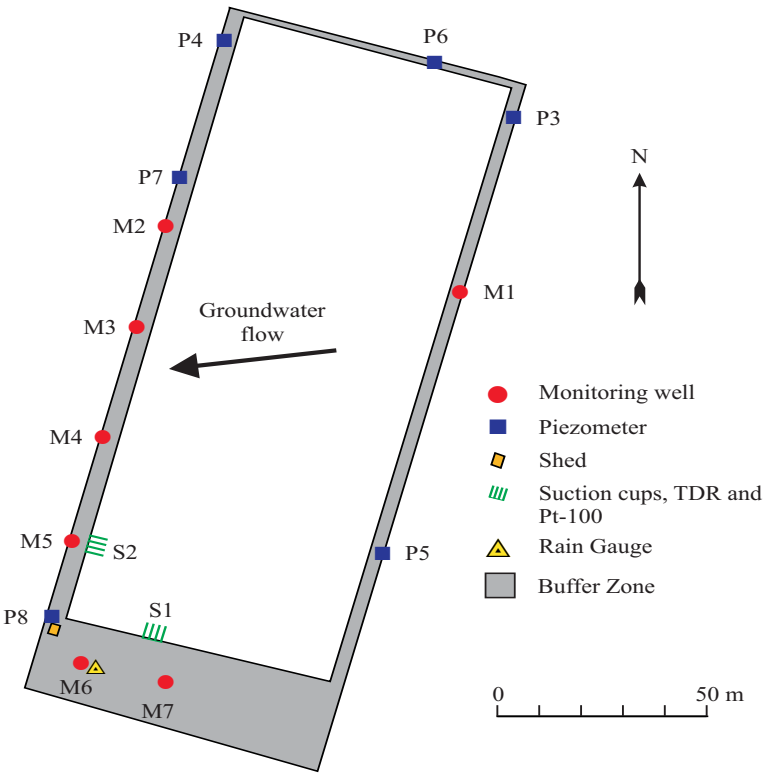

Figure 2.Overview of the Tylstrup test site. The innermost white area indicates the cultivated land, while the grey area indicates the surrounding buffer zone. The positions of the various installations are indicated, as is the direction of groundwater flow (by an arrow).

2.1.2 Agricultural management

Management practice during the 2005 and 2006 growing seasons is briefly summarized below and detailed in Appendix 3 (Table A3.1). For information about management practice during the previous monitoring periods see Kjær *et al*. (2002, 2003, 2004, 2005c & 2007).

A crop of maize (cv. Vernal) was established on 28 April 2005. The crop emerged on 14 May, and on 18 May a first spraying of weeds using terbutylazine took place when two leaves had unfurled (Figure 6). On 6 June, when the maize had five unfurled leaves, 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 t/ha of 100% dry matter was harvested. This was similar to yields obtained in experiments undertaken by the Farmers' Association (Pedersen, 2005).

Maize debris was incorporated by rotary cultivation in November 2005 and in April 2006 the field was ploughed. A crop of spring barley (cv. Cabaret) was sown on 23 April. Two weeks later the barley emerged. Weeds were sprayed with tribenuron-methyl on 6 June when the first node was detectable. The fungicide epoxiconazole was applied on 3 July at the end of heading. Due to a precipitation deficit the crop was irrigated twice with 29 mm/ha on 19 June and 9 July. Harvest of the spring barley took place on 24 August yielding 55.6 hkg/ha of grain (85% dry matter), which was similar to the average for the year and location (Plantedirektoratet, 2006). The straw, 33.2 hkg/ha (100% dry matter), was shredded at harvest and incorporated the following day using a rotary cultivator. On 26 August the field was ploughed and on the same day sown with winter rape seeds (cv. Lioness) dressed with the insecticide thiamethoxam, and sprayed with the herbicide clomazone (the latter, however, not included in the programme). Due to a heavy precipitation event shortly after sowing the surface of the soil was severely crusted. The crust impeded the emergence of the rape and on 6 September the field was resown (cv. Castille). The herbicides propyzamide and clopyralid were applied on 9 February and 27 March, respectively, the latter not included in the monitoring programme.

2.1.3 Model set-up and calibration

The numerical model MACRO (version 5.1) 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 2007 and to establish an annual water balance.

Compared to Kjær *et al.* (2007), a year of validation was added to the MACRO-set-up for the Tylstrup site. The set-up was hereby calibrated for the monitoring period May 1999-June 2004 and validated for the monitoring period July 2004-June 2007. 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. were used in the calibration and validation process. Data acquisition, model set-up and results related to simulated bromide transport are described in Barlebo *et al. (*2007) 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 (Figure 3). The overall trends in soil water saturation 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 25, 60 and 110 cm b.g.s. was, however, less well captured. The dynamics of groundwater table were captured with some exceptions, but as with previous simulations the amplitude of the fluctuations was less well described (Figure 3B).

The resulting annual water balance is shown for each hydraulic year of the monitoring period (July–June) in Table 2. Precipitation and actual evapotranspiration of the latest hydraulic year, July 2006–June 2007, was the highest since the monitoring began at the site. The precipitation was characterized by July and April being very dry and August, October-January, and June being very wet (Appendix 4). Compared to previous hydraulic years, the precipitation pattern of this year resulted in increased percolation 1 m b.g.s. except for August 2006 and May 2007.

Table 2. Annual water balance for Tylstrup (mm/y). Precipitation is corrected to 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
1.7.04–30.6.05	773	854	57	477	434
1.7.05–30.6.06	773	725	67	488	304
1.7.06–30.6.07	773	1147	59	591	615

[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.*

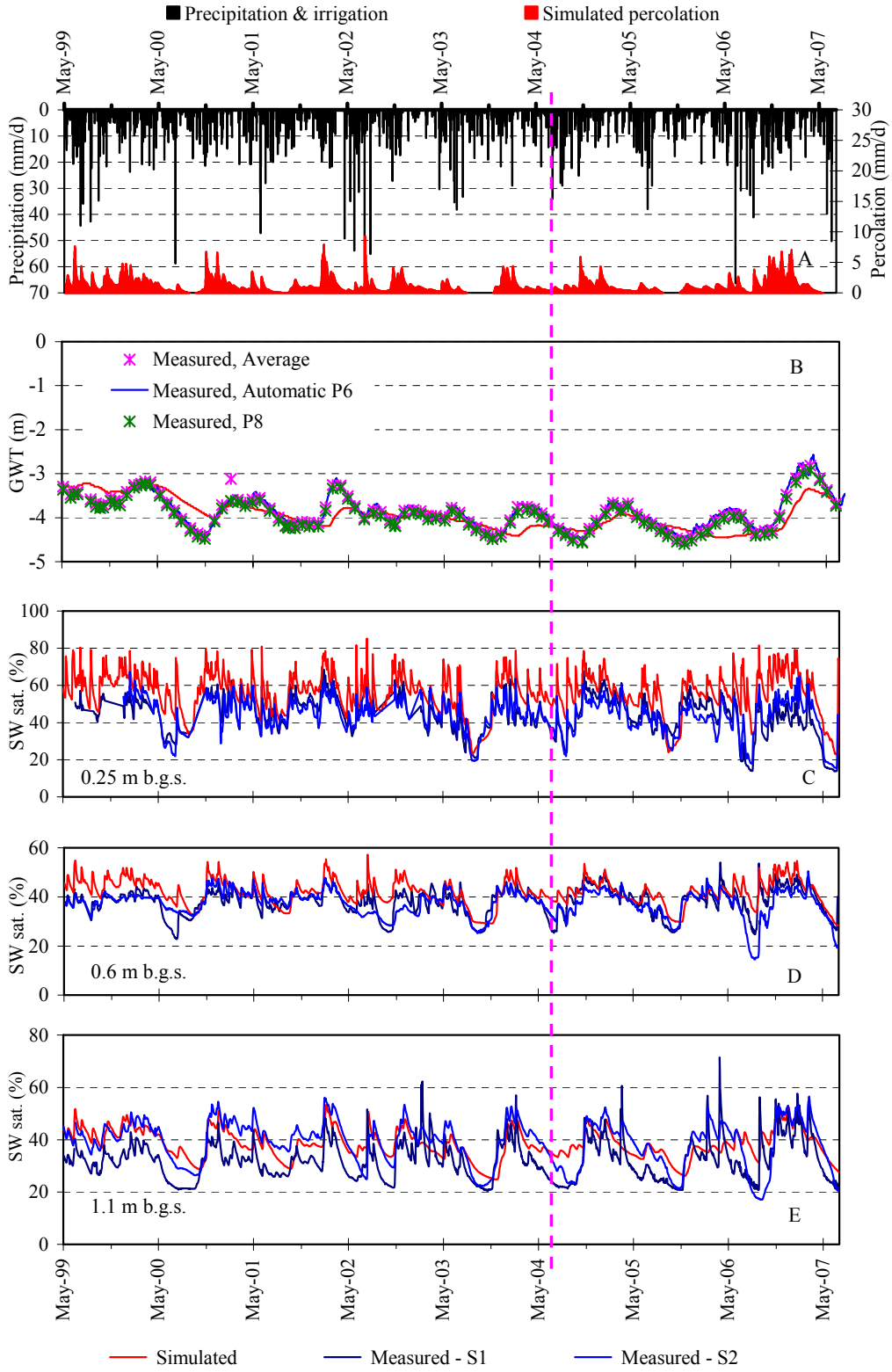

Figure 3. Soil water dynamics at Tylstrup: Measured precipitation, irrigation and simulated percolation 1 m b.g.s. (A), simulated and measured groundwater level GWT (B), and simulated and measured soil water saturation (SW sat.) at three different soil depths (C, D and E). The measured data in B derive 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 2007).

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.* (2007) and Rosenbom *et al.* (In prep.)

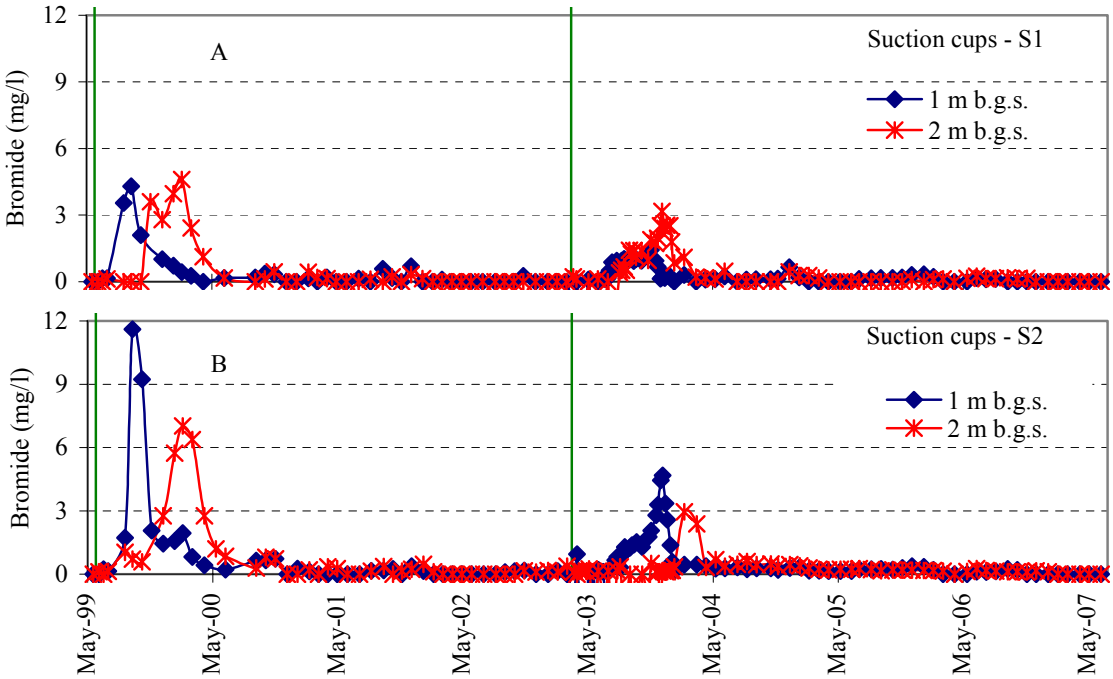

Figure 4. Measured bromide concentration in the unsaturated zone at Tylstrup. The measured data derive from suction cups installed 1 m b.g.s. and 2 m b.g.s. at locations S1 (A) and S2 (B) indicated in Figure 2. The green vertical lines indicate the dates of bromide applications.

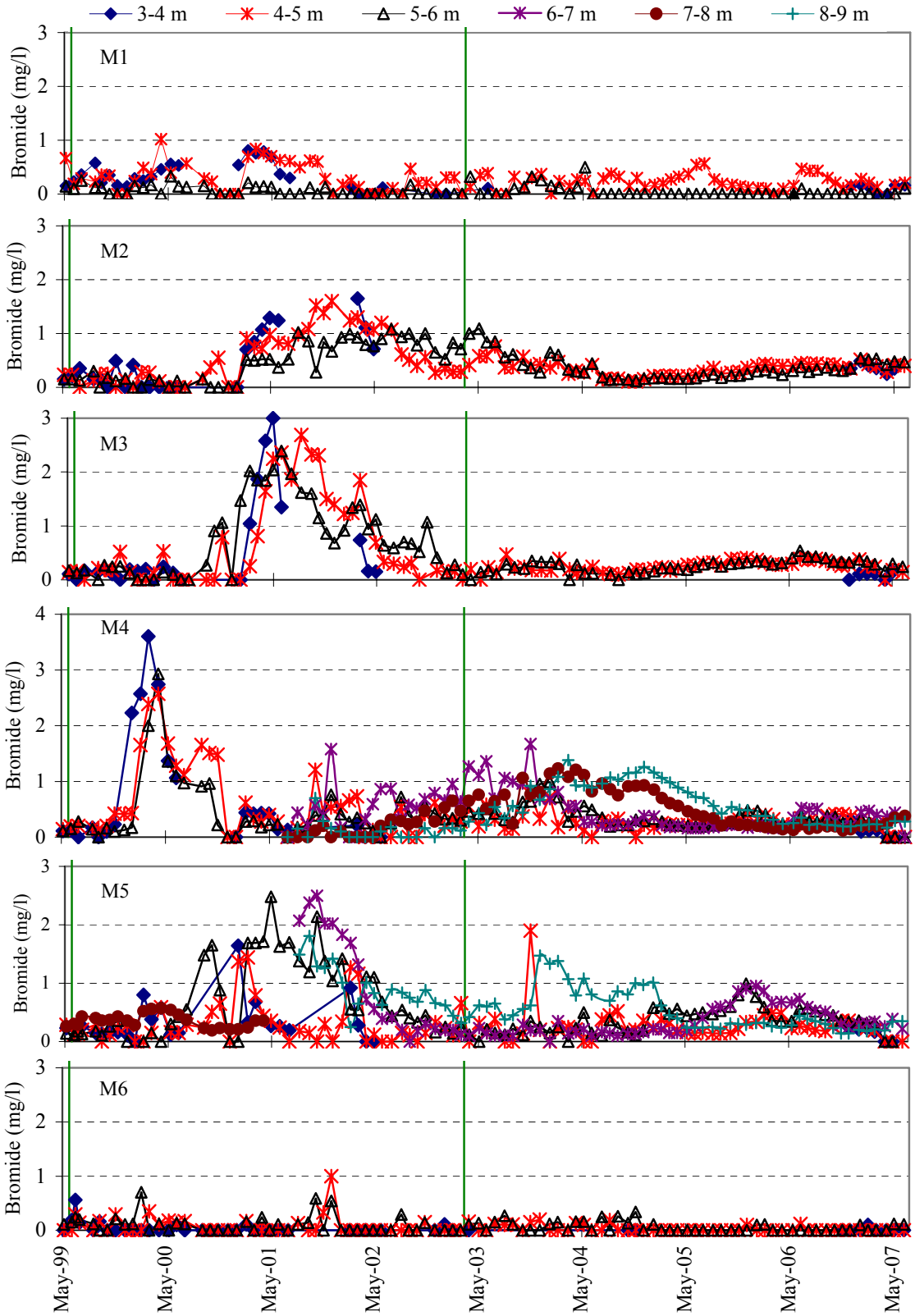

Figure 5. Bromide concentration in the groundwater at Tylstrup. The data derive from monitoring wells M1–M6. Screen depth is indicated in m b.g.s. The green vertical lines indicate the dates of bromide application.

2.2.3 Pesticide leaching

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

It should be noted that precipitation in Table 3 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 mancozeb (applied here as Dithane DG), tribenuron-methyl (applied here as Express) and rimsulfuron (applied here as Titus) degrade rapidly, the risk of leaching risk is more associated with their respective degradation products, ETU, triazinamin-methyl, PPU and PPU-desamino. This is why the degradation products and not the parent compounds are monitored in the PLAP (Table 3). Pesticides applied later than April 2007 are not evaluated in this report and hence are not included in Table 3 and Figure 6.

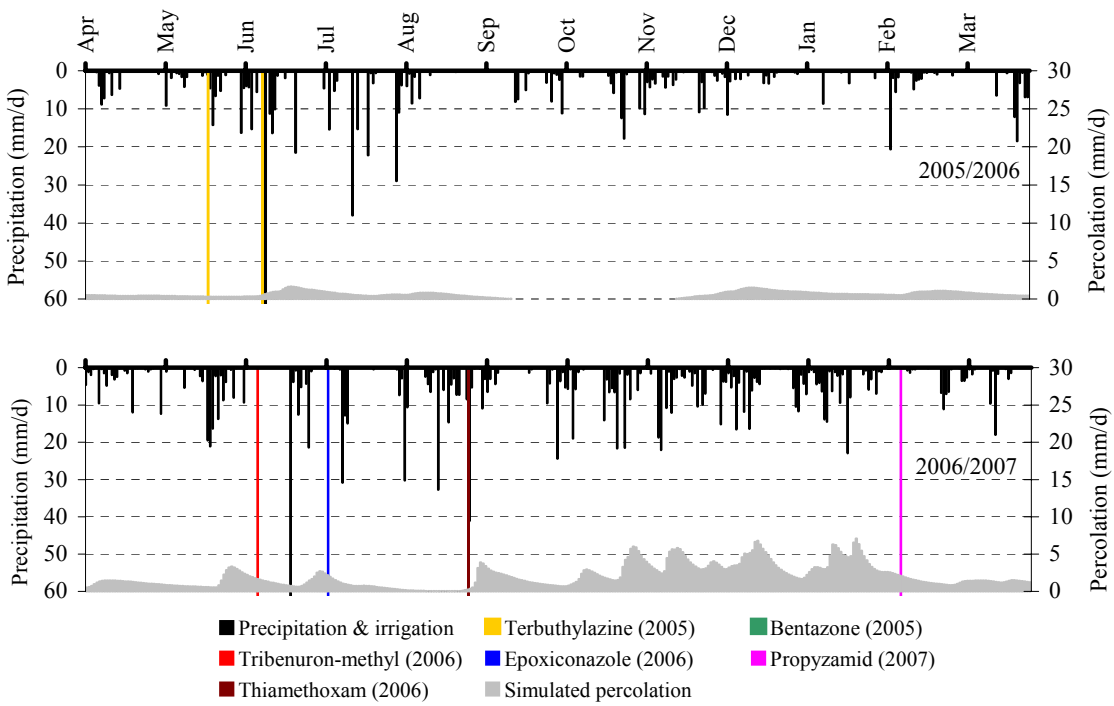

Figure 6. Pesticide application, precipitation and irrigation (primary axis) together with simulated percolation 1 m b.g.s. (secondary axis) at Tylstrup in 2005/2006 (upper) and 2006/2007 (lower).

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)
Metribuzine (Sencor WG)	Jun 99	Jul 03	4223	2097	85	<0.01 (3)
- *metribuzine-diketo*		Jul 07†	7891	3722	85	0.05–0.36 (630)
- *metribuzine-desamino*		Jul 03	4223	2097	85	<0.02 (0)
- *metribuzine-desamino-diketo*		Jul 07†	7891	3722	85	0.14–0.97 (317)
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 2007.

The leaching risk of pesticides applied during 2000, 2001, 2002, 2003 and 2004 has been evaluated in Kjær *et al.* (2002, 2003, 2004, 2005c & 2007),. The leaching of metribuzin is further detailed in Kjær *et al.* (2005b).

Since one of the pesticides (rimsulfuron) applied in 2004 continued to leach during this monitoring period, the results of this 2004 application are, however, summarised below.

Rimsulfuron degrades rapidly in the soil, and the leaching risk is therefore more associated with the degradation products PPU and PPU-desamido. PPU has been found several times in suction cups situated 1 m b.g.s. at both S1 and S2. The first detection of PPU occurred at S1 10 months after the application (Figure 7B), whereafter PPU was found in 20 out of 27 analysed samples, concentrations ranging between 0.021 and 0.092 µg/l. A little more than two years after application PPU was found at S2 in several samples, concentrations ranging between 0.01 and 0.067 µg/l (Figure 7D). Elevated concentrations of PPU were seen at the end of the monitoring period, indicating that leaching had not yet ceased. Average concentrations did not exceed 0.1 µg/l in any of the three years for either of the metabolites, however (Table 4). Minor leaching of PPU-desamido was also seen at Tylstrup, but the number of detections as well as concentration levels were low (Figure 7 and Appendix 5).

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]	Jun 04	Jul 07†	2960	1343	13	<0.01 (40) [3]
- PPU- desamino [2]	Jun 04	Jul 07†	2960	1343	13	<0.01 (14) [3]
Maize 2005						
Terbutylazine (Inter-Terbutylazine)	May 05	Jul 07	2145	933	16	<0.01 (0)
-desethyl-terbutylazine						<0.01 (2)
-2-hydroxy-terbutylazine						<0.01 (1)
-desisopropyl-atrazine						<0.01 (18) [3]
-2-hydroxy-desethyl-terbutylazine						<0.01 (6)
Bentazone (Laddok TE)	Jun 05	Jul 07	2061	927	33	<0.01 (1)
-AIBA						<0.01 (0)
Spring barley 2006						
-triazinamin-methyl [4] (Express ST)	Jun 06	Jul 07†	1321	671	43	<0.02 (0)
Epoxiconazole (Opus)	Jul 06	Jul 07†	1206	635	24	<0.01 (0)
Winter rape 2007						
Thiamethoxam (Cruiser raps)	Aug 06	Jul 07†	1003	610	57	<0.01 (0)
-CGA 322704						<0.02 (0)
Propyzamide (Kerb 500 SC)	Feb 07	Jul 07†	358	87	40	<0.01 (0)
-RH-24644						<0.01 (0)
-RH-24580						<0.01 (0)
-RH-24655						<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.
[3] Leaching increased the second year after application (see Figure 7B and Figure 8B).
[4] 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 2007.

Whereas PPU has been found in the suction cups 2 m b.g.s. at S1 (Figure 7C) in all of the nine samples taken between 11. May 2005 and 9 May 2007, it has not been found at S2 (Figure 7E). Whereas PPU was found in a single groundwater sample (0.045µg/l on 7 December 2005 in a monitoring screen of M4 located 4.4-5.4 m b.g.s.), PPU-desamido has not been seen in the groundwater (Table A5.1 in Appendix 5).

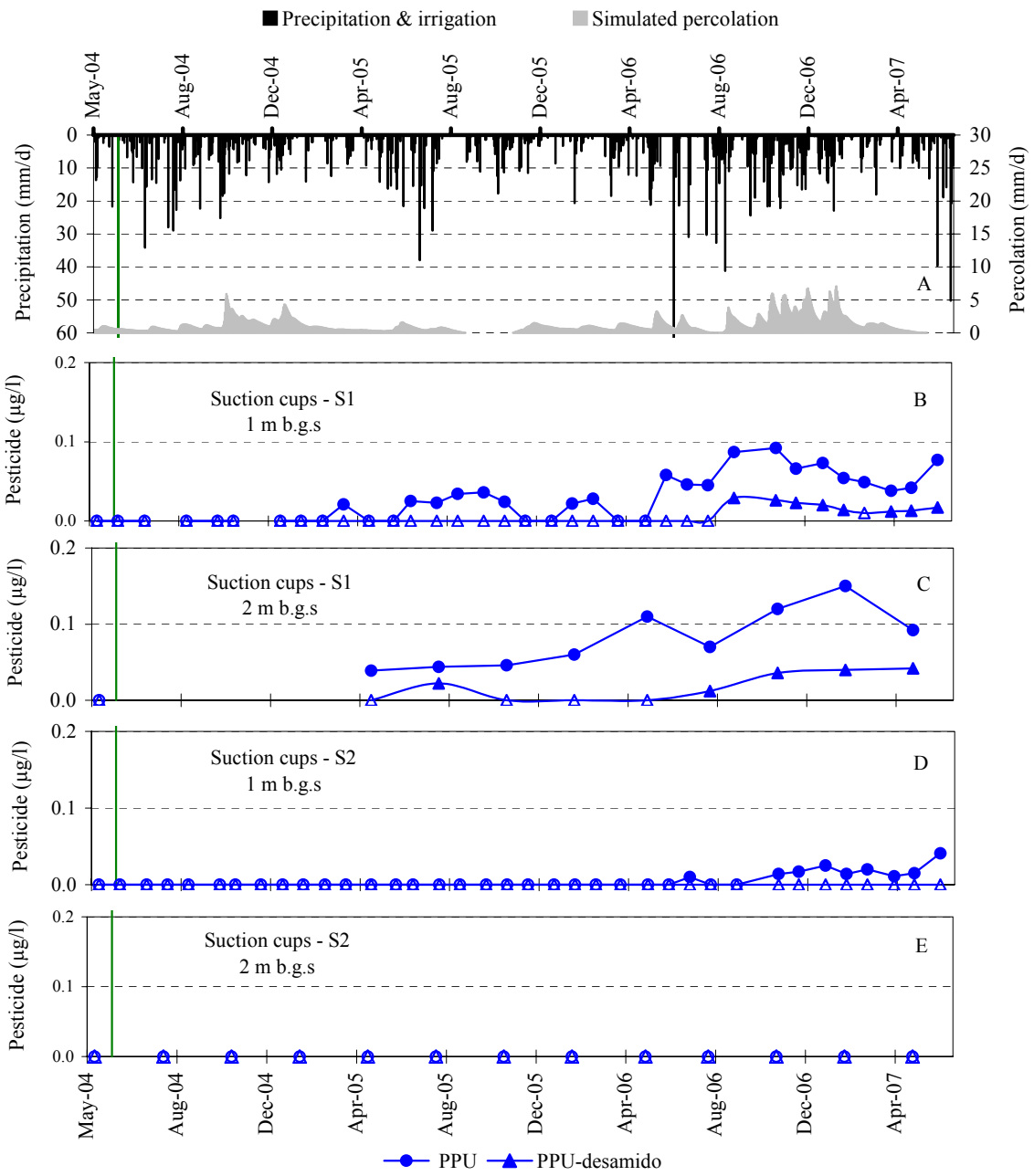

Figure 7. Precipitation, irrigation and simulated percolation 1 m b.g.s. (A) together with measured concentration of *PPU* and *PPU* – desamino (µg/l) in suction cups installed on location S1 at 1m b.g.s. (B) and 2 m b.g.s. (C) and location S2 at 1m b.g.s. (D) and 2 m b.g.s. (D) at Tylstrup. The green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

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 2004 (20% higher than normal) and 51 mm in June 2004 (21% lower than normal). Precipitation and percolation following the application at Tylstrup were thus much lower than that observed at Jyndevad in 2003 where rimsulfuron was also applied. Finally, it should be noted that the concentration of PPU is likely to be underestimated by 14 - 47% (Kjær *et al.* 2007). 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 on 18 May and 8 June 2005 (Figure 8), at the later application in combination with bentazone. Terbutylazine as well as several of its metabolites were monitored. Terbutylazine itself was never detected and the degradate 2-*hydroxy-terbutylazine* just once (Table 3 & Figure 8B). Occasionally, there were detections of low levels of some of the other metabolites. *Desisopropyl-atrazine* was detected in the monitoring screen M1 upstream of the area on 9 August 2006 (data not shown). Between 14 June 2006 and 11 October it was found in suction cups at S2 at a depth of 1 m b.g.s., concentrations ranging between 0.023 and 0.031 µg/l (Figure 8C). After having disappeared for half a year, it reappeared in a concentration of 0.01 µg/l on 9 May 2007 and on 13 June the concentration was 0.013 µg/l. Similar low concentrations (0.04 µg/l) were also found in suction cups at S1 . The metabolite 2-*hydroxy-desethyl-terbutylazine* has been found four times at 1 m b.g.s at S1 in concentrations ranging from 0.013 to 0.016 µg/l from 14 June to 8 November 2006 (Figure 8 B). At S2 there has been only one detection; 0.013 µg/l on 11 October (Figure 8C) and 0.026 µg/l was found at M5.2 in groundwater (data not shown). *Desethyl-terbutylazine* was found twice at S1 in concentrations of 0.01 and 0.012 µg/l on 17 May and 14 June 2006, respectively (Figure 8B).

Bentazone, applied concomitantly with terbutylazine on 8 June 2005, was only detected once within the two-year period, at a level of 0.012 µg/l on 10 April 2006, 1 m b.g.s. at S1 (data not shown).

Table 4. Percolation together with estimated average concentration (µg/l) of PPU and PPU-desamido 1 m b.g.s. at Tylstrup. Leached mass refers to the total mass (% of applied rimsulfuron) leached during the monitoring period 1.7.04–30.6.07.

	Percolation	PPU		PPU-desamido	
	(mm/y)	Suction cup – S1	Suction cup – S2	Suction cup – S1	Suction cup – S2
1.7.04–30.6.05	468	<0.02	<0.02	<0.02	<0.02
1.7.05–30.6.06	276	0.02	<0.02	<0.02	<0.02
1.7.06–30.6.07	613	0.07	0.02-0.03	<0.02	<0.02
Leached mass[1)]		70-77%	21-33%	15-27%	6-25%

1) Expressed as rimsulfuron equivalent.

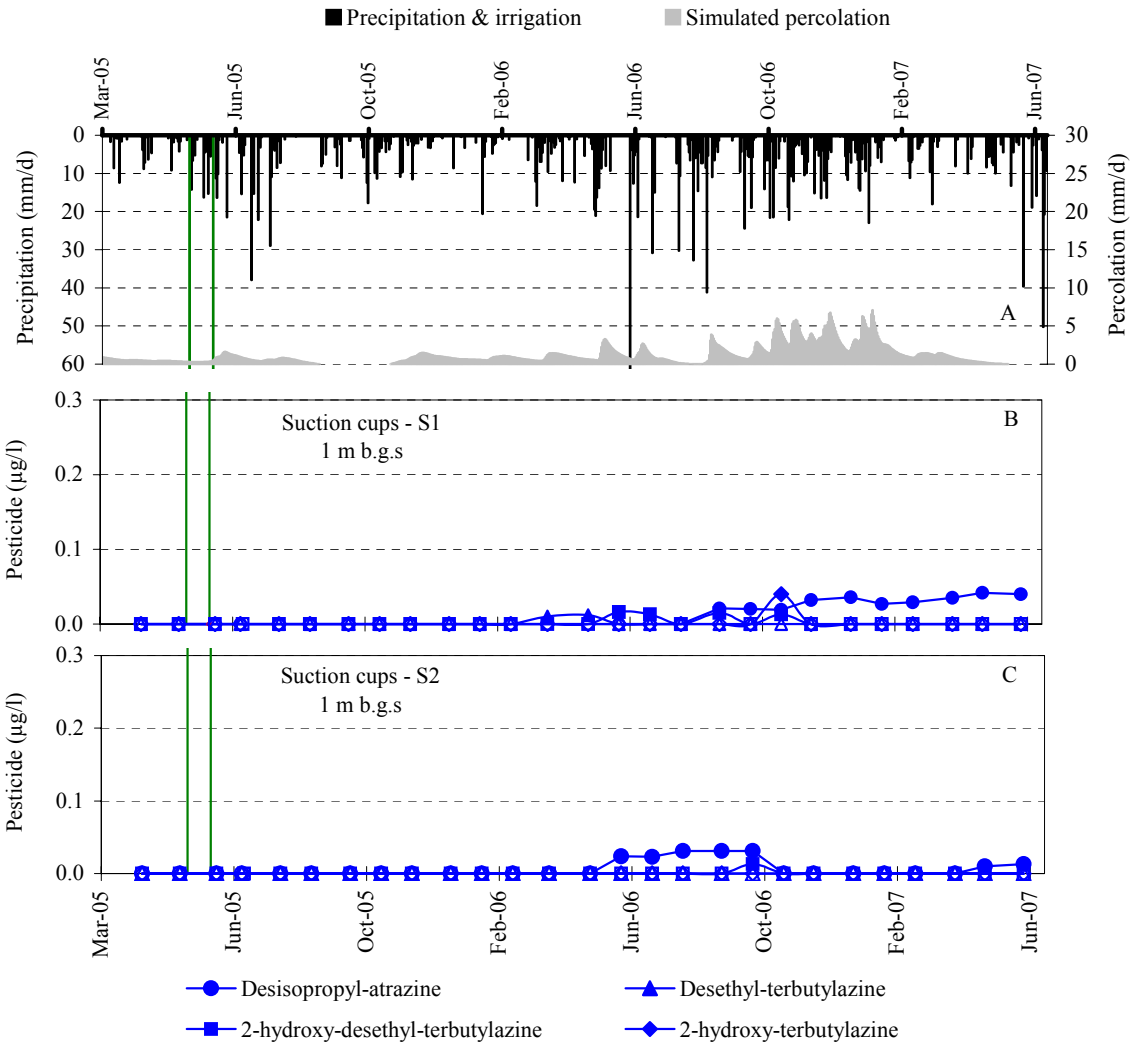

Figure 8. Precipitation, irrigation and simulated percolation 1 m b.g.s. (A) together with measured concentration terbutylazine, desethyl-terbutylazine, 2-hydroxy-desethyl-terbutylazine and desisopropyl-atrazine (µg/l) in suction cups installed at 1m b.g.s. at location S1 (B) and location S2 (C) at Tylstrup. The green vertical lines indicate the dates of pesticide application. Open circles and triangles indicate concentrations below the detection limit of 0.01 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 1). The test site covers a cultivated area of 2.4 ha (135 x 184 m) and is practically flat. A windbreak borders the eastern side of the test site. The area has a shallow groundwater table ranging from 1 to 3 m b.g.s. (Figure 10 B) The overall direction of groundwater flow is towards northwest (Figure 9). 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 occurrences 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 2005 - 2006 growing seasons is briefly summarized below and detailed in Appendix 3 (Table A3.2). For information about management practice during the previous monitoring periods see Kjær *et al.* (2002, 2003, 2004, 2005c & 2007).

After ploughing in the pea stubble, the field was sown with winter wheat (cv. Biscay) on 24 September 2004 using a combined rotavator and drilling machine. Eight days later the wheat emerged. On 19 October 2004, when the plants had two unfurled leaves, weeds were sprayed with a mixture of ioxynil and bromoxynil (Figur 13). An additional spraying was carried out in the spring using amidosulfuron on 15 April 2005 and fluroxypyr on 3 May 2005. Fungicidal treatment was carried out on 18 May using 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 on 18 May did not suffice and an additional spraying with propiconazole was carried out 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. The grain yield was somewhat disappointing and may be attributed to the dry summer and to problems with fungal diseases being resistant to strobin.

The field was limed on 13 March 2006 using 3.3 t/ha of dolomite chalk (92%). The field was rotary-cultivated on 29 March and ploughed the subsequent day. Two weeks later spring barley (cv. Simba) was sown. The barley emerged on 21 April. The herbicide florasulam was sprayed on 26 May when the second node was detectable. On 8 June, at heading, the fungicide epoxiconazole was applied. Due to a dry growing season, the field was irrigated five times. An amount of 27, 30, 27 mm was applied on 6, 12 and 26 June. On 2 and 7 July 30 mm was applied. Harvest of barley took place on 7 August yielding 60.5 hkg/ha of grain (85% dry matter) and 26.8 hkg/ha of straw, which was approximately 5 hkg/ha grain more than similar, irrigated soils in the region (Plantedirektoratet, 2006).

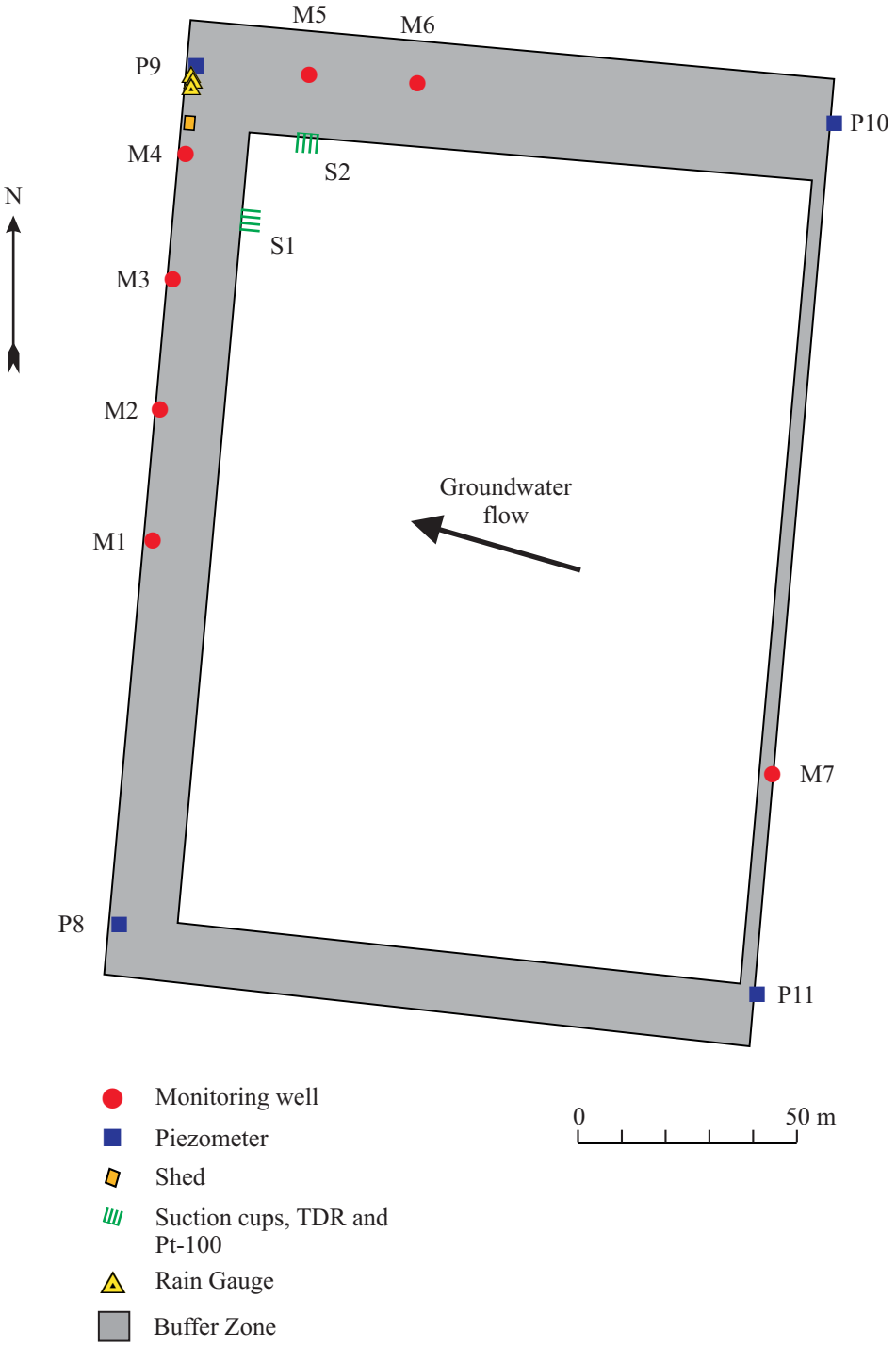

Figure 9. Overview of the Jyndevad test site. The innermost white area indicates the cultivated land, while the grey area indicates the surrounding buffer zone. The positions of the various installations are indicated, as is the direction of groundwater flow (by an arrow).

3.1.3 Model set-up and calibration

The numerical model MACRO (version 5.1, Larsbo *et al.* (2005)) 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 2007 and to establish an annual water balance.

Compared with the set-up in Kjær *et al.* (2007), a year of validation was added to the MACRO-set-up for the Jyndevad site. The set-up was hereby calibrated for the monitoring period May 1999-June 2004 and validated for the monitoring period July 2004-June 2007. 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 (location indicated at Figure 8), and the bromide concentration measured in the suction cups located 1 and 2 m b.g.s (Figure 11). Data acquisition, model set-up as well as results related to simulated bromide transport are described in Barlebo *et al.* (2007) 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 10). The dynamics of the simulated groundwater table was well described with MACRO 5.1 (Figure 10B). As noted earlier (Kjær *et al.*, 2007), 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 (Figure 10E). As in the Tylstrup scenario, the decrease in water saturation observed during the summer periods at 25 and 60 cm b.g.s. was less well captured.

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

	Normal 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
1.7.06–30.6.07	995	1301	114	571	847

1) Normal values based on time series for 1961–1990.
2) Groundwater recharge is calculated as precipitation + irrigation - actual evapotranspiration.

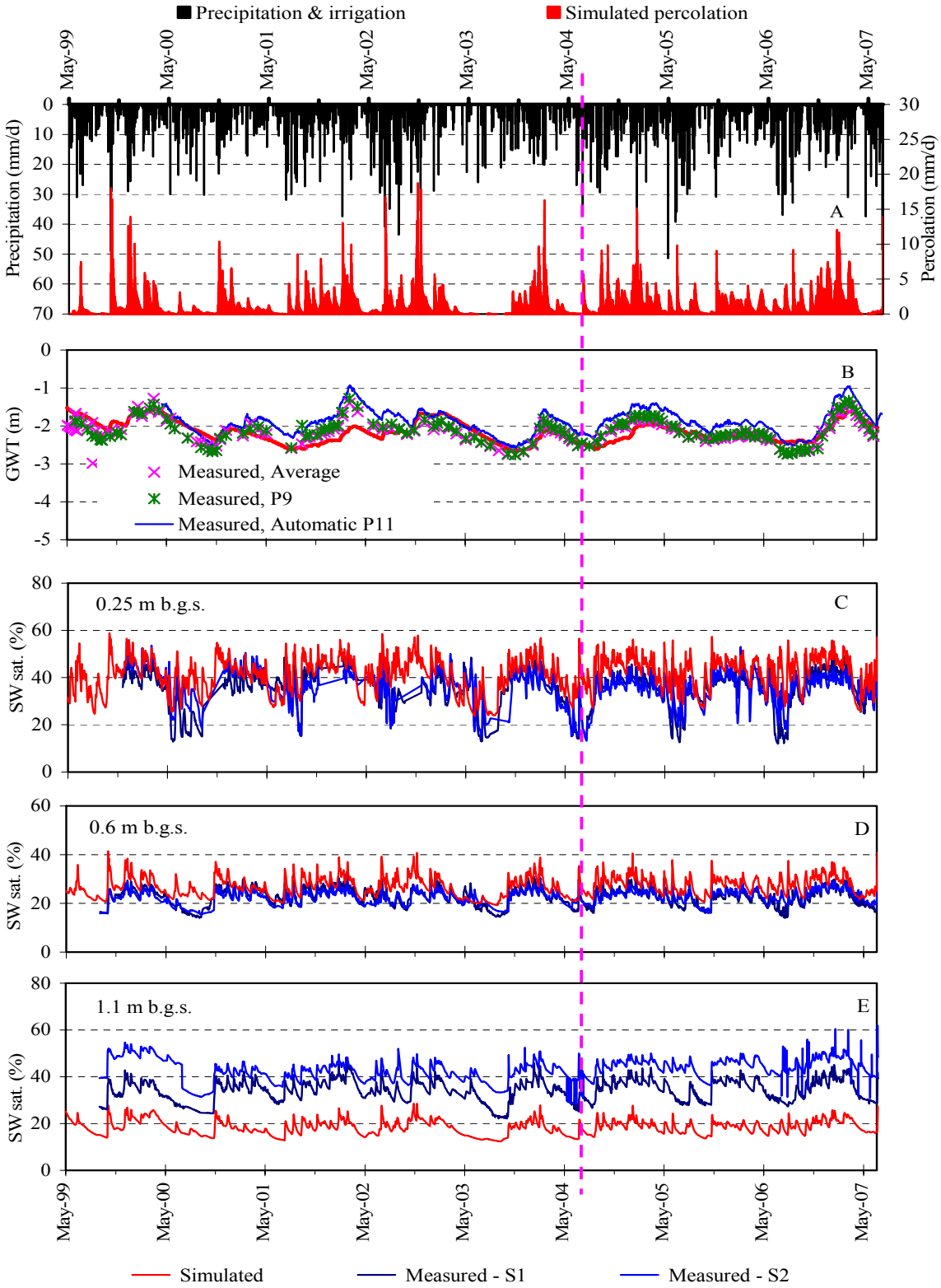

Figure 10. Soil water dynamics at Jyndevad: Measured precipitation, irrigation and simulated percolation 1 m b.g.s. (A), simulated and measured groundwater level (B), and simulated and measured soil water saturation (SW sat.) at three different soil depths (C, D and E). The measured data in B derive 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 9). The broken vertical line indicates the beginning of the validation period (July 2004- June 2007).

The resulting water balance for Jyndevad for the eight monitoring periods is shown in Table 5. Compared with the previous seven years, the latest hydraulic year July 2006-June 2007 was characterised by having the highest precipitation, the second highest simulated actual evapotranspiration and the second highest irrigation value. Precipitation in the latest hydraulic year was characterized by August, December-February, and June being very wet and April being very dry (Appendix 4). Due to this precipitation pattern, continuous percolation was simulated throughout the year discounting April. Additionally, the climatic setting of this year gave rise to the largest observed change in groundwater table within any hydraulic year of the monitoring period.

3.2.2 Bromide leaching

Bromide has now been applied twice at Jyndevad. The bromide concentrations measured up to April 2003 (Figure 11 and Figure 12) 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.).

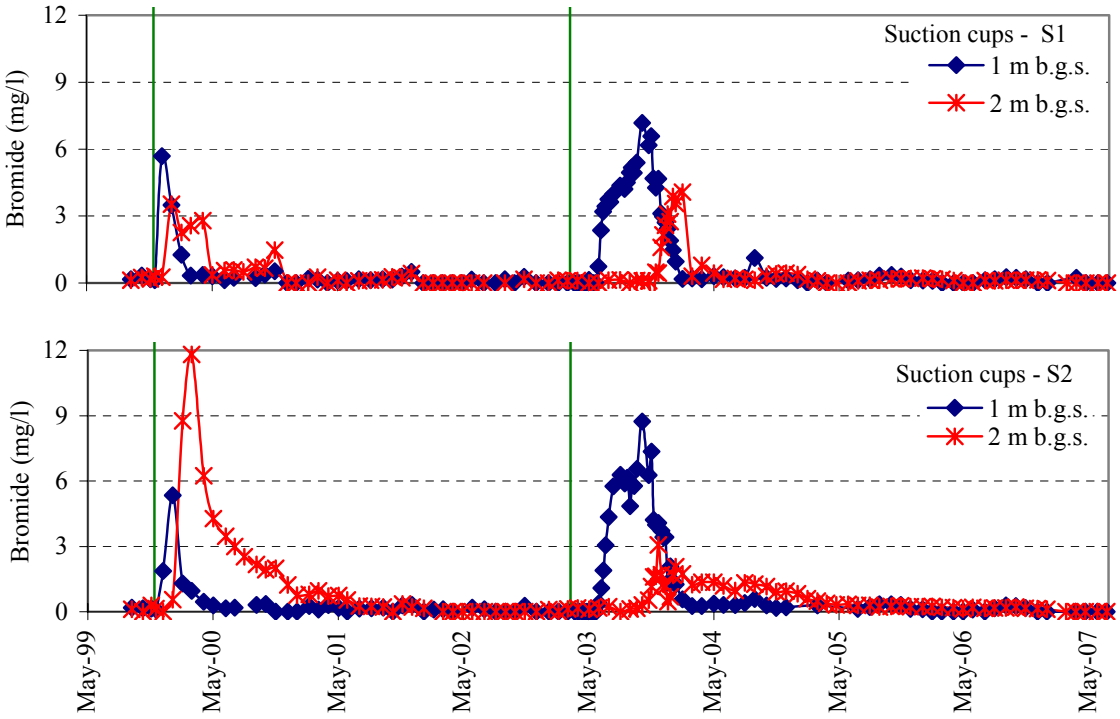

Figure 11. Bromide concentration in the unsaturated zone at Jyndevad. The measured data derive from suction cups installed (A) 1 m b.g.s. and (B) 2 m b.g.s. at locations S1 and S2 (Figure 8). The green vertical lines indicate the dates of bromide applications.

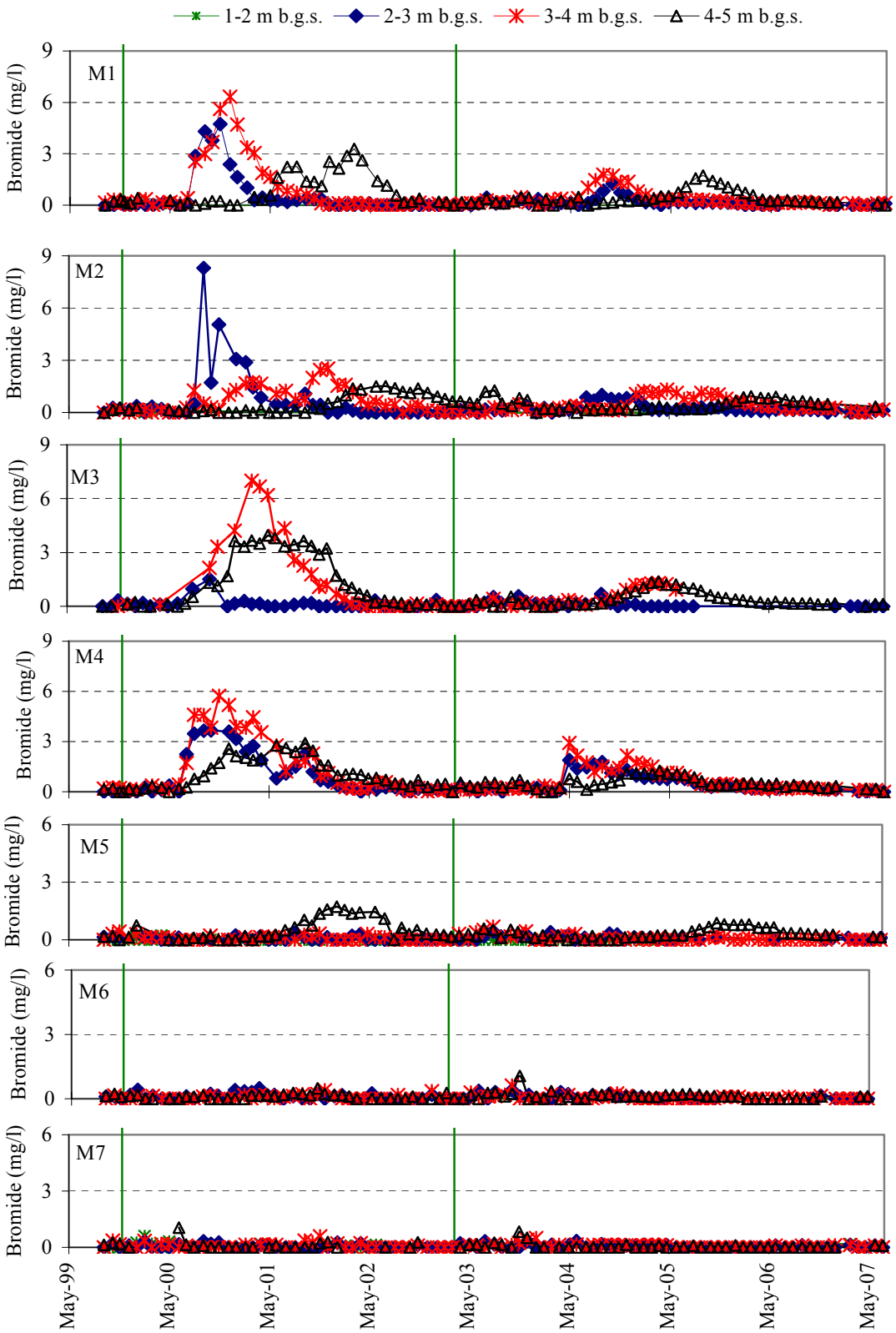

Figure 12. Bromide concentration in the groundwater at Jyndevad. The data derive from monitoring wells M1–M7. Screen depth is indicated in m b.g.s. The green vertical lines indicate the dates of bromide applications.

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 6. Pesticide application during the two most recent growing seasons is shown together with precipitation and simulated precipitation in Figure 13. It should be noted that precipitation is corrected to the soil surface according to Allerup and Madsen (1979), whereas percolation (1 m b.g.s.) refers to accumulated 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-desamido. For the same reasons it is the degradation products and not the parent compounds that are monitored in the PLAP (Table 6). Pesticides applied later than April 2006 are not evaluated in this report and hence are not included in Table 6 and Figure 13.

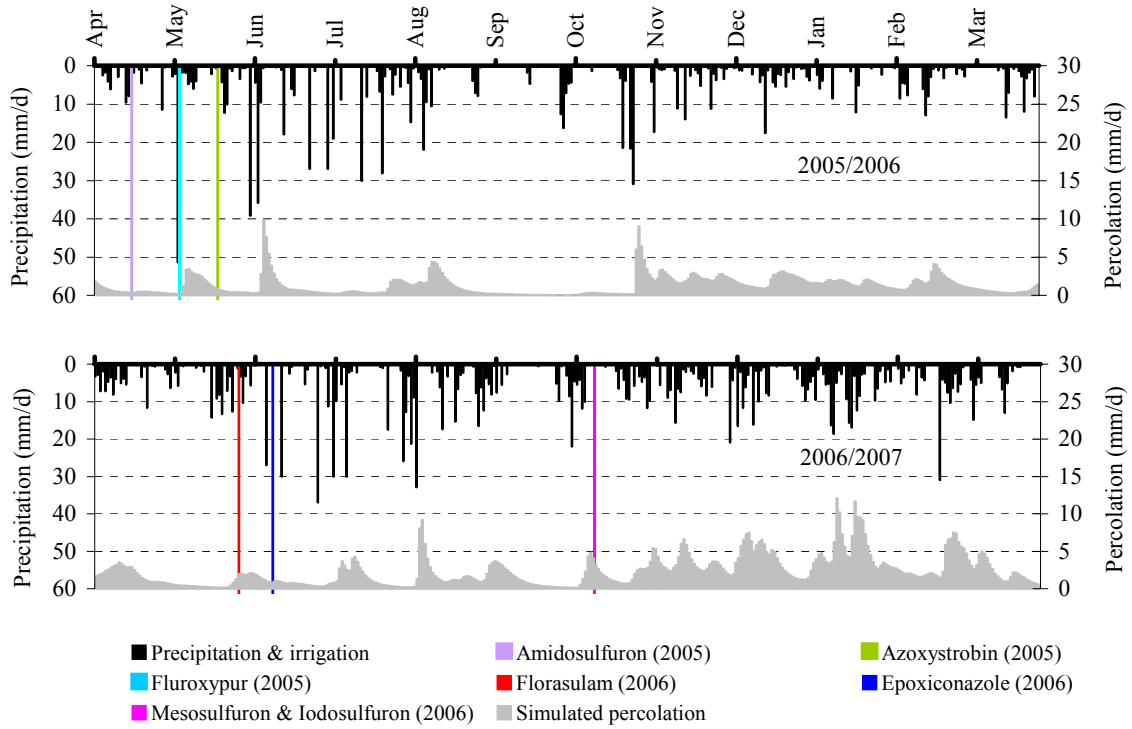

Figure 13. Pesticide application, precipitation and irrigation (primary axis) together with simulated percolation 1 m b.g.s. (secondary axis) at Jyndevad in 2005/2006 (upper) and 2006/2007 (lower).

Table 6. 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	1451	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	Apr 04	3118	1809	4	<0.01 (0)
- *desethyl-terbutylazine*	May 01	Apr 07	6742	3826	4	<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 07†	5865	3229	11	0.06[4)]–0.13 (204)
- *PPU-desamido*		Jul 07†	5865	3229	11	0.01–0.03 (109)
Spring barley 2003						
MCPA (Metaxon)	Jun 03	Jul 05	2340	1233	0	<0.01 (0)
- *4-chlor,2-methylphenol*						<0.01 (0)
Dimethoate (Perfekthion 500 S)	Jun 03	Jul 05	2278	1232	1	<0.01 (0)
Pea 2004						
Bentazone (Basagran 480)	May 04	Jul 07	3888	2044	4	0.02-0.13 (30)
- *AIBA*						<0.01 (2)
Pendimethalin (Stomp)	May 04	Apr 07	3557	1996	4	<0.01 (0)
Pirimicarb (Pirimor)	Jun 04	Apr 07	3493	1993	27	<0.01 (0)
- *Pirimicarb-desmethyl*						<0.01 (1)
- *Pirimicarb-desmethyl-formamido*						<0.02 (0)
- *fluazifop-P(free acid)* [5)] (Fusilade X-tra)	Jun 04	Jul 06	2395	1233	27	<0.01 (0)
Winter wheat 2005						
Ioxynil (Oxitril CM)	Oct 04	Apr 07	2955	1791	81	<0.01 (0)
Bromoxynil (Oxitril CM)	Oct 04	Apr 07	2955	1791	81	<0.01 (0)
Amidosulfuron (Gratil 75 WG)	Apr 05	Jul 07	1070	515	33	<0.01 (3)
Fluroxypyr (Starane)	May 05	Jul 07	2683	1360	37	<0.02 (0)
Azoxystrobin (Amistar)	May 05	Apr 07	2274	1283	49	<0.01 (0)
- *CyPM*						<0.02 (0)
Spring barley 2006						
Florasulam (Primus)	May 06	Jul 07†	1559	843	34	<0.01 (0)
- *florasulam-desmethyl*						<0.03 (0)
Epoxiconazole (Opus)	Jun 06	Jul 07†	1508	821	31	<0.01 (0)
Mesosulfuron-methyl(AtlantisWG)	Oct 06	Jul 07†	986	647	73	<0.01 (0)
- *mesosulfuron*						<0.01 (0)

Systematic chemical nomenclature for the analysed pesticides is given in Appendix 1.
[1)] Degradation product of tribenuron-methyl. The parent compound degrades too rapidly to be detected by monitoring.
[2)] Degradation product of pyridate. The parent compound degrades too rapidly to be detected by monitoring.
[3)] 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 14).
[5)] Degradation product of fluazifop-P-butyl. The parent compound degrades too rapidly to be detected by monitoring.
† Monitoring will continue for an additional year. The values for prec. and perc. are accumulated up to July 2007.

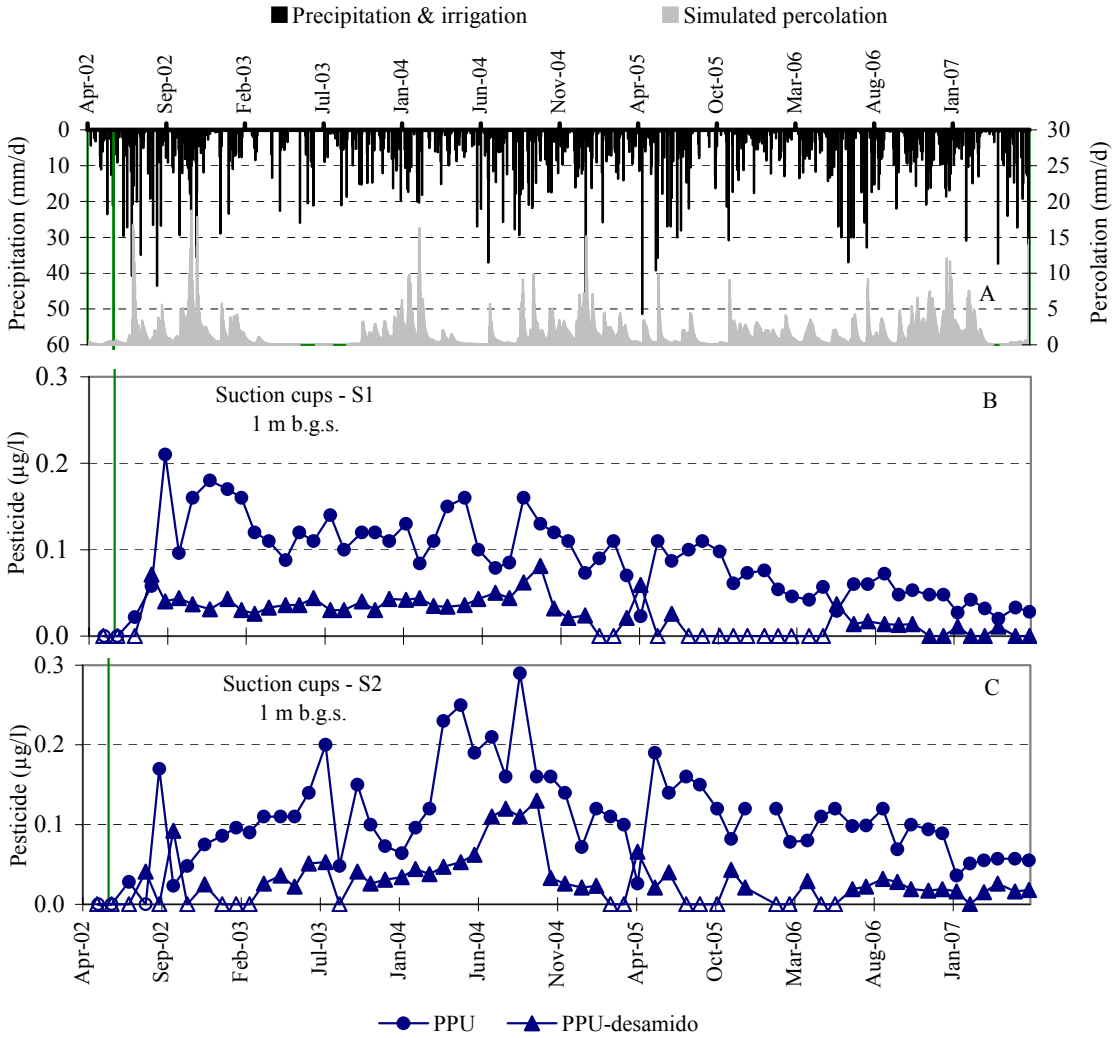

Figure 14. Precipitation, irrigation and simulated percolation 1 m b.g.s. (A) together with measured concentrations of *PPU* and *PPU-desamido (*µg/l) in suction cups installed 1 m b.g.s. at location S1 (B) and S2 (C) at Jyndevad. The green vertical line indicates the date of pesticide application. Open circles and triangles indicate concentrations below the detection limit of 0.02 µg/l.

The leaching risk of pesticides applied during 2000, 2001, 2002, 2003 and 2004 has been evaluated in Kjær et al. (2002, 2003, 2004, 2005c & 2007). Since bentazone (applied in 2004) and PPU and PPU-desamido (metabolites of rimsulfuron applied in 2003) were still included in the current monitoring period, the results of these applications are, however, summarised 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 14). Both compounds were characterized by continuous leaching over a long period of time. Although the concentration decreased during the last monitoring year, elevated concentrations, in particular of PPU, were still seen towards the end of 2007, i.e. five years after application. Average yearly concentrations of PPU reaching 0.1 µg/l were seen as long as three years after application and the quantity leached amounted to 35-65% of applied rimsulfuron (Figure 14 and Table 7). With an overall travel time of about four years PPU also reached the downstream monitoring screens (Figure 15). Elevated concentrations of PPU were seen in

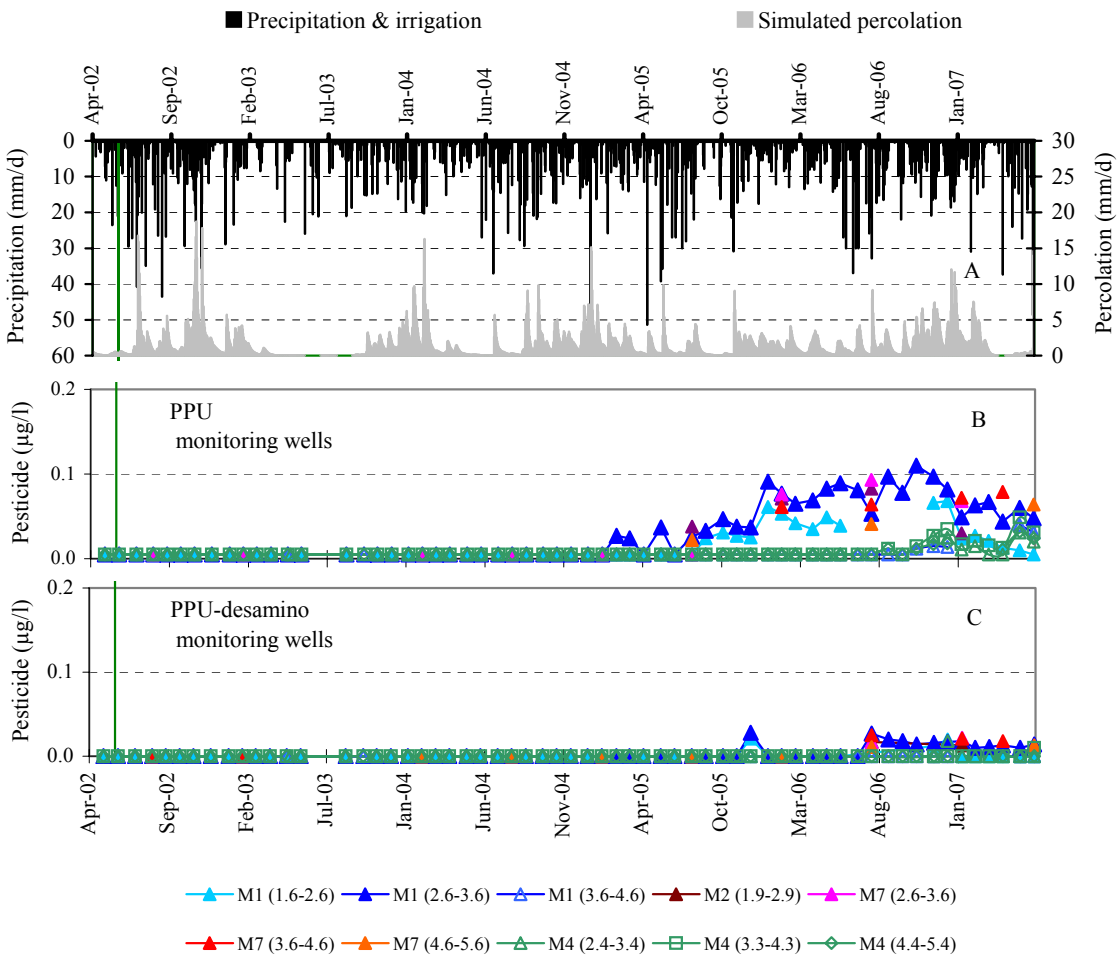

Figure 15. Precipitation, irrigation and simulated percolation 1 m b.g.s. (A) together with measured concentrations (µg/l) in monitoring wells M1, M2, M4 and M7 of *PPU* (B) and *PPU-desamido* (C) at Jyndevad. The numbers in parentheses indicate the depths of the analysed screens. The green vertical line indicates the date of pesticide application. Open circles and triangles indicate concentrations below the detection limit of 0.02 µg/l.

M1 (sampled monthly), M2 (sampled half-yearly) and from 2006 in M4 (sampled monthly). PPU was also found in low concentrations in M7, which receives water from the upstream neighbouring field (Figure 9 and Figure 15). The PPU found in this well likely originated from the neighbouring upstream fields. This is because the tracer test suggested that water sampled in M7 had not infiltrated at the PLAP site, and because rimsulfuron was also applied at the neighbouring upstream area (Kjær et al. 2007). In addition to the leaching observed at the PLAP site, this result thus indicates that leaching also occurred in the neighbouring upstream field. Furthermore, PPU-desamino was detected in monitoring wells, the number of detections and concentration level being lower than that of PPU-desamido, however (Figure 15C and Table A5.2 in Appendix 6).

Finally, it should be noted that the concentration of PPU is likely to be underestimated by 14 - 47% (Kjær *at al.* 2007) due to stability problems as described in Section 3.1.3.

Bentazone did leach from the root zone. A concentration reaching 1.6 µg/l was found in suction cups of S2 only two months after application and concentrations exceeding 0.1 µg/l were seen four months after application. Following this, the leaching decreased with measured concentrations all being below 0.1 µg/l (Figure 16). The rapid transport, which allowed the high concentration of bentazone to be found only two months after application, did not occur in the suction cups at S1.

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. The metabolite AIBA was only found in S2 on two occasions during the period with high leaching of bentazone in July to August 2004.

The leaching risk of the five pesticides applied during the 2005 growing season (*ioxynil, bromoxynil, amidosulfuron, fluroxypyr, azoxystrobin* and its metabolite *CyPM)* was found to be negligible. Apart from three samples (soil water sampled in suction cups at S2 in June – August 2005) containing 0.012; 0.7 and 0.11 µg/l amidosulfuron, none of these compounds have yet been detected. It should be noted that the findings on amidosulfuron are of very limited use since its degradation products – with which the leaching risk is mainly associated – are not included, as methods for their analysis are not yet available.

The pesticides used on spring barley in 2006 have not yet been found in any of the analysed water samples. The final evaluation awaits an additional year of monitoring.

Table 7. Percolation together with estimated average concentrations (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 1.7.02–30.6.07.

	Percolation	PPU		PPU-desamido	
	(mm/y)	Suction cup – S1	Suction cup – S2	Suction cup – S1	Suction cup – S2
1.7.02–30.6.03	706	0.13	0.06	0.03-0.04	0.02-0.03
1.7.03–30.6.04	468	0.12	0.10	0.04	0.04
1.7.04–30.6.05	759	0.10	0.14	0.03	0.05
1.7.05–30.6.06	465	0.07	0.09	<0.02	<0.02
1.7.06–30.6.07	815	0.05	0.08	0.02	0.02
Leached mass[1)]		45-65%	47-54%	18-19%	17-20%

[1)] *Expressed as rimsulfuron equivalent.*

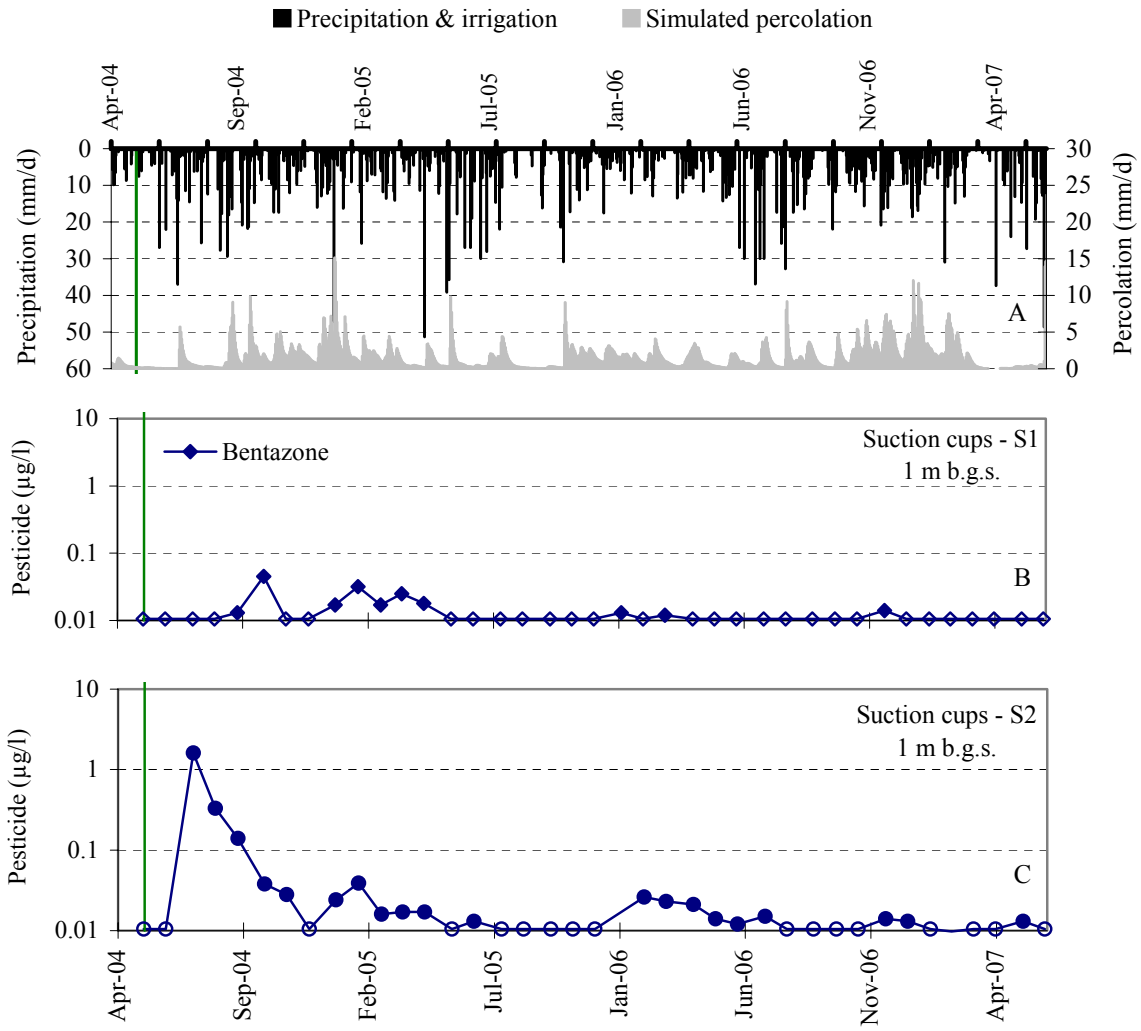

Figure 16 Precipitation, irrigation and simulated percolation 1 m b.g.s. (A) together with measured concentrations of bentazone at Jyndevad (B & C). The measured data derive from suction cups installed 1 m b.g.s. at locations S1 and S2 (see figure 9). The green vertical line indicates the date of pesticide application. Open circles and squares indicate concentrations below the detection limit of 0.01 µg/l.

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 17). 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 and 26%, and the organic carbon content was 3.4 and 2.8%, respectively, Table 1. 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 2005 - 2006 growing seasons is briefly summarized below and detailed in Appendix 3 (Table A3.3). For information about management practice during the previous monitoring periods see Kjær *et al*. (2002, 2003, 2004, 2005c & 2007).

On 23 April 2005, the day before the sowing of spring barley (cv Cabaret), pig slurry was applied by injection. The barley emerged on 7 May. On 27 May, when two tillers were detectable, the herbicide fluroxypyr was applied. When 20% of the inflorescence had emerged on 30 June, the crop was sprayed with the fungicide azoxystrobin. The pesticide pirimicarb was applied against aphids on 14 July when the first grains had reached half their 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 trailer hose application of pig slurry on 29 August 2005, the field was ploughed and sown with winter rape (cv. Calypso) on 1 September. Before the emergence of the rape, the herbicide clomazone was sprayed onto the bare soil. On 17 November, when the rape had six unfurled leaves, the herbicide propyzamide was applied. On 20 April 2006, when the rape had nine visible internodes, the herbicide clopyralid was used. Pest control was performed on 5 May using alpha-cypermethrin. However, this substance was not included in the monitoring programme. The crop was fertilised with 23.8 t/ha pig slurry on 26 April 2006. On 24 July, when nearly all pods had reached the final size, the crop was windrowed. The crop was threshed on 7 August, yielding 37.3 hkg/ha of seeds (91% dry matter), a yield similar to the average on this type of soil within the region (Plantedirektoratet. 2006). All of the straw, 67.7 hkg/ha 100% dry matter, was shredded on the day of harvest. The field was ploughed on 20 September and two days later sown with winter wheat (cv. Skalmeje) as well as sprayed with the herbicide pendimethalin.

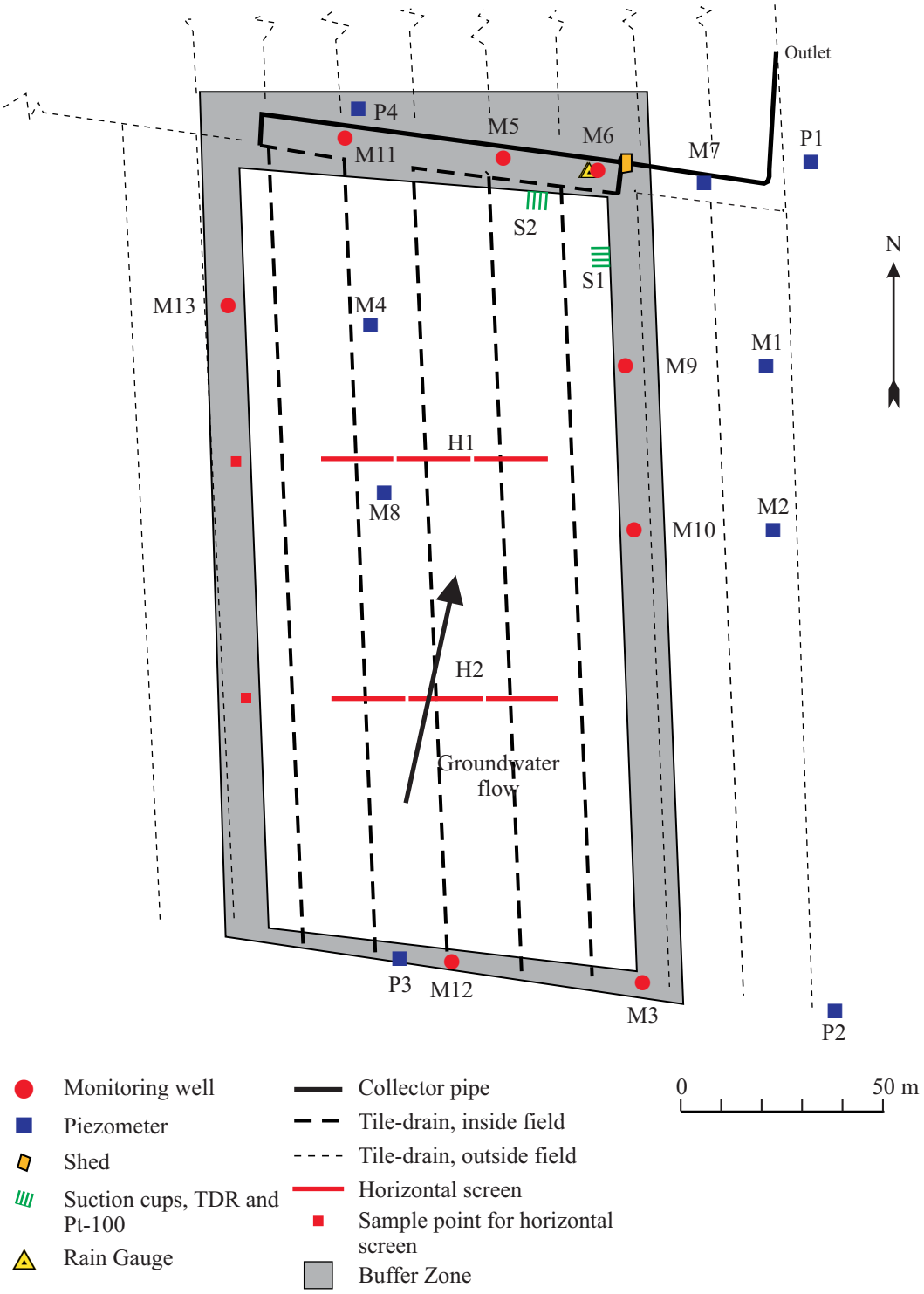

Figure 17. Overview of the Silstrup site. The innermost white area indicates the cultivated land, while the grey area indicates the surrounding buffer zone. The positions of the various installations are indicated, as is the direction of groundwater flow (by an arrow).

4.1.3 Model set-up and calibration

The numerical model MACRO (version 5.1, Larsbo *et al.* (2005)) was applied to the Silstrup site covering the soil profile to a depth of 5 m b.g.s., always including the groundwater table. The model is used to simulate the water flow in the unsaturated zone during the full monitoring period April 2000–June 2007 and to establish an annual water balance.

Compared with the setup in Kjær et al. (2007), a year of validation was added to the MACRO-set-up for the Silstrup site. The set-up was hereby calibrated for the monitoring period May 1999-June 2004 and validated for the monitoring period July 2004-June 2007. 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 17), and the measured drainage flow. Data acquisition, model set-up and results related to simulated bromide transport are described in Barlebo *et al.* (2007) and Rosenbom *et al.* (In prep.). Given impounding of water in the drainwater monitoring well, estimates for the measured drainage on 11 December 2006, 13 – 14 December, 2006 and 28 February 2007 were based on expert judgment.

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 18). As in Kjær *et al.* (2007), the simulated groundwater table of this hydraulic year was validated against the much more fluctuating groundwater table measured in piezometer P3, which yielded the best description of measured drainage (Figure 18B and 18C). The earlier reported delay in the initial increase in simulated drainage flow was still present in October and January (Figure 18C). As in the previous monitoring periods, the overall trends in soil water content were described reasonably well (Figure 18D, 18E, and 18F), though the model still tended to describe the subsoil as being much dryer during the summer period than measured by the deeper TDR probes (Figure 18E and 18F).

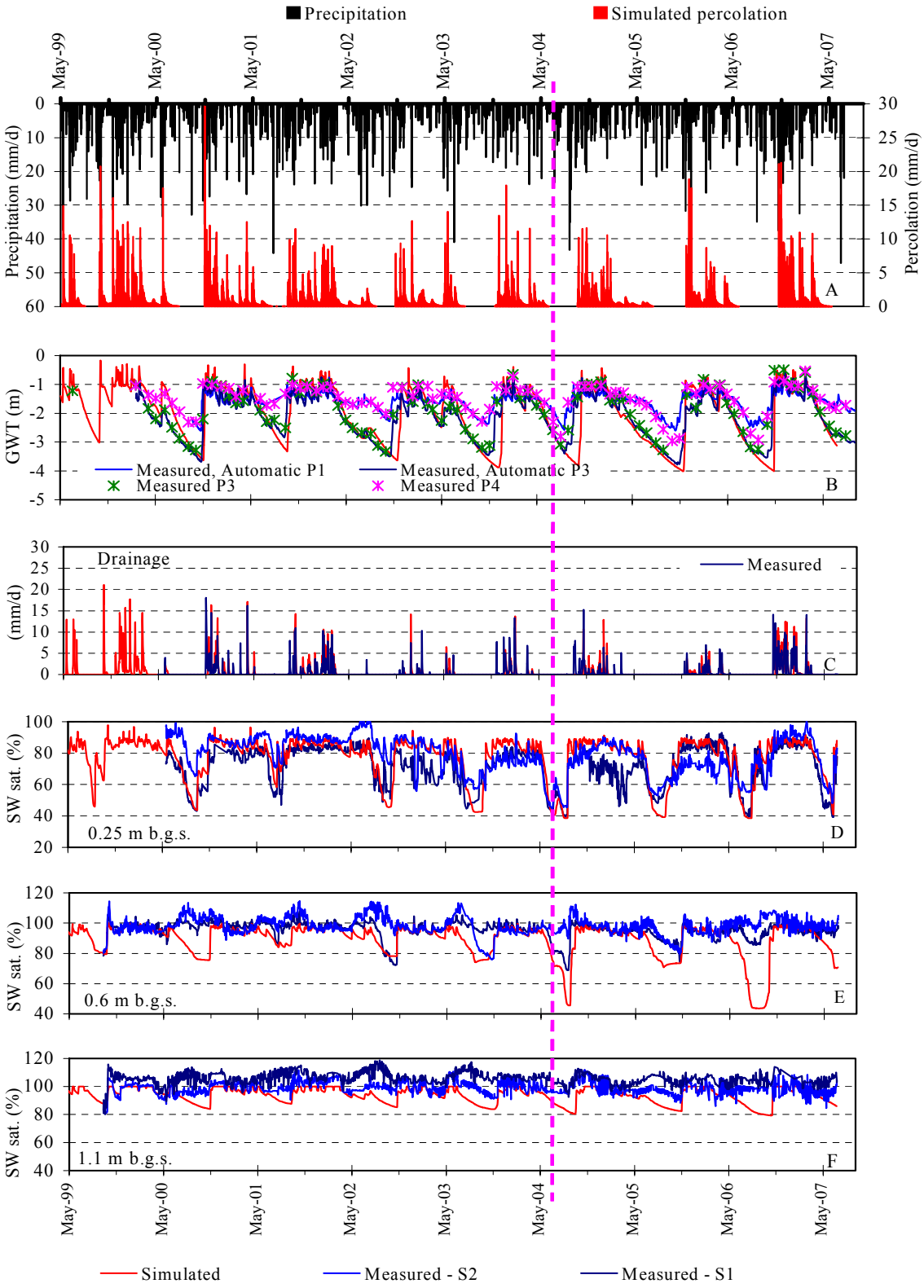

Figure 18. Soil water dynamics at Silstrup: Measured precipitation and simulated percolation 1 m b.g.s. (A), simulated and measured groundwater level GWT (B), simulated and measured drainage flow (C), and simulated and measured soil water saturation (SW sat.) at three different soil depths (D, E and 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 17). The broken vertical line indicates the beginning of the validation period (July 2004- June 2007).

Table 8. 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 evapotranspiration	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
1.7.06–30.6.07	976	1150	539	361	307	249

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

Hydraulic conductivity and water content were 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.*, 2007).

The resulting water balance for Silstrup for the eight monitoring periods is shown in Table 8. Compared with the previous seven years, the latest hydraulic year July 2006-June 2007 was characterised by having the second highest precipitation, the highest simulated actual evapotranspiration and the highest measured drainage. Precipitation in this year was characterized by July and April being very dry and October-December and June being very wet (Appendix 4). Due to this precipitation pattern, the simulated percolation pattern of the year July 2006-June 2007 was similar to the pattern of earlier years in the monitoring period, and was represented by continuous percolation throughout the period October-April (Figure 18A), leaving the summer months without percolation. The climatic setting of this year gave rise to long periods with groundwater table above drainage level causing the largest measured drainage since monitoring started in July 2000 (Figure 18B and 18C). Apart from small differences in measured and simulated yearly amount of drainage, the overall pattern of drainage levels in the hydraulic years was captured.

4.2.2 Bromide leaching

The bromide concentrations shown in Figure 19 and Figure 20 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.* (2007).

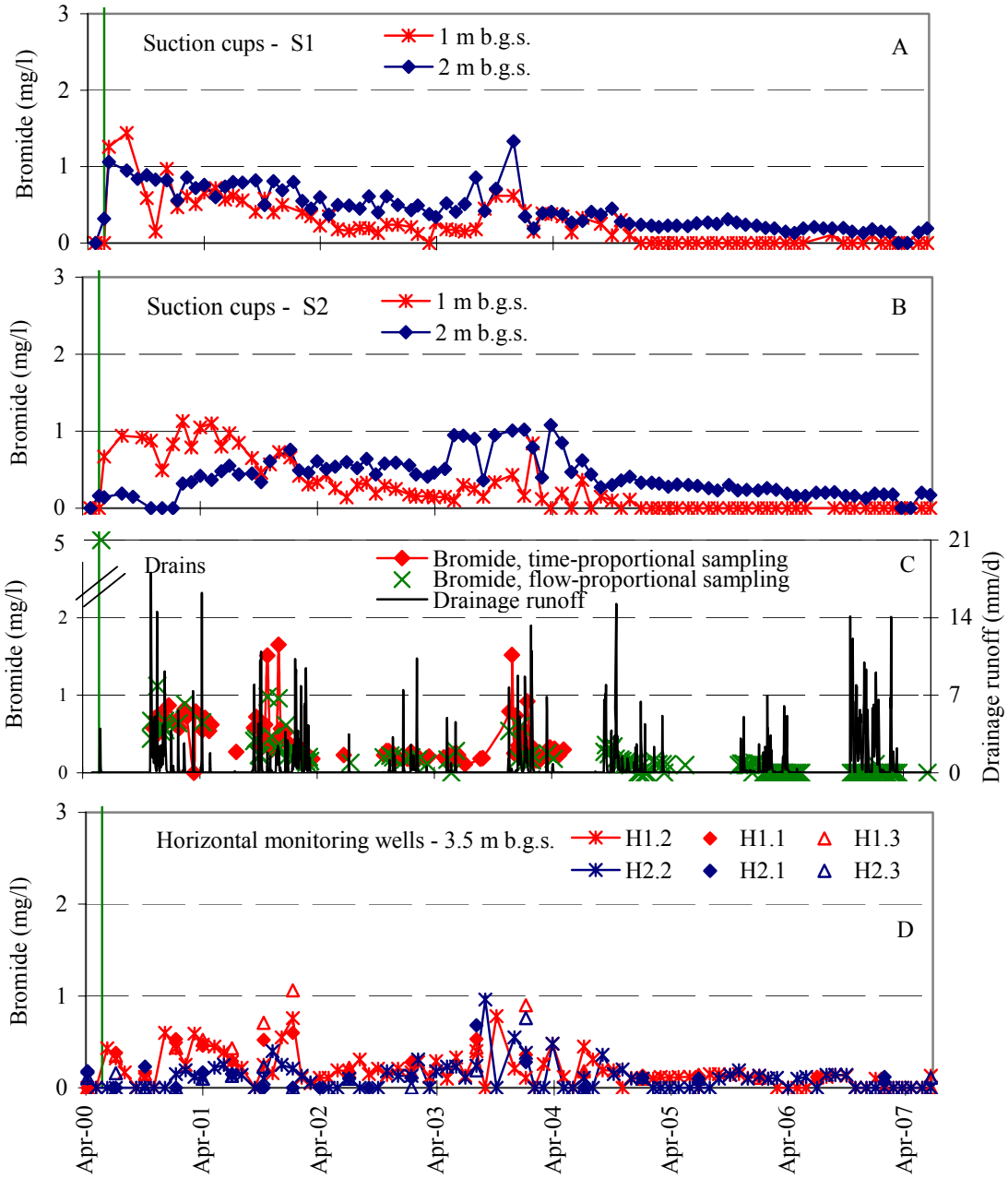

Figure 19. Bromide concentration at Silstrup. A and B refer to suction cups located at S1 and S2. The bromide concentration is also shown for drainage runoff (C) and the horizontal monitoring wells H1 and H2 (D). The green vertical line indicates the date of bromide application.

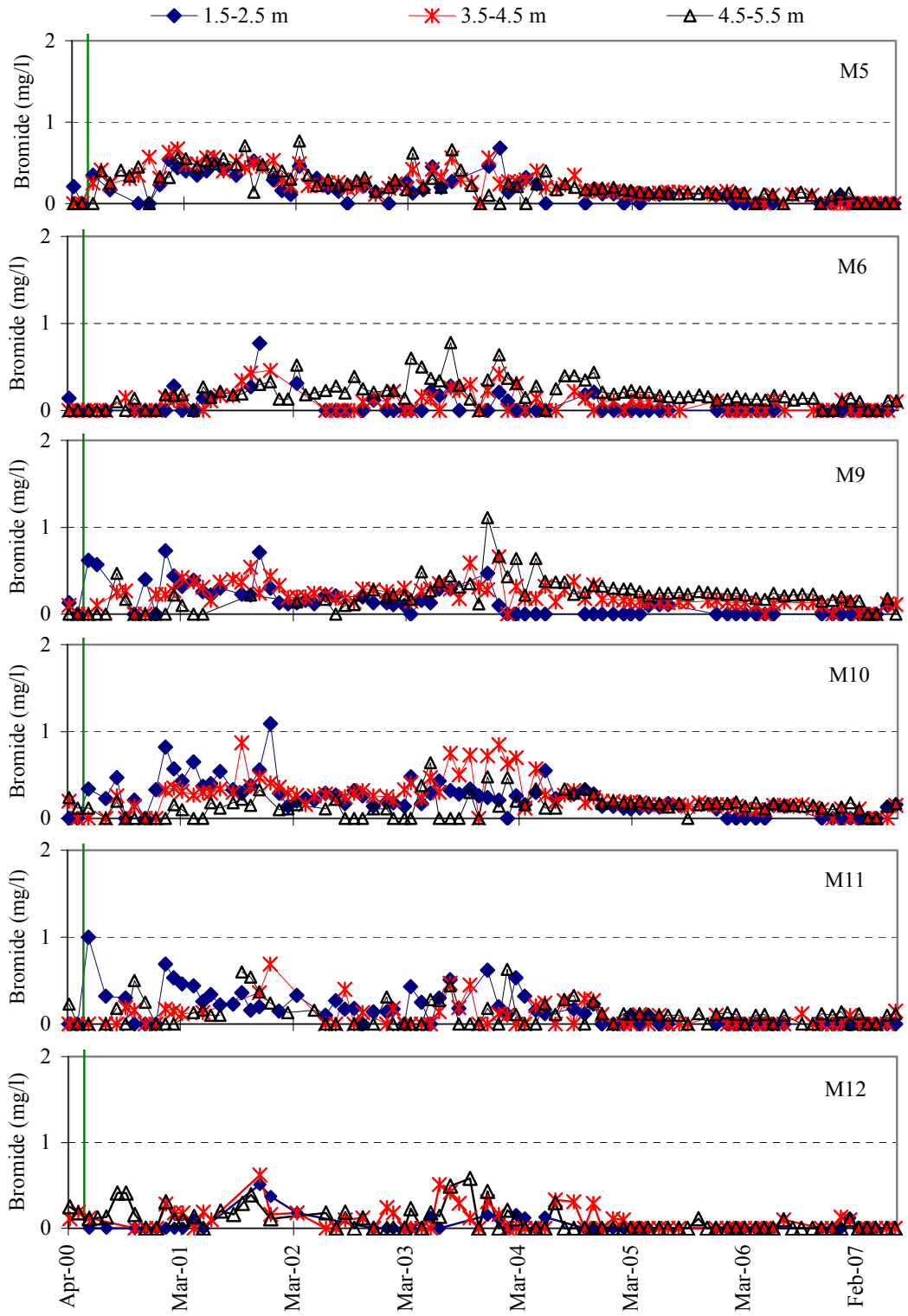

Figure 20. Bromide concentration at Silstrup. The data derive from the vertical monitoring wells (M5–M12). Screen depth is indicated in m b.g.s. The green vertical line indicates the date of bromide application.

4.2.3 Pesticide leaching

Monitoring at Silstrup began in May 2000 and presently encompasses several pesticides and their degradation products, Table 9. Pesticide application during the two most recent growing seasons is shown together with precipitation and simulated precipitation in Figure 21. It should be noted that precipitation in Table 9 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 9).

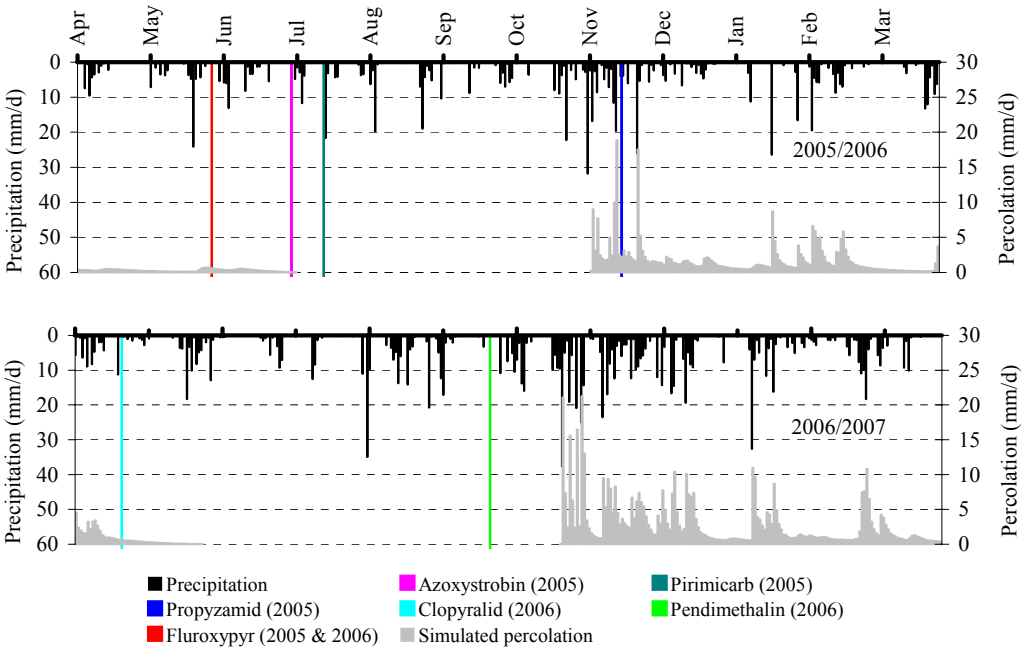

Figure 21. Pesticide application, precipitation and irrigation (primary axis) and simulated percolation 1 m b.g.s. (secondary axis) at Silstrup in 2005/2006 (upper) and 2006/2007 (lower).

Table 9. 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 07	6452	2825	1	<0.01 (17*)
- pirimicarb-desmethyl						<0.01 (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.
** Pesticide has been applied more than once, and the findings are not necessarily related to one specific application.*

Table 9 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 07	2931	1202	0	0.09 (62*)
Pirimicarb (Pirimor G)	Jul 04	Jul 07	2818	1205	0	<0.01 (17*)
- *pirimicarb-desmethyl*						<0.01 (1*)
- *pirimicarb-desmethyl-formamido*						<0.02 (0)
Spring barley 2005						
Fluroxypyr (Starane 180)	May 05	Jul 07	2012	830	11	<0.02 (0)
Azoxystrobin (Amistar)	Jun 05	Jul 06	862	332	10	0.01 (6*)
- *CyPM*	Jun 05	Jul 07	2012	828	10	0.02 (62*)
Pirimicarb (Pirimor G)	Jul 05	Jul 07	1933	818	0	<0.01 (17*)
- *pirimicarb-desmethyl*						<0.01 (1*)
- *pirimicarb-desmethyl-formamido*						<0.01 (0*)
Winter rape 2006						
Propyzamide (Kerb 500 SC)	Nov 05	Jul 07†	1601	760	75	0.22 (32) 1)
- *RH-24644*						0.01 (17) 1)
- *RH-24580*						<0.01 (2) 1)
- *RH-24655*						<0.01 (0) 1)
Clopyralid (Matrigon)	Apr 06	Jul 07†	1265	503	8	<0.01 (0)
Pendimethalin (Stomp)	Sep 06	Jul 07†	942	509	0	<0.04 (14)

** Pesticide has been applied more than once, and the findings are not necessarily related to one specific application.*
1) Drainage runoff commenced two weeks prior to the application of propyzamide, and the weighted concentrations refer to the period from the date of application until 1 July 2007.
† Monitoring will continue for an additional year. The values for prec. and perc. are accumulated up to July 2007.

The leaching risk of pesticides applied during 2000, 2001, 2002, 2003 and 2004 has been evaluated in Kjær *et al.* (2002, 2003, 2004, 2005c & 2007), respectively.

The insecticide *pirimicarb*, was applied in July 2000, 2004 and in July 2005. While minor leaching of pirimicarb was observed after the application in 2000 (Kjær *et al.* , 2003), the two latter applications (2004, 2005) did not induce any leaching. Neither pirimicarb itself nor its two metabolites, pirimicarb-desmethyl and pirimicarb-desmethyl-formamido, were found in any of the water samples taken after the two latter applications (Table 9, Table A5.3 in appendix 5).

The herbicide *fluroxypyr* applied in May 2005 has not been detected in any of the analysed water samples.

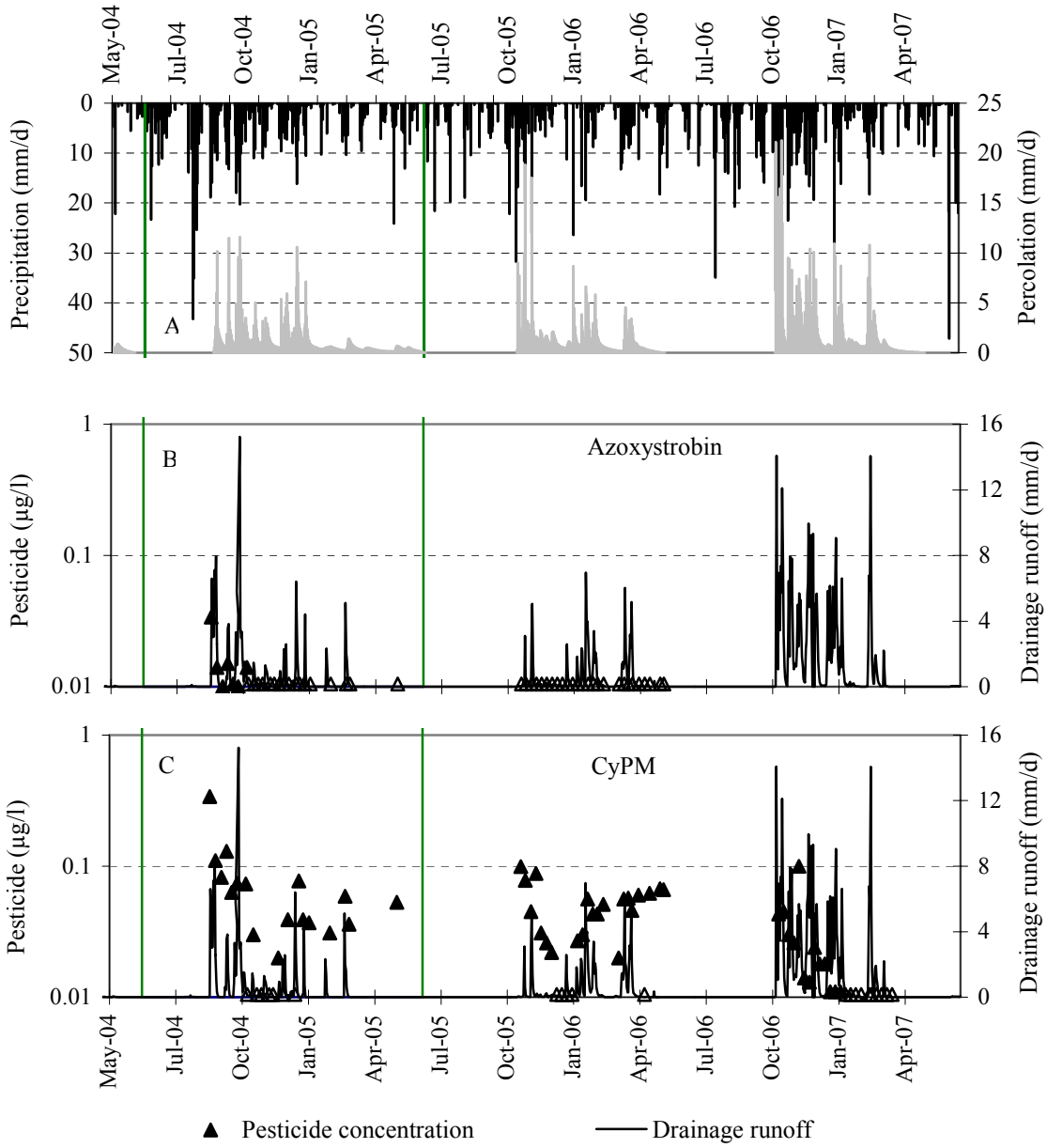

Figure 22 Precipitation and simulated percolation 1 m b.g.s. (A) together with the concentration of azoxystrobin (B) and CyPM (C) in the drainage runoff at Silstrup. The green vertical line indicates the date of azoxystrobin application. Open diamonds indicate values below the detection limit of 0.01 µg/l.

Figure 22 illustrates the findings in drainage water of *azoxystrobin* and its metabolite *CyPM***.** Azoxystrobin was applied twice: on 14 June 2004 and 30 June 2005. On neither occasion was there any drainage water flow when spraying. Azoxystrobin as well as CyPM were found in the first samples of drainage water taken mid September after the first application. Following the second application only CyPM was found. The maximum concentration of azoxystrobin (0.034 µg/l) and CyPM (0.34 µg/l) was measured at the initial sampling in 2004. After the application in June 2004, six of the samples contained azoxystrobin, whereas none of the samples held detectable amounts of azoxystrobin after the second application in the June 2005. Both applications of azoxystrobin caused leaching of the metabolite CyPM. Concentrations in drainage water followed the same pattern with a high initial content followed be a steep drop, and finally a rise to a somewhat higher

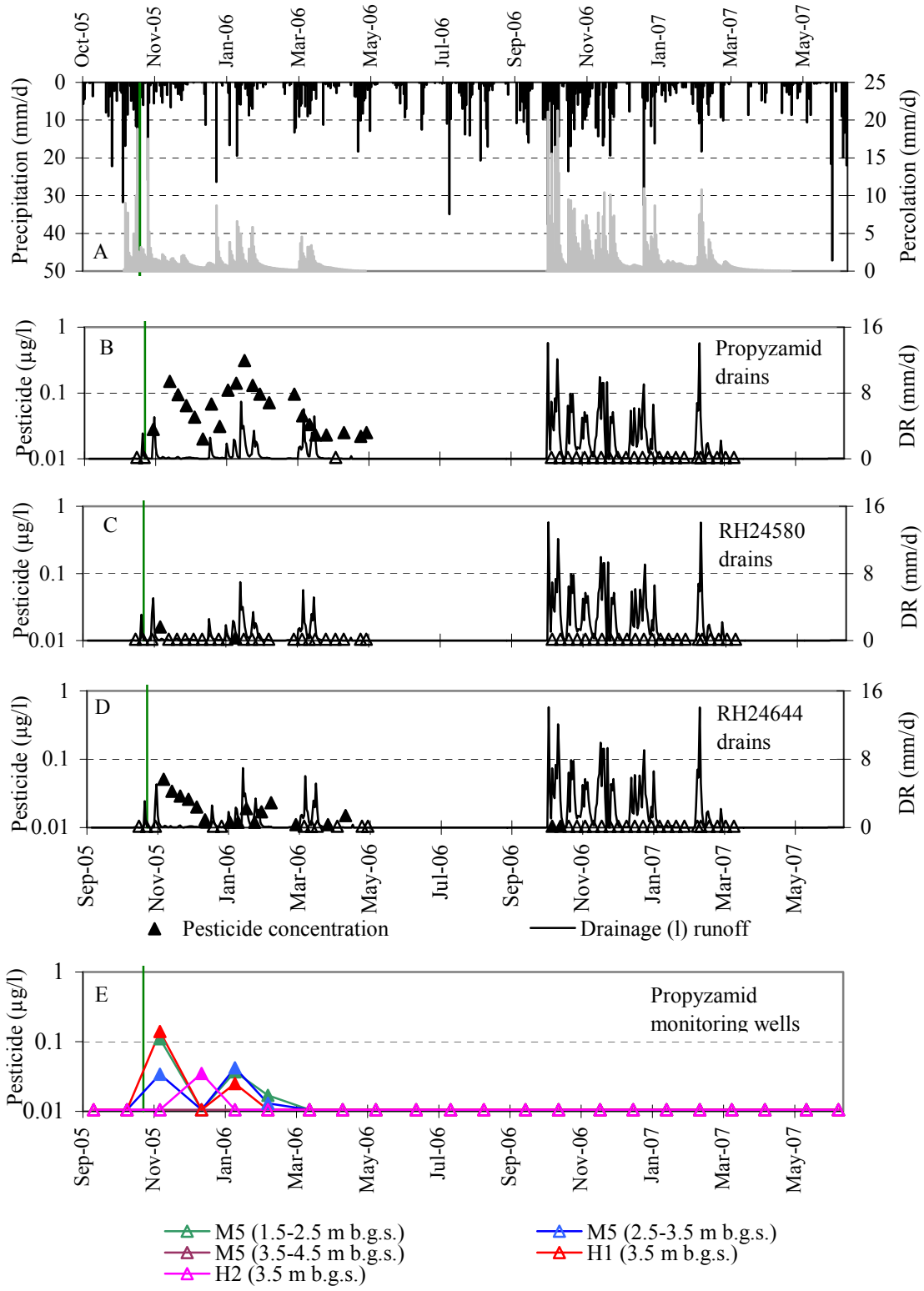

Figure 23. Precipitation and simulated percolation 1 m b.g.s. (A) together with the concentration of propyzamide (B), RH24580 (C) and RH 24644 (D) in the drainage runoff at Silstrup. The concentration of propyzamide in monitoring well M5, H1 and H2 is given in E, the numbers in parentheses indicating the screen depth. Open diamonds indicate values below the detection limit of 0.01 µg/l. The green vertical line indicates the date of propyzamide application.

level-(Figure 22C). Although the initial leaching was marked, the average, yearly concentrations did not exceed the 0.1µg/l in either of the two years, Table 9. Whereas azoxystrobin has not been found in groundwater, CyPM has been detected twice in a horizontal groundwater monitoring screen at 0.036 and 0.016 µg/l on 2 November 2006 and 7 December 2006, respectively. In the uppermost screens of the vertical monitoring well M5 (depth 1.5 – 2.5 m b.g.s.) CyPM has been found in four of nine samples taken between 1 December 2005 and 7 December 2006, concentrations ranging between 0.022 and 0.051 µg/l. In well M5.2 (2.5-3.5 m b.g.s.) concentrations were in the range 0.01 to 0.032 µg/l within the period 6 April 2006 to 4 January 2007, with four of nine samples being positive. At the 3.5-4.5 m depth there was a single detection of 0.01 µg/l on 1 March 2007. None of the data from groundwater are shown, but the number of analysed samples and detections are given in Table 5.3 in Appendix 5.

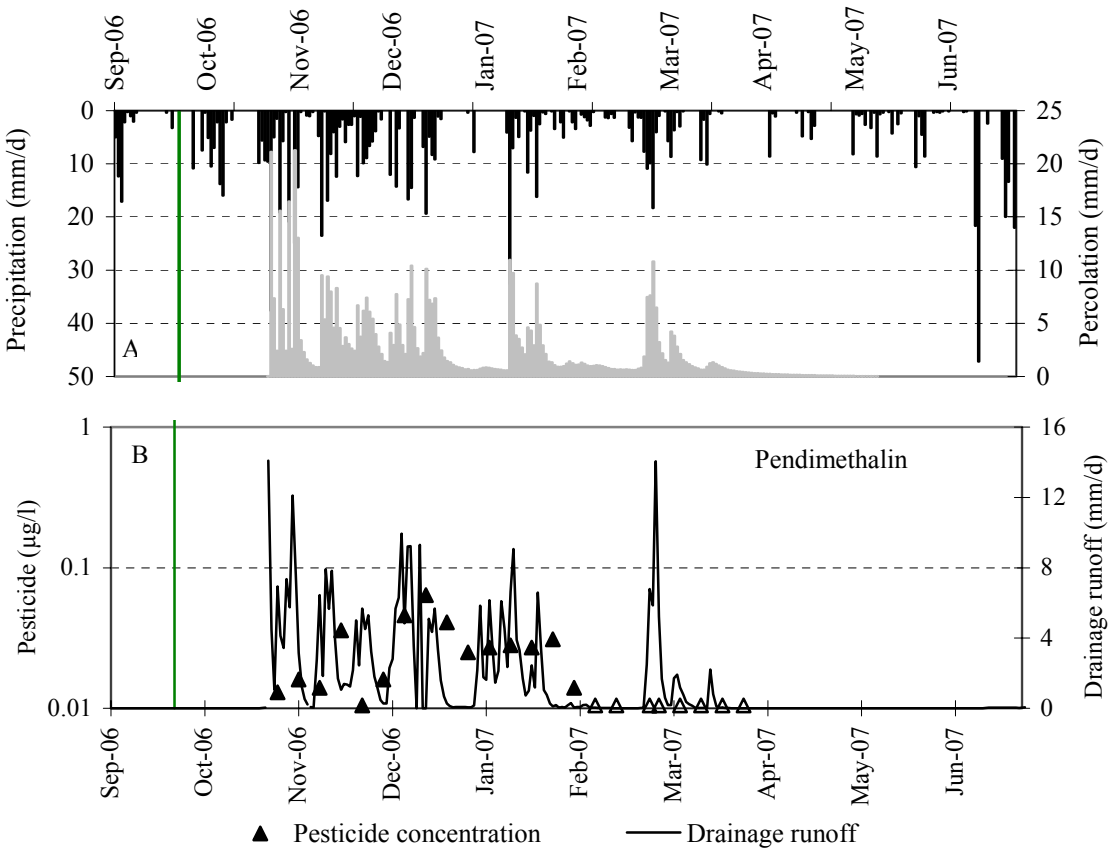

Figure 24. Precipitation and simulated percolation 1 m b.g.s. (A) together with the concentration of pendimethalin (B) in the drainage runoff at Silstrup. The green vertical line indicates the date of pendimethalin application. Open diamonds indicate values below the detection limit of 0.01 µg/l.

Propyzamide, a herbicide applied late autumn/beginning of the winter 2005, together with its three metabolites RH24580, RH 24644 and RH24655, has now been monitored for nearly two years. Figure 23 shows that leaching from the root zone to the drainage system in particular relates to propyzamide (Figure 23B), followed by RH24644 (Figure 23D) and RH 24580 (Figure 23C). The metabolite RH24655 was not detected at all. Only propyzamide concentrations exceeded the 0.1µg/l limit (Figure 23B). The only metabolite detected in groundwater was RH24644 (data not shown) on 1 December 2005 at 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.). Propyzamide was found in groundwater nine times, Figure 23E. The limit of 0.1µg/l was exceeded twice, both samples taken on 1 December 2005 (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.). It should be noted that drainage runoff commenced two weeks prior to the

application of propyzamide. The weighted concentrations given in Table 9 refer to the period from the date of application until 1 July 2007, whereas the average concentration for a 12-month period amounted to 0.1 µg/l for propyzamide.

The leaching risk of pesticides applied in 2006 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 clopyralid did not leach during the first year following application, whereas leaching of pendimethalin was observed as illustrated in Figure 24 and Appendix 5 (Table A5.3).

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 Weichselian Glaciation. Estrup has thus been exposed to weathering, erosion, leaching and other geomorphological processes for a much longer period than the other sites. The test field covers a cultivated area of 1.26 ha (105 x 120 m) and is virtually flat (Figure 25). 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 a clay content of 10–20% and an organic carbon content of 1.7–7.3%. A C-horizon of low permeability also characterizes the site. 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 2005 - 2006 growing seasons is briefly summarized below and detailed in Appendix 3 (Table A3.4). For information about management practice during the previous monitoring periods see Kjær *et al*. (2002, 2003, 2004, 2005c & 2007).

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 was sprayed at emergence on 26 May with the herbicide terbutylazine. A mixture of terbutylazine and bentazone was used when four leaves had unfurled on 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 strongly sorbing glyphosate compounds, pendimethalin and a tracer of bromide were applied on 9 November. The joint application of the two substances was done for scientific reasons rather than as common agricultural practice. Whereas glyphosate was applied in accordance with the regulations, pendimethalin was not. The result related to the application of pendimethalin is therefore not included in this report, but will be published in a forthcoming scientific publication.

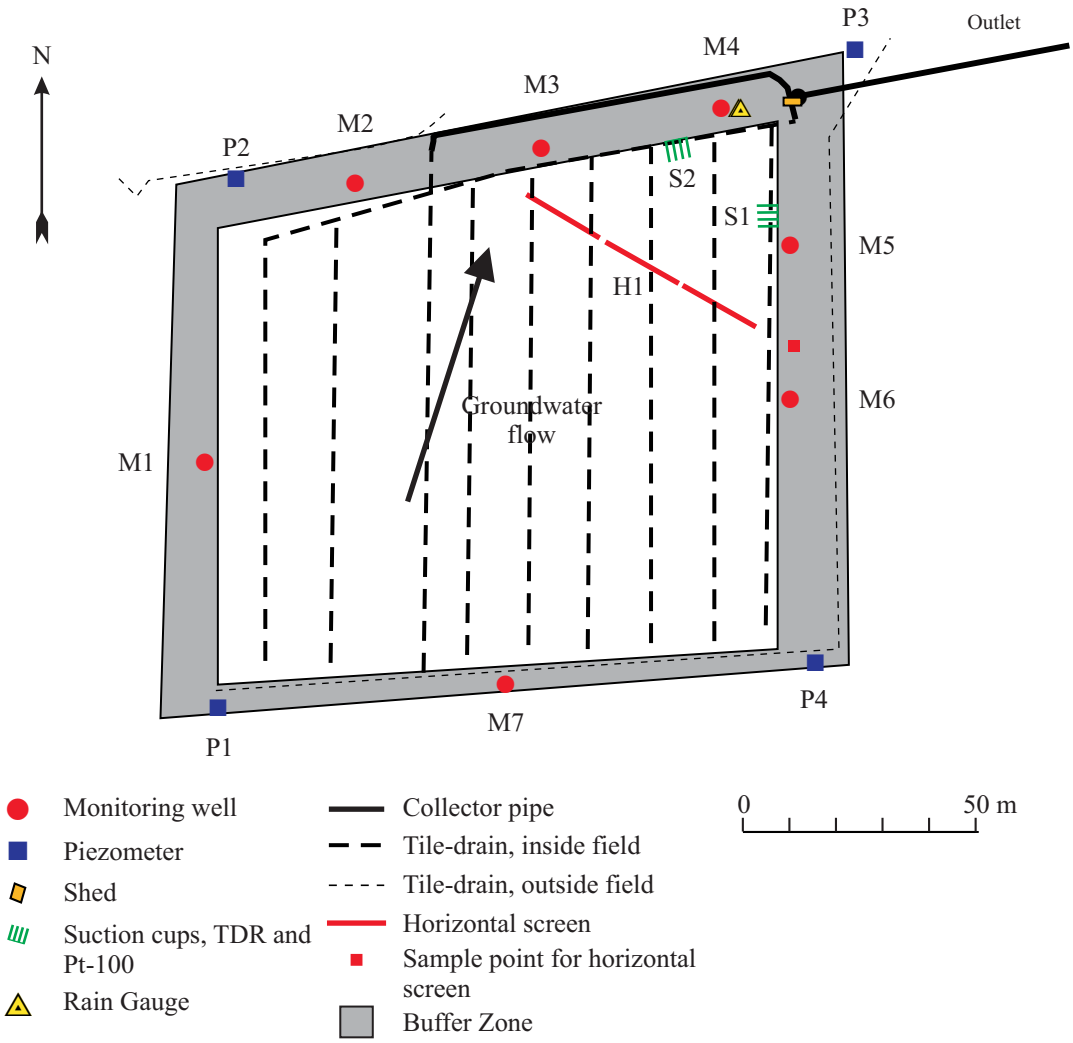

Figure 25. Overview of the Estrup site. The innermost white area indicates the cultivated land, while the grey area indicates the surrounding buffer zone. The positions of the various installations are indicated, as is the direction of groundwater flow (by an arrow).

Ploughing of the field took place on 12 April 2006 and on 27 April spring barley was sown (cv. Simba), which emerged on 6 May. Weeds were treated twice with fluroxypyr on 17 May and 2 June, but the substance was not included in the monitoring. On 6 June, at the beginning of stem elongation, the herbicide florasulam was applied. On 29 June at 70% emergence of inflorescence, the fungicide azoxystrobin was used. The amount of grain harvest on 17 August was 59.2 hkg/ha, a roughly average yield (Plantedirektoratet, 2006). Straw, 26.8 hkg/ha, was removed on 11 September and two days later the field was ploughed. On 14 September winter wheat (cv. Smuggler) was sown.

5.1.3 Model set-up and calibration

The numerical model MACRO (version 5.1, Larsbo *et al.* (2005)) was applied to the Estrup site covering the soil profile to a depth of 5 m b.g.s., always including the groundwater table. The model is used to simulate the water flow in the unsaturated zone during the monitoring period from July 2000–June 2007 and to establish an annual water balance.

Compared to the setup in Kjær *et al.* (2007), a year of validation was added to the MACRO-set-up for the Estrup site. The set-up was hereby calibrated for the monitoring period May 1999-June 2004 and validated for the monitoring period July 2004-June 2007. 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 25). 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.* (2007) 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 26). The model provided an acceptable simulation of the overall level of the groundwater table. A drop in measured groundwater table was seen after short periods of low precipitation (Figure26B). 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. However, the overall soil water saturation at 25 and 40 cm b.g.s. was captured excluding periods with drastic drops in the level of saturation (Figure 26D and 26E). Especially the water saturation drop in April-June 2007 was not captured. Nothing special is noted for the groundwater table in the latest monitoring period (July 2006–June 2007). As in previous years (Kjær *et al.*, 2007), the simulated groundwater table often fluctuates slightly above the drain depth during periods of drainage flow.

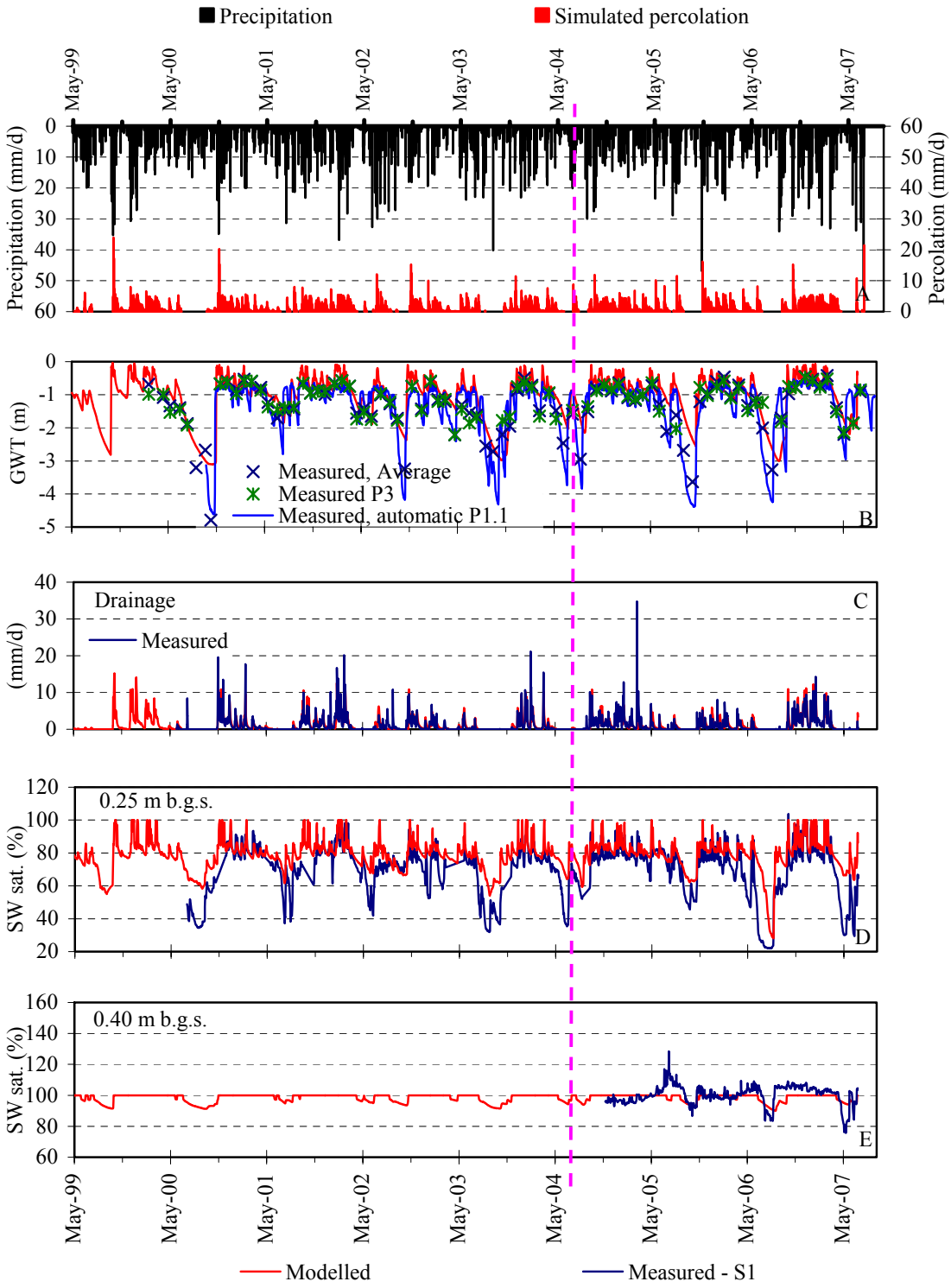

Figure 26. Soil water dynamics at Estrup: Measured precipitation and simulated percolation 0.6 m b.g.s. (A), simulated and measured groundwater level (B), simulated and measured drainage flow (C), and simulated and measured soil saturation (SW sat.) at two different soil depths (D and E). The measured 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 25). The broken vertical line indicates the beginning of the validation period (July 2004- June 2007).

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

	Normal precipitation [2)]	Precipitation	Actual evapotranspiration	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
1.7.06–30.6.07	968	1365	515	547	618	303

[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 26C) matched the measured drainage flow quite well. Drainage runoff over the whole monitoring period was high compared to that of the other two till sites being investigated in the PLAP. This was due to a significantly lower permeability of the C-horizon than of the overlying A and B horizons (se Kjær *et al.* 2005c for details).

The resulting water balance for Estrup for the eight monitoring periods is shown in Table 10. Compared with the previous seven years, the latest hydraulic year July 2006-June 2007 was characterised by having the highest precipitation, the second highest simulated actual evapotranspiration and the highest measured and simulated drainage. Precipitation in this year was characterized by July and April being very dry and August, October-January and May-June being very wet (Appendix 4). Due to this precipitation pattern, the simulated percolation pattern of the year July 2006-June 2007 was similar to the pattern of earlier years in the monitoring period, and was represented by continuous percolation throughout the period September-Marts (Figure 26A), leaving the summer months with spatial periods of percolation. The climatic setting of this year gave rise to periods with groundwater table high above drainage level causing the largest measured drainage since July 2000 (Figure 26B and 26C). Apart from small differences in measured and simulated yearly amount of drainage, the overall trend in drainage amount pattern of the hydraulic years was captured.

5.2.2 Bromide leaching

Bromide has now been applied twice at Estrup. The bromide concentrations measured up to October 2005 (Figure 27 and Figure 28) 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.).

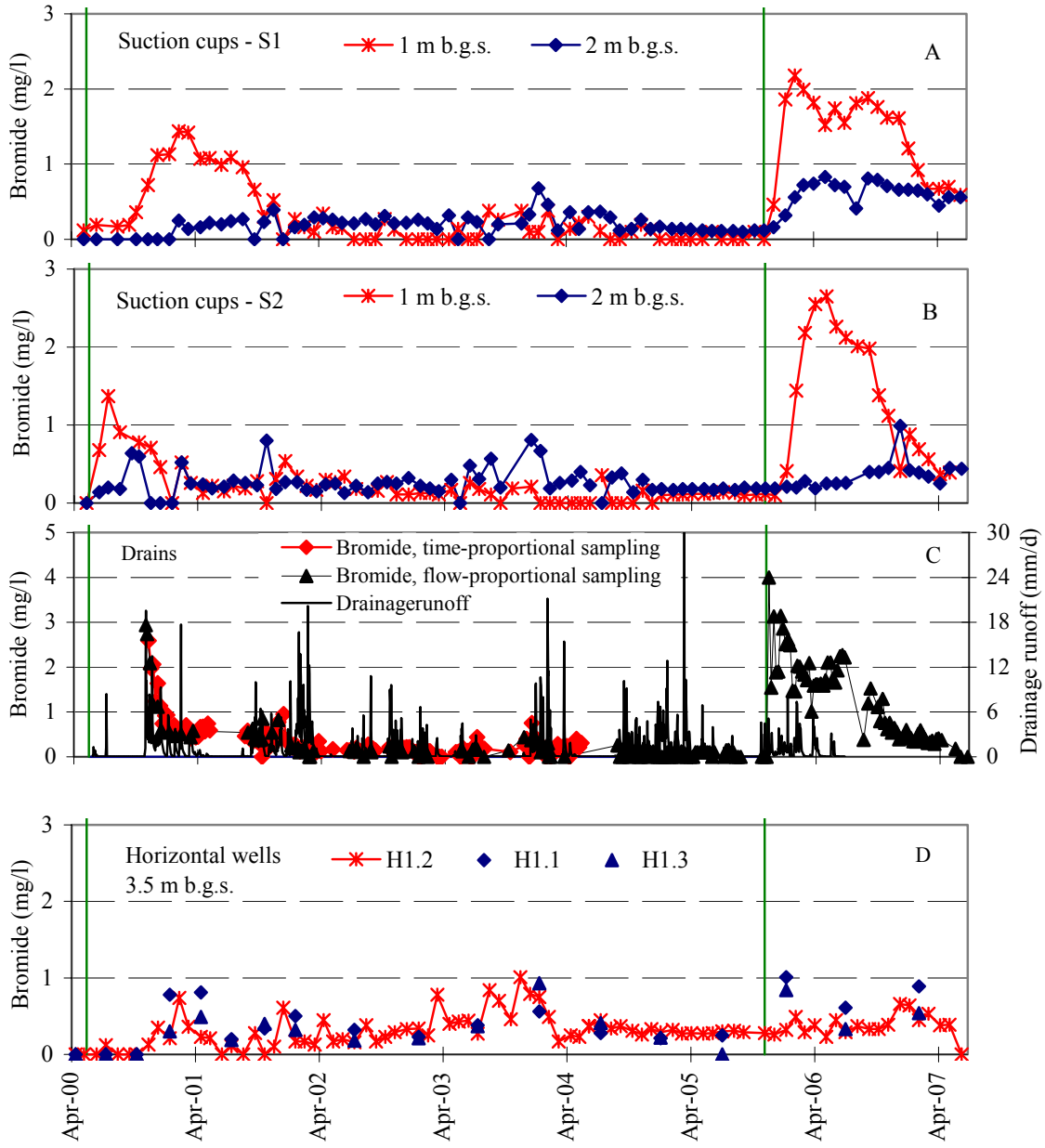

Figure 27. Bromide concentration at Estrup. A and B refer to suction cups located at S1 and S2, respectively. The bromide concentration is also shown for drainage runoff (C) and the horizontal monitoring well H1 (D). The green vertical lines indicate the dates of bromide applications.

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 11. Pesticide application during the two most recent growing seasons (2005 – 2006) is shown together with precipitation and simulated precipitation in

Figure 29. It should be noted that precipitation 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 11.

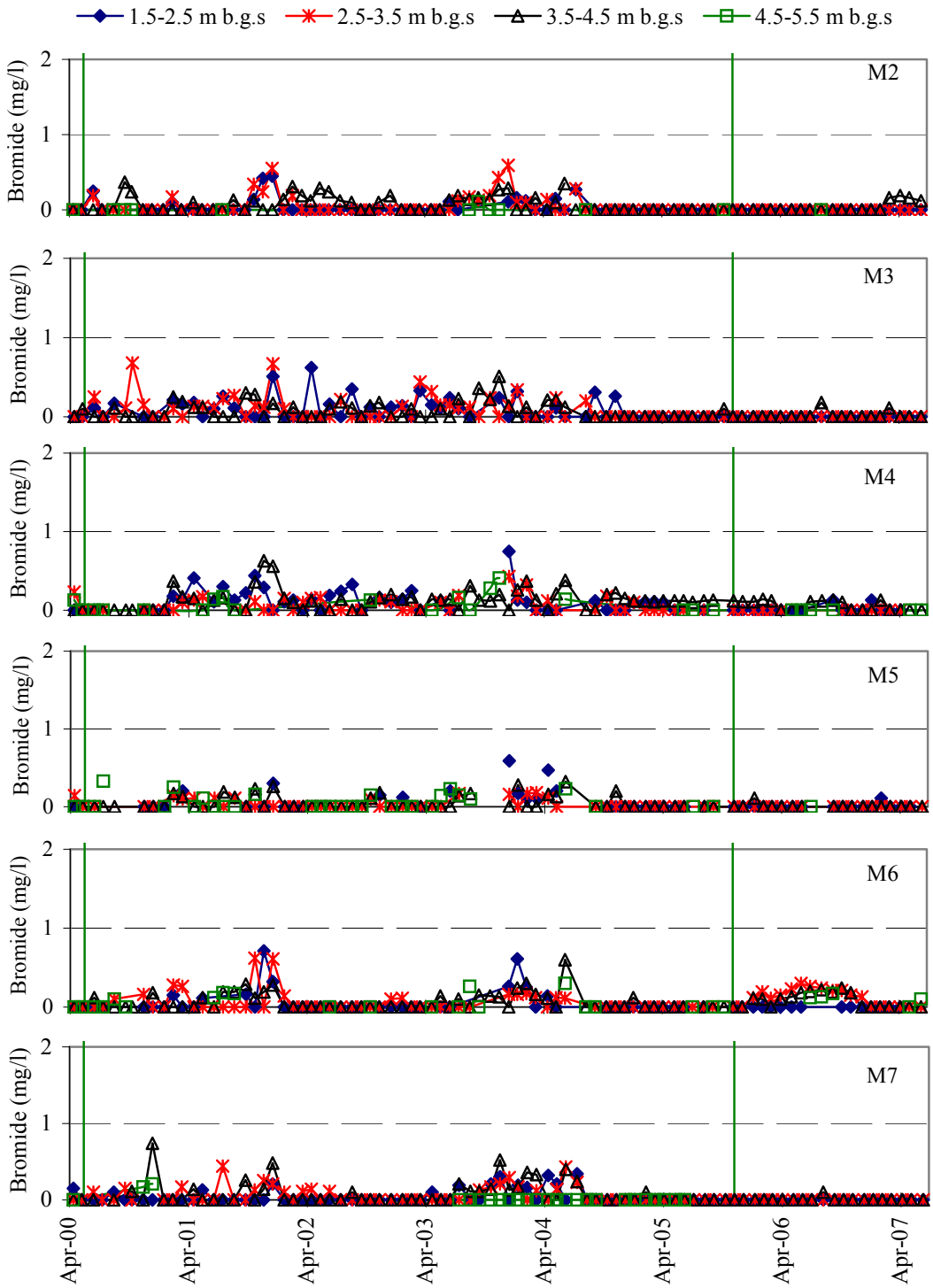

Figure 28. Bromide concentration at Estrup. The data derive from the vertical monitoring wells (M2–M7). Screen depth is indicated in m b.g.s. The green vertical lines indicate the dates of bromide applications.

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

Crop and analysed pesticides	Application 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 07†	7177	3479	123	0.54(232*)
- *AMPA*						0.17(283*)
Bentazone (Basagran 480)	May 01	Jul 07†	6580	3063	9	0.03 (125)
- *AIBA*						<0.01 (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.
** Pesticides 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.

The leaching risk of pesticides applied during 2000, 2001, 2002, 2003 and 2004 has been evaluated in Kjær *et al.* (2002, 2003, 2004, 2005c & 2007).

Terbutylazine and bentazone were applied during the growing of maize in 2005. Applied pesticides and all measured metabolites leached (Figure 30, 31 and 32).

Terbutylazine, desethyl-terbutylazine, 2-hydroxy-desethyl-terbutylazine and 2-hydroxy-terbutylazine were leached in high average concentrations (>0.1µg/l), while desisopropyl-atrazine was found frequently but in low concentrations (Table 11, Figure 31) .

Table 11 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 07†	4983	2402	0	0.43(232*)
- *AMPA*						0.19(283*)
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 07†	3402	1650	38	0.12 (61*)
- *CyPM*						0.23 (95*)
Maize 2005						
Terbutylazine (Inter-Terbutylazin)	May 05	Jul 07†	2334	1092	32	0.48 (77)
- *desethyl-terbutylazine*						0.31 (83)
- *2-hydroxy-terbutylazine*						0.11 (67)
- *desisopropyl-atrazine*						0.02 (84)
- *2-hydroxy-desethyl-terbutylazine*						0.24 (70)
Bentazone (Laddok TE)	Jun 05	Jul 07†	2289	1069	10	0.18 (125)
- *AIBA*						<0.01 (2)
Glyphosate (Roundup Bio	Nov 05	Jul 07†	1884	962	68	4.04(232*)[1)]
- *AMPA*						0.42(283*)[1)]
Spring barley 2006						
Florasulam (Primus)	Jun 06	Jul 07†	1393	605	0	<0.01 (0)
- *florasulam-desmethyl*						<0.03 (0)
Azoxystrobin (Amistar)	Jun 06	Jul 07†	1365	612	0	0.03 (61*)
- *CyPM*						0.13 (95*)
Mesosulfuronmethyl (Atlantis WG)	Oct 06	Jul 07†	1010	536	63	<0.01 (13) [1)]
- *mesosulfuron*						<0.02 (0)

Systematic chemical nomenclature for the analysed pesticides is given in Appendix 1.
** Pesticide have been applied more than once, 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 prior to the application of glyphosate and mesosulfuronmethyl and the weighted concentrations refer to the period from the date of application until 1 July the following year.

Desisopropyl-atrazine was found frequently in groundwater monitoring wells, the frequency of detection and concentration level in the upper most screen of M4 being somewhat similar to that found in the drainage system (Figure 31E and 32B). Unlike desisopropyl-atrazine, the frequency of detection and the concentration level of desethyl-terbutylazine was much lower in the monitoring well than in the drainage system. Despite the marked leaching to the drainage system, desethyl-terbutylazine was only found in seven water samples from the groundwater monitoring wells (Figure 31C and 32C, appendix 5). A similar leaching pattern was seen for terbutylazine, 2-hydroxy-desethylterbutylazine and 2-hydroxy-terbutylazine Apart from one sample containing a detectable amount of terbutylazine, neither of these compounds was detected in samples collected from groundwater monitoring wells (Appendix 5, Table A5.4).

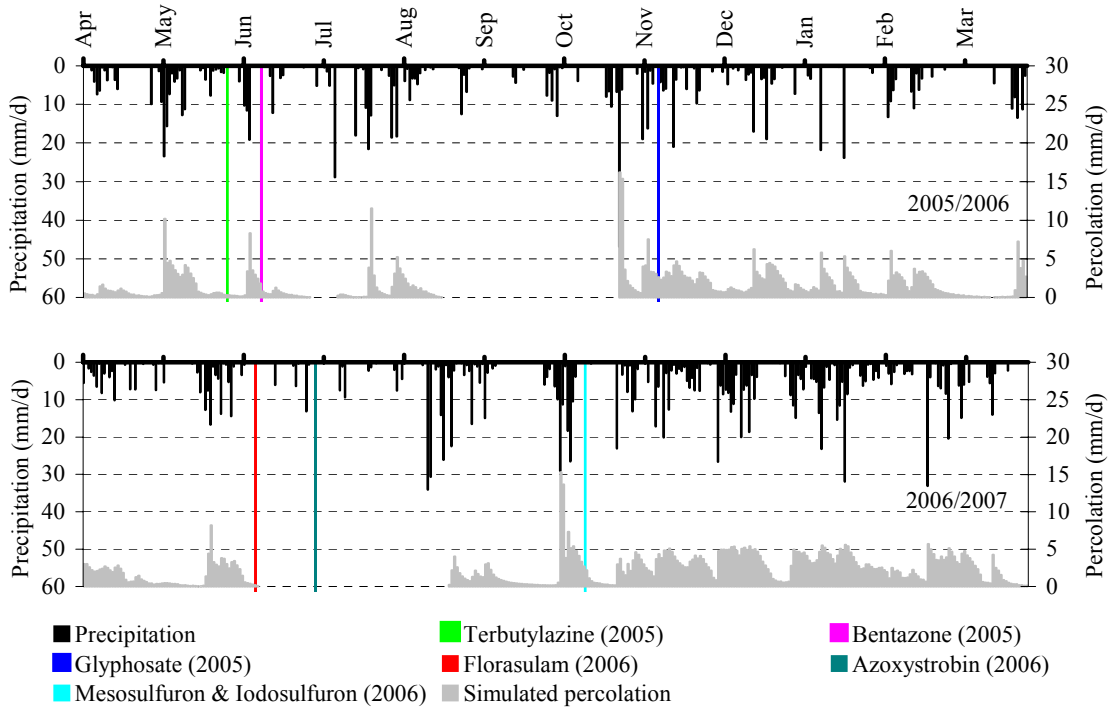

Figure 29. Pesticide application and precipitation (primary axis) together with simulated percolation 0.6 m b.g.s. (secondary axis) at Estrup in 2005/2006 (upper) and 2006/2007 (lower).

In addition to terbutylazine and desethylterbutylazine, also bentazone (applied in June 2005) leached in average concentrations exceeding 0.1 µg/l (Table 11 and Figure 30B). Leaching of bentazone was confined to the drainage depth. Bentazone has been detected in groundwater monitoring wells, but at low concentration level and frequency of detection (Figure 32D and Appendix 5, Table A5.4). The leaching pattern of bentazone differs from that of terbutylazine and desethylterbutylazine. Bentazone leached in high concentrations, but the concentration decreased rapidly and concentrations exceeding 0.1 were only found during a three-month period. Compared to bentazone, the leaching of terbutylazine and desethylterbutylazine continued during a much longer period of time. Although the concentration level also decreased during the first month, concentrations exceeding 0.1 µg/l were found more than one year after application.

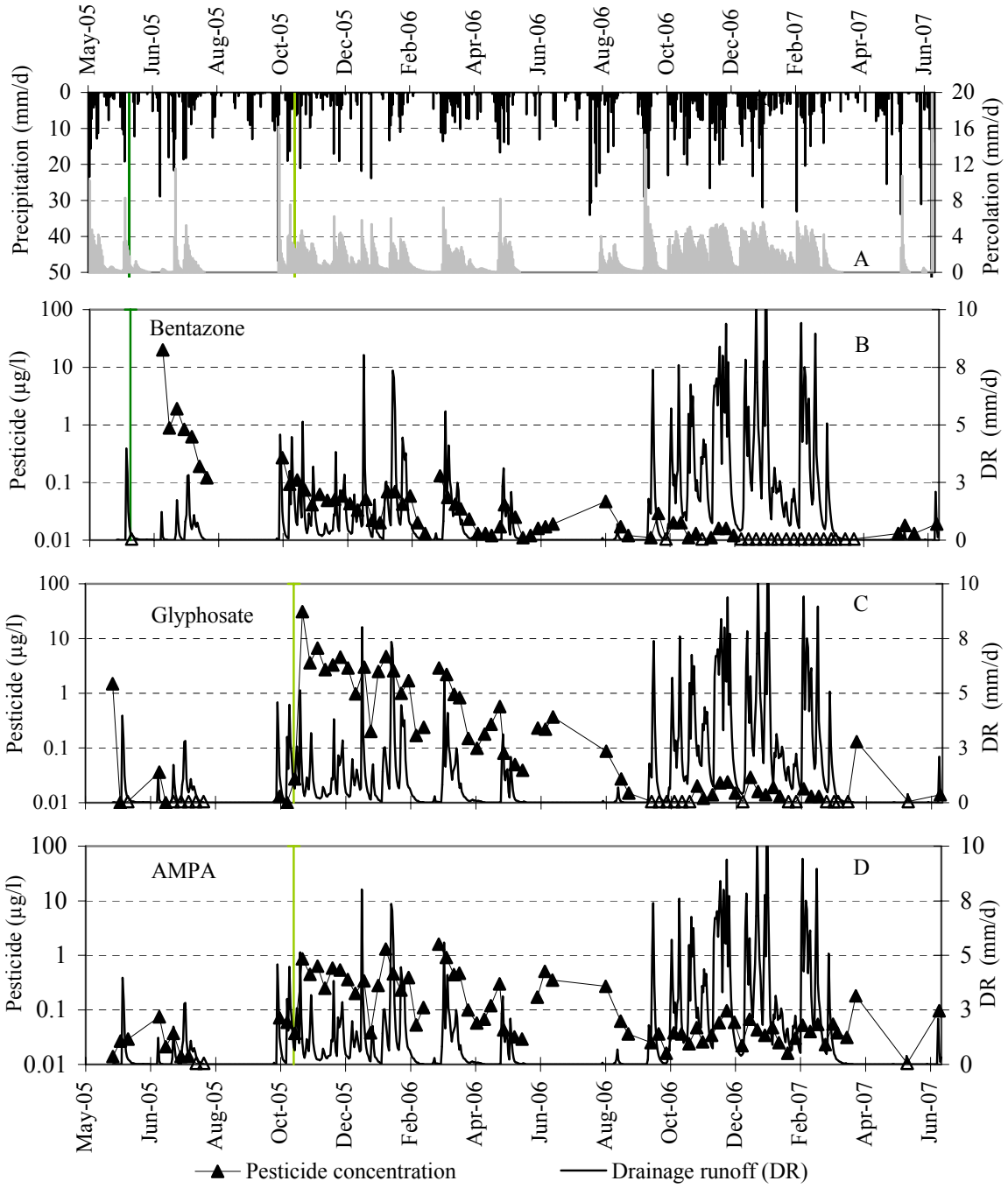

Figure 30. Precipitation and simulated percolation (A) together with concentration of bentazone (B), glyphosate (C) and AMPA (D) in the drainage runoff (DR on the secondary axis) at Estrup in 2005/2007. The green vertical lines indicate the dates of applications. Open diamonds and triangles indicate values below the detection limit of 0.01 µg/l.

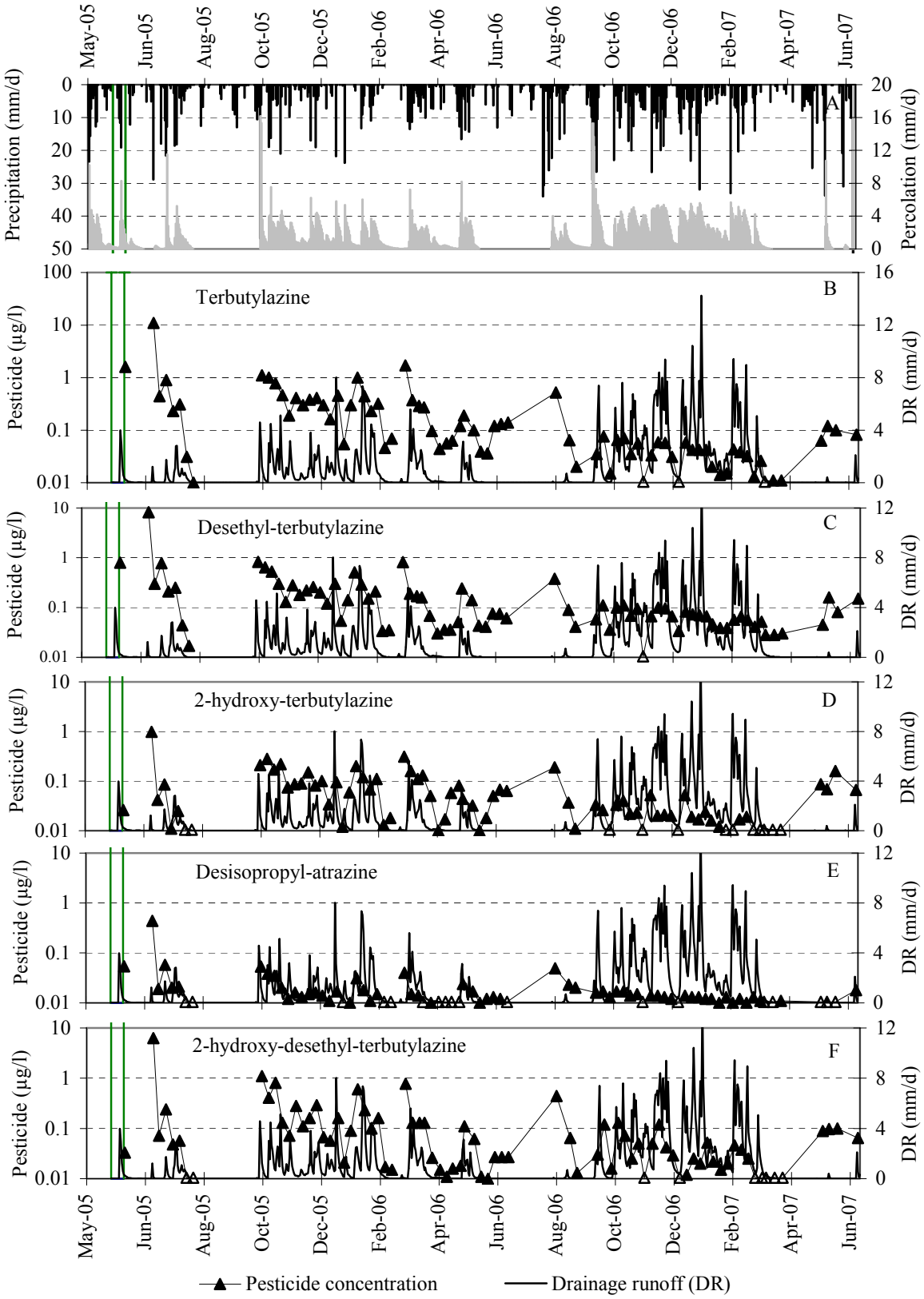

Figure 31 Precipitation and simulated percolation (A) together with concentration of terbutylazine (B), desethyl-terbutylazine (C), 2-hydroxyl-terbutylazine (D), desisopropyl-atrazine (E) and 2-hydroxy-desethyl-terbutylazine (F) in the drainage runoff (DR on the secondary axis) at Estrup in 2005/2007. The green vertical lines indicate the dates of applications. Open triangles indicate values below the detection limit of 0.01 µg/l.

The leaching risk of pesticides applied in autumn 2005 and 2006 will not be evaluated until the 2008 monitoring results become available, i.e. when two years of monitoring data have been collected. Never the less, the following leaching pattern was observed:

- Azoxystrobin, as well as its metabolite CyPM, leached to drain depth in average concentrations reaching 0.03 and 0.13 µg/l respectively (Table 11). The leaching pattern during the 2006 application was very similar to that following the previous application occurring in 2004 (Figure 33 and Kjær *et al*, 2007). Apart from two detections of CyPM, neither CyPM nor azoxystrobin have been detected in any samples collected from the groundwater monitoring screen.

- High levels of glyphosate leaching (applied late November 2005) as well as the metabolite AMPA were observed (Figure 30C and 30D and Table 11). Leaching patterns of AMPA and glyphosate during 2006 were similar to that following the previous two applications at Estrup (Figure 34). The high leaching levels have so far been confined to the depth of the drainage system, as the frequency of detection and concentration level found in samples from groundwater monitoring screens was very low (Appendix 5, Table A5.4). As reported in Kjær *et al.* 2007, pendimethalin (applied togeter with glyphosate late November 2005) also leached from the root zone at Estrup. When evaluating the results presented in Kjær *et al*. 2007, it should be noted, however, that pendimethalin was not applied in accordance with current regulations (see section 5.1.2.). The leaching results regarding pendimethalin have therefore been omitted from the present report.

- Low concentrations (<0.1µg/l) of mesosulfuronmethyl (applied October 2006) were found in a few samples from the drainage system, whereas florasulam (applied June 2006) and its metabolite florasulam-desmethyl were not detected in any of the analysed samples.

Pesticide leaching at Estrup is generally confined to the depth of the drainage system. Apart from glyphosate and desisopropylatrazin being detected in 25 and 22 groundwater samples, pesticides have only sporadically been detected in groundwater monitoring screens below the depth of the drainage system (Appendix 5, Table A5.4). Due to decreased hydraulic conductivity and a lower degree of preferential flow, transport of water and solutes at Estrup are 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).

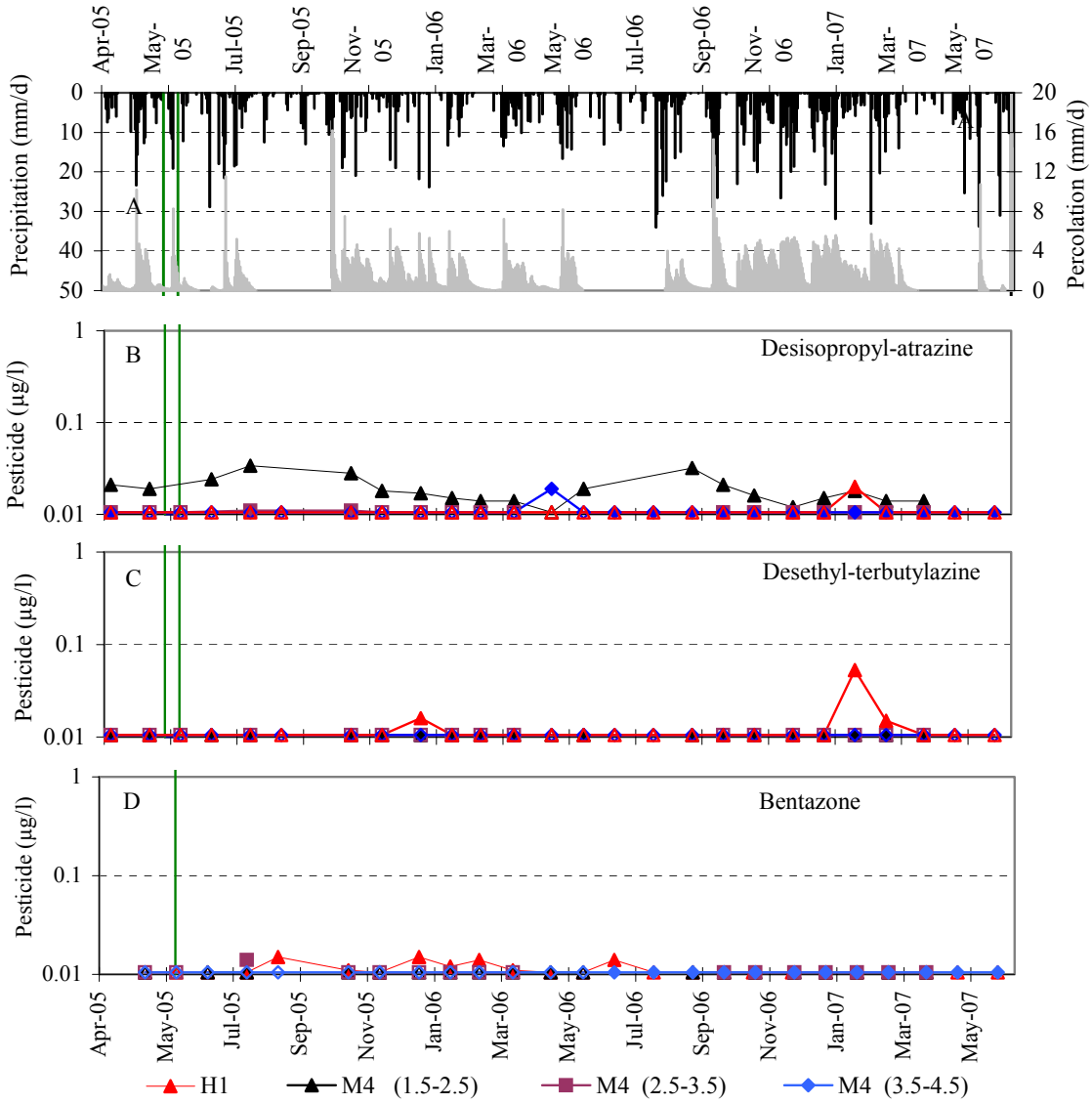

Figure 32. Precipitation and simulated percolation (A) together with concentration of desisopropyl-atrazine (B), desethyl-terbutylazine (C) and bentazone (D) in groundwater monitoring screens at Estrup in 2005/2007. The green vertical lines indicate the dates of applications, and numbers in parentheses the screen depth.

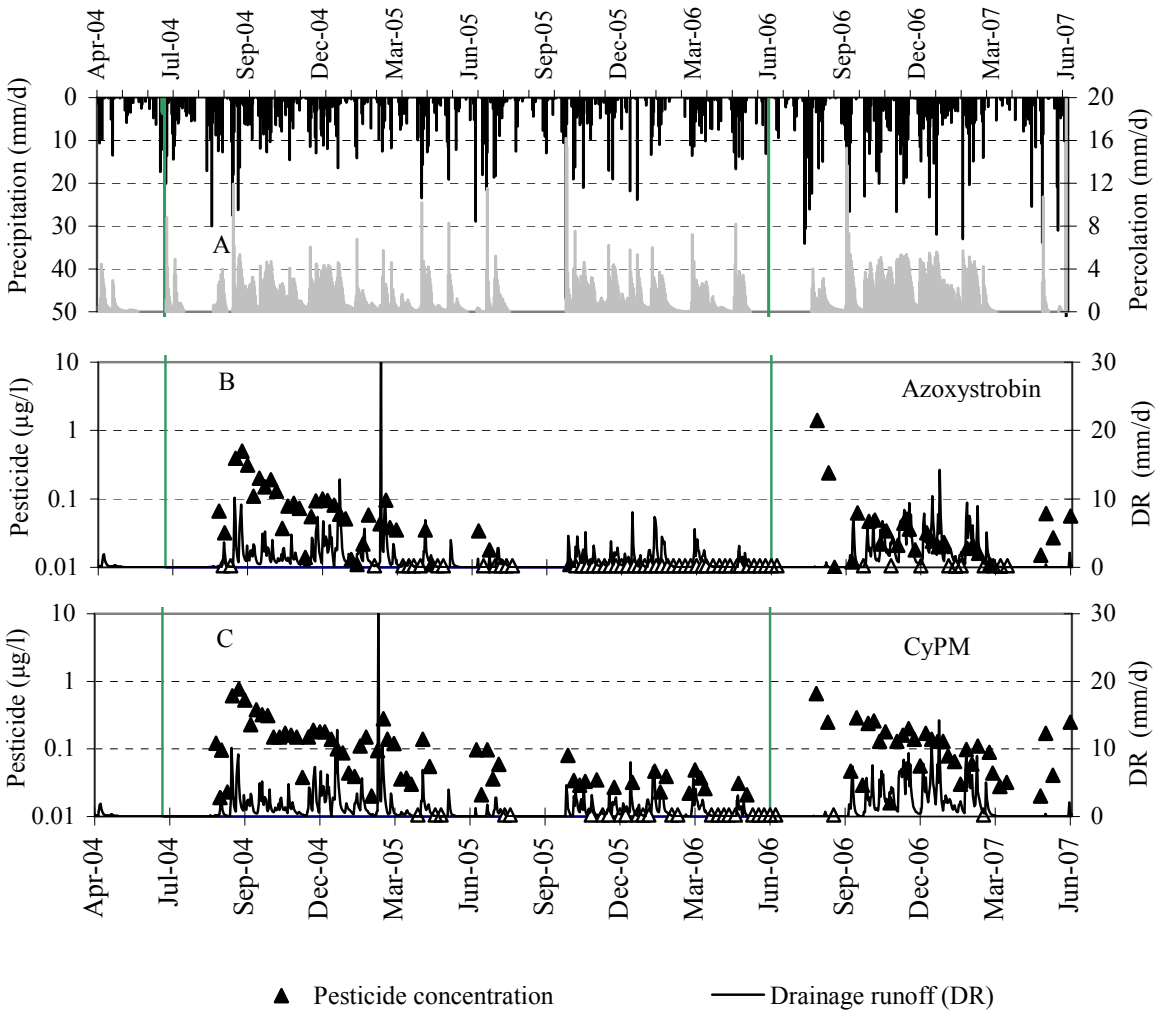

Figure 33. Precipitation and simulated percolation (A) together with concentration of azoxystrobin (B) and CyPM (C) in the drainage runoff (DR on the secondary axis) at Estrup in 2004/2007. The green vertical lines indicate the date of application. Open diamonds and triangles indicate values below the detection limit of 0.01 µg/l.

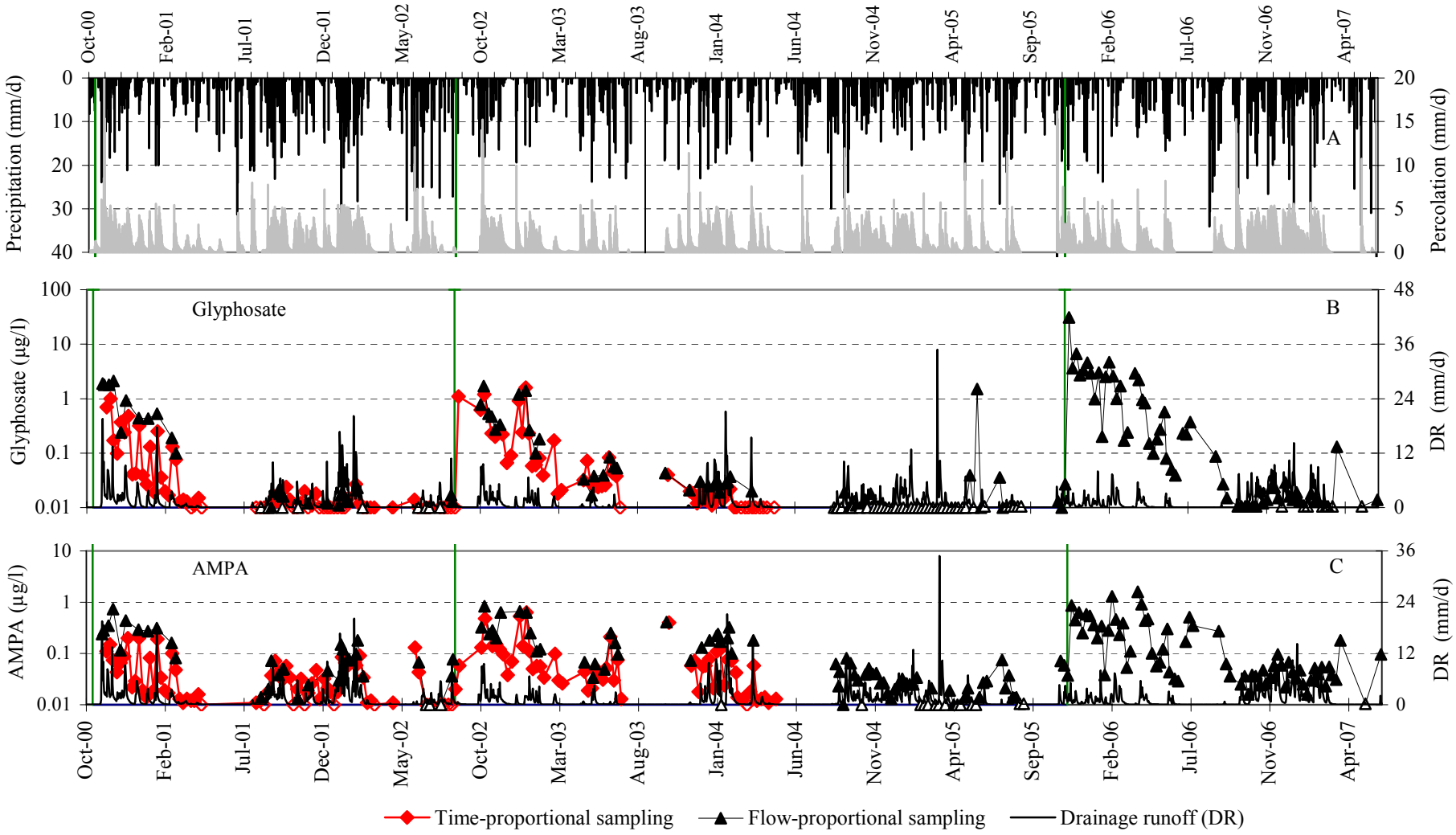

Figure 34. Precipitation and simulated percolation (A) together with the concentration of glyphosate (B) and AMPA (C) in the drainage runoff (DR. on the secondary axis) at Estrup. Data represent a seven-year period including three applications of glyphosate as indicated by the green vertical lines. Open 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 35). 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 35). 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, however, that virtually none of the applied bromide reached the vertical monitoring well (M6) located in the sand-filled basin (Figure 36 and Figure 39), 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).

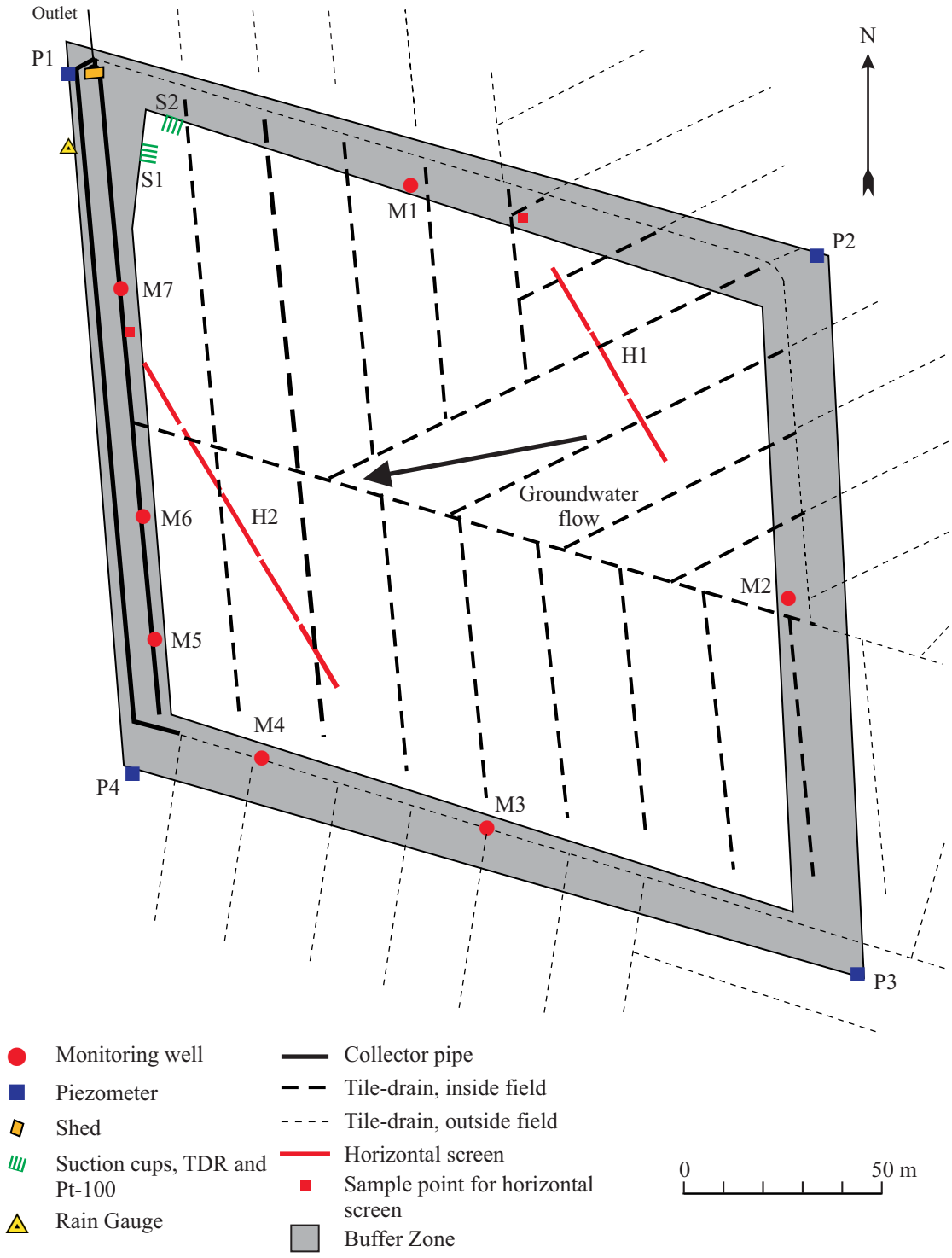

Figure 35. Overview of the Faardrup site. The innermost white area indicates the cultivated land, while the grey area indicates the surrounding buffer zone. The positions of the various installations are indicated, as is the direction of groundwater flow (by an arrow).

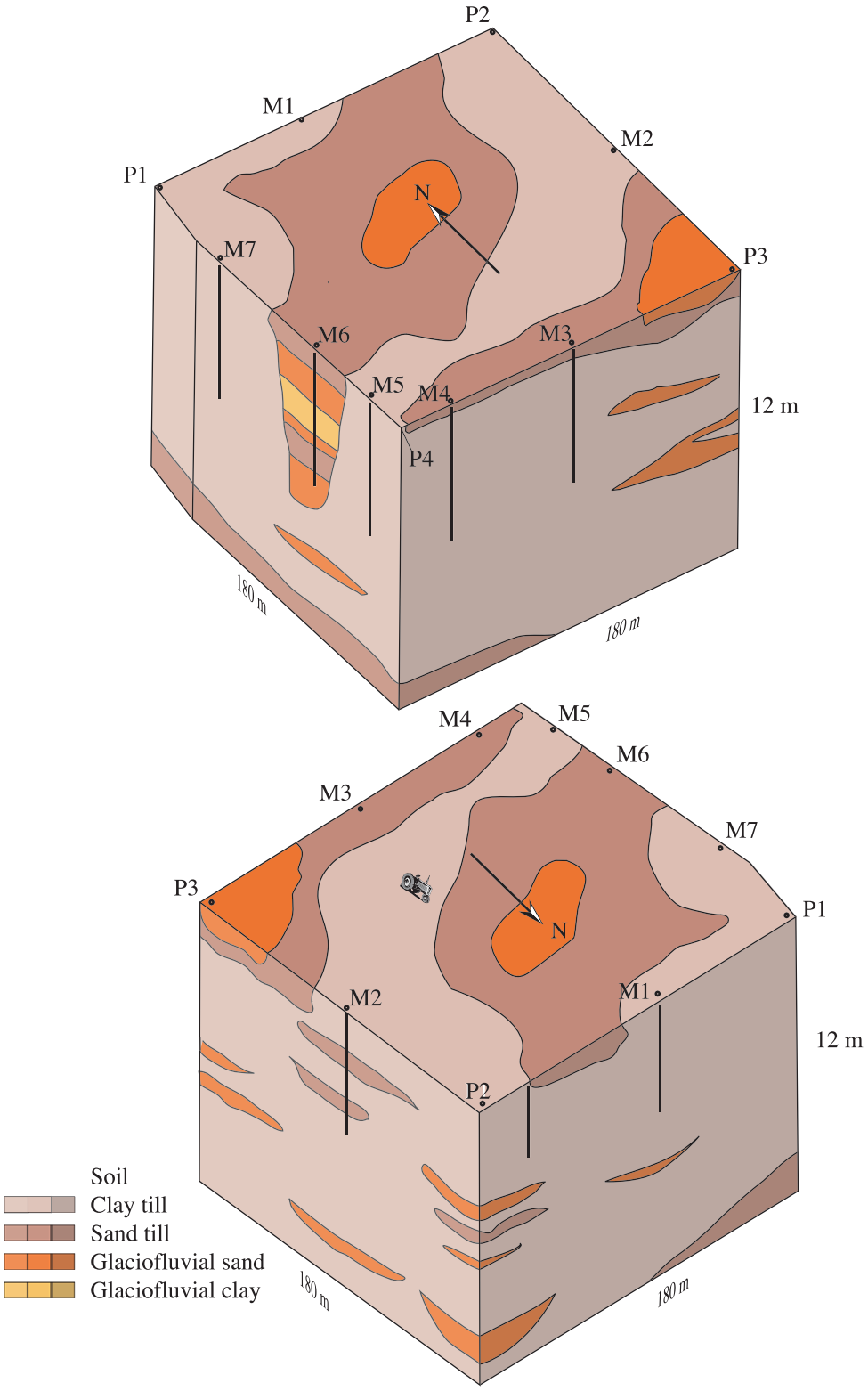

Figure 36. Geological description of Faardrup (Lindhardt *et al.* 2001).

6.1.2 Agricultural management

Management practice during the two recent growing seasons is briefly summarized below and detailed in Appendix 3 (Table A3.5). For information about management practice during the previous monitoring periods see Kjær *et al*. (2002, 2003, 2004, 2005c & 2007).

The field was ploughed in the autumn of 2004 and sown with maize (cv. Nescio) on 26 April 2005. At emergence on 17 May weeds were treated with terbutylazine and further, when two leaves had unfurled, with a mixture of terbutylazine and bentazone on 27 May. 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).

The field was ploughed on 30 November. After seedbed preparation on 20 April 2006 spring barley was sown on 28 April (cv. Scandium). Emergence took place eight days later. Weeds were treated with fluroxypyr on 26 May when the barley had five unfurled leaves. Treatment with the fungicide epoxiconazole was done on 29 June when 20% of the inflorescence had emerged. A yield of 67.3 hkg/ha of grain and 51.1 hkg/ha of straw, 85 and 100% dry matter, respectively, was harvested on 11 August. The average yield of spring barley within the region on this type of soil was nearly 10 hkg/ha less (Plantedirektoratet, 2006).

On 17 August the field was ploughed and sown with winter rape (cv. Labrador) and the following day sprayed with the herbicide clomazone. This substance was not included in the monitoring, however. The rape was sprayed again on 19 February 2007, when the rape had six unfurled leaves, using the herbicide propyzamide, and again on 30 March when the rape had seven visibly extended internodes, using clopyralid (not included in the monitoring programme).

6.1.3 Model set-up and calibration

The numerical model MACRO (version 5.1) 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 2007 and to establish an annual water balance.

Compared to the set-up in Kjær *et al.* (2007), a year of validation was added to the MACRO-set-up for the Faardrup site. The set-up was accordingly calibrated for the monitoring period May 1999-June 2004 and validated for the monitoring period July 2004-June 2007. 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 35) and measured drainage flow. Data acquisition and model set-up are described in Barlebo *et al. (*2007) and Rosenbom *et al.* (In prep.).

Due to electronic problems, precipitation measured at Flakkebjerg located 3 km east of Faardrup was used for the monitoring periods: July 1999 - June 2002, July 2003 - June 2004, in January and February of both 2005 and 2006, and July 2006 - June 2007.

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 level and dynamics of the soil water saturation in all three horizons in the hydraulic year July 2006 – June 2007 were generally well described by the model (Figure 37D, 37E and 37F), alhough at 0.25 and 0.6 m b.g.s. the model did not capture the exact drop in water saturation in the summer period of 2006. For that period, a similar pattern was registered for the dynamics and level of the measured groundwater table.(Figure 37B). This lack of resemblance between measured and simulated water saturation/level of the groundwater table could be caused by the precipitation values used being measured 3 km from the Faardrup site and not on site. As a result of the too high simulated groundwater table/water saturation in the summer 2006, drainage flow was simulated but not measured in November 2006.

The resulting water balance for Faardrup for the eight monitoring periods is shown in Table 12. Compared with the previous seven years, the latest hydraulic year July 2006-June 2007 was characterised by having the highest precipitation, the third highest simulated actual evapotranspiration and the second highest measured and simulated drainage. Precipitation in this year was characterized by April being very dry and January and May-June being very wet (Appendix 4). Due to this precipitation pattern, the duration of the simulated percolation period of the year July 2006-June 2007 was longer than earlier years in the monitoring period, and was represented by continuous percolation throughout the period (Figure 37A), except for the month of September 2006. Compared to the other years, the climatic setting of this year gave rise to a longer period with groundwater table much higher than the drainage level, causing the largest measured drainage since the monitoring started in July 2000 (Figure 37B and 37C). Apart from small differences in measured and simulated yearly amount of drainage, the overall trend in the drainage pattern of the hydraulic years was captured.

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

	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	505	36	18	144
1.7.04–30.6.05	626	671	469	131	55	72
1.7.05–30.6.06	626	557	372	28	15	157
1.7.06–30.6.07	626	790	515	202	212	72

[1)] Normal values based on time series for 1961–1990.
[2)] For July 1999 - June 2002, July 2003 - June 2004, in January and February of both 2005 and 2006, and July 2006 - June 2007, measured at the DIAS Flakkebjerg meteorological station located 3 km from the test site (see detailed text above).
[3)] Groundwater recharge is calculated as precipitation - actual evapotranspiration - measured drainage.

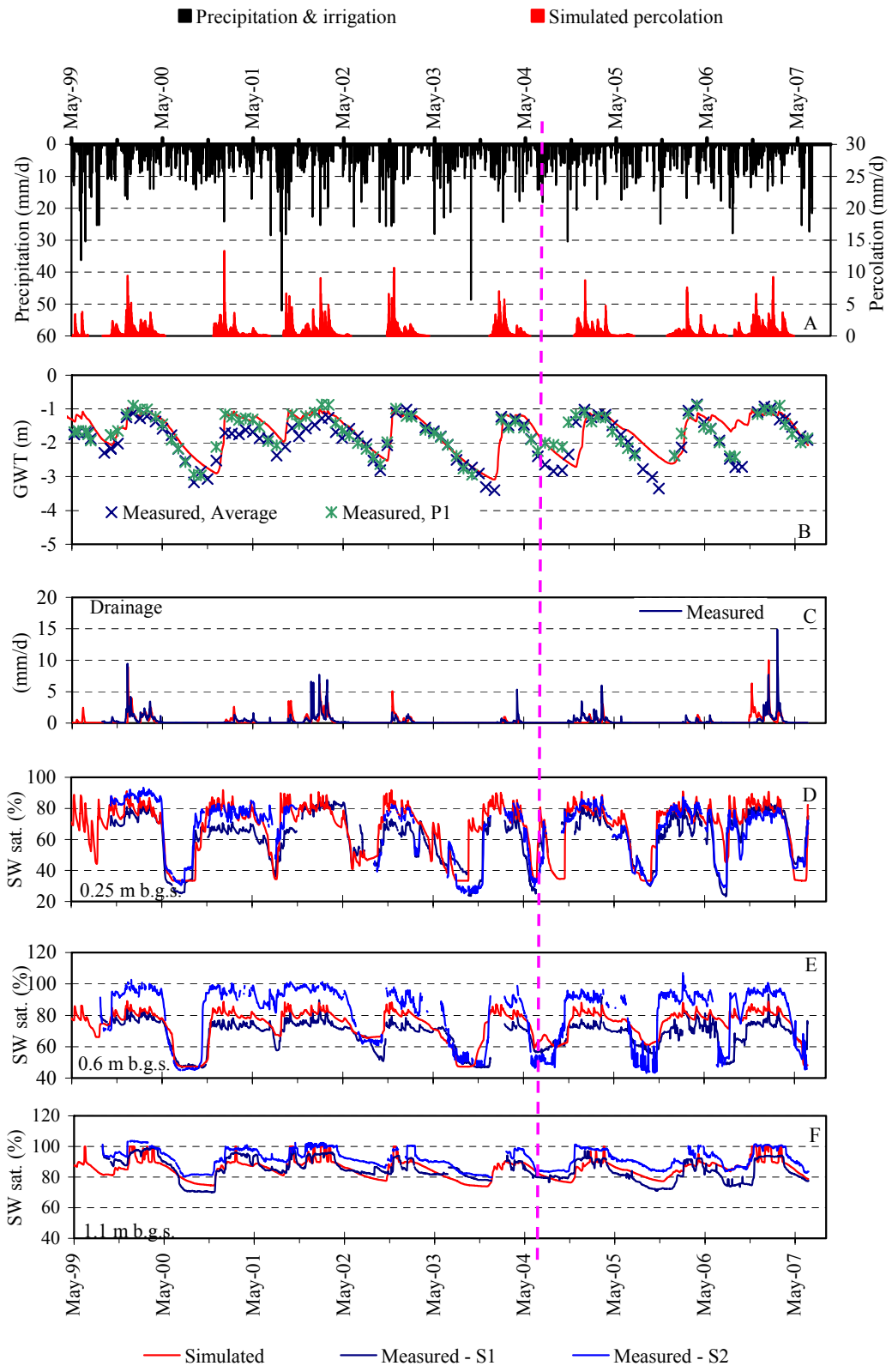

Figure 37. Soil water dynamics at Faardrup: Measured precipitation and simulated percolation 1 m b.g.s. (A), simulated and measured groundwater level GWT (B), simulated and measured drainage flow (C) and simulated and measured soil water saturation (SW sat.) at three different soil depths (D, E, and 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 35). The broken vertical line indicates the beginning of the validation period (July 2004-June 2007).

6.2.2 Bromide leaching

The bromide concentration shown in Figure 38 and Figure 39 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).

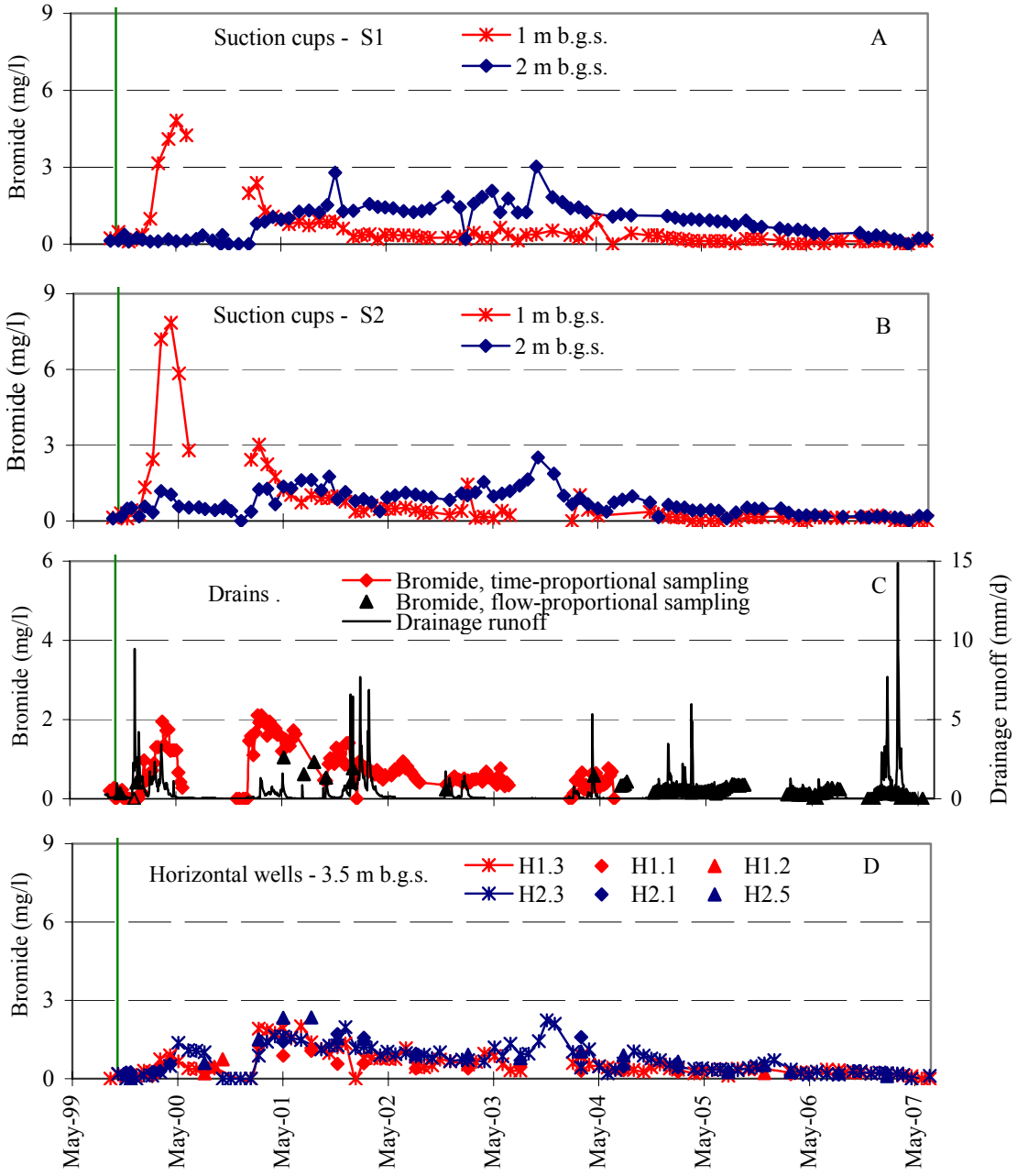

Figure 38. Bromide concentrations at Faardrup. A and B refer to suction cups located at S1 and S2. The bromide concentration is also shown for drainage runoff (C) and the horizontal monitoring wells (D). The green vertical line indicates the date of bromide application.

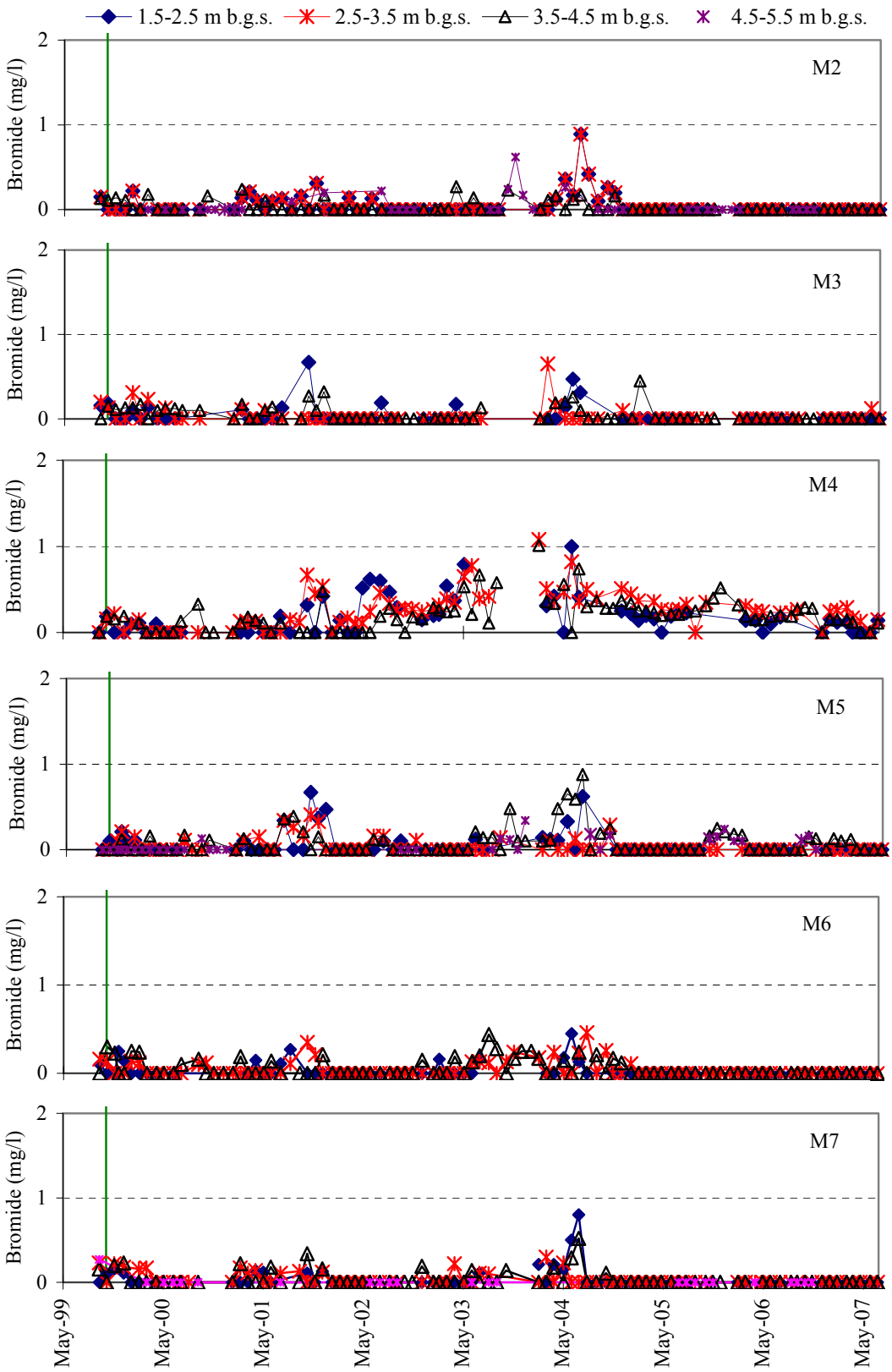

Figure 39. Bromide concentrations at Faardrup. The data derive from the vertical monitoring wells (M2–M7). Screen depth is indicated in m b.g.s. The green vertical line indicates the date of bromide application.

6.2.3 Pesticide leaching

Monitoring at Faardrup began in September 1999 and presently encompasses several pesticides and their degradation products, as indicated in Table 13. Pesticide application during the two most recent growing seasons is shown together with precipitation and simulated precipitation in Figure 40. 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 13).

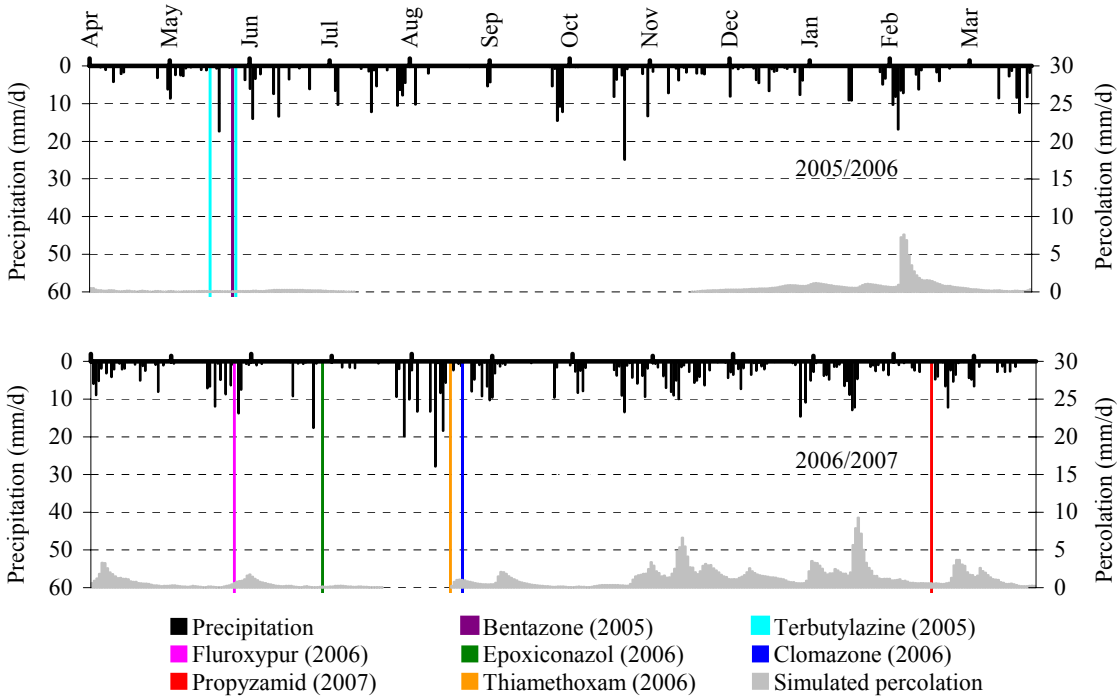

Figure 40. Pesticide application, precipitation (primary axis) together with simulated percolation (secondary axis) at Faardrup in 2005/2006 (upper) 2006/2007 (lower).

Table 13. Pesticides analysed at Faardrup with the product used shown in parentheses. Degradation products are in italics. Precipitation (prec.) and percolation (perc.) are accumulated from the date of first application (app. date) until the end of monitoring. 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 2000)	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

The leaching risk of pesticides applied during 2000, 2001, 2002, 2003 and 2004 has been evaluated in Kjær *et al.* (2002, 2003, 2004, 2005c & 2007),.

Terbutylazine and bentazone were applied in May 2005 on a maize crop, Table 13, Figure 40, 41, 42 and 43. Pesticides and their metabolites leached both to the drainage system and to groundwater monitoring screens. Mean concentrations were calculated, and terbutylazine and desethyl-terbutylazine concentrations of 0.67 and 0.59 µg/l were found. A very high bentazone mean concentration, 2.82 µg/l was recorded. There was only one finding of the bentazone metabolite AIBA.

Table 13 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	1761	509	4	<0.02(1)
- propanamide-clomazone (FMC65317)						<0.02(1)
Winter wheat 2004						
Prosulfocarb (Boxer EC)	Oct 03	Apr 06	1542	454	0	<0.01 (0)
MCPA (Metaxon)	Jun 04	Jul 06	1307	331	0	<0.01 (2*)
- 4-chlor,2-methylphenol						<0.01(1*)
Azoxystrobin (Amistar)	Jun 04	Jul 07	2098	636	0	<0.01 (0)
- CyPM						<0.01 (4)
Maize 2005						
Terbutylazine (Inter-Terbutylazin)	May 05	Jul 07†	1428	465	4	0.67 (74)
- desethyl-terbutylazine						0.59 (96)
- 2-hydroxy-terbutylazine						0.04 (35)
- desisopropyl-atrazine						0.03 (72)
- 2- hydroxy-desethyl-terbutylazine						0.07 (16)
Bentazone (Laddok TE)	May 05	Jul 07	1408	464	6	2.82 (28)
- AIBA						<0.01 (1)
Spring barley 2006						
Fluroxypyr (Starane 180 S)	May 06	Jul 07†	846	323	17	<0.02 (2)
Epoxiconazole (Opus)	Jun 06	Jul 07†	790	306	3	<0.01 (0)
Winter Rape 2007						
Thiamethoxam (Cruiser RAPS)	Aug 06	Jul 07†	654	304	27	<0.01 (0)
- CGA 322704						<0.02 (0)
Propyzamide (Kerb)	Feb 07	Jul 07†	266	33	46	0.138 (4) 1)
- RH-24644						<0.01 (4) 1)
- RH-24580						<0.01 (0) 1)
- RH-24655						<0.01 (0) 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.
1) Drainage runoff commenced prior to the application of propyzamide and the weighted concentrations refer to the period from the date of application (Feb 07) until 1 July 2007.

Leaching of terbutylazine and metabolites to the drainage system follows the same patterns and concentrations of being above or near 0.1 µg/l within the drainage season of 2005. At the start of the drain season 2006 (January and February) high concentrations of terbutylazine and desethyl-terbutylazine were also measured. However, the concentration decreased rapidly below 0.1µg/l. In November 2006 desethyl-terbutylazine was found frequently, but in rather small concentrations, Figure 41 C. Terbutylazine and desethyl-terbutylazine were also found in high concentrations (>0.1 µg/l) in the groundwater monitoring well M5 (Figure 42B and C). Figure 42B and 42C show that desethyl-terbutylazine was found in high concentrations during 2005–2007. Desisopropyl-atrazine, 2-hydroxy-desethyl-terbutylazine and 2-hydroxy-terbutylazine were found in the groundwater, but in low concentrations (<0.1 µg/l). 2-hydroxy-terbutylazine occurred more frequently in 2006/2007 and the monitoring of 2007/2008 will show whether this metabolite leaches to groundwater over a longer period of time.

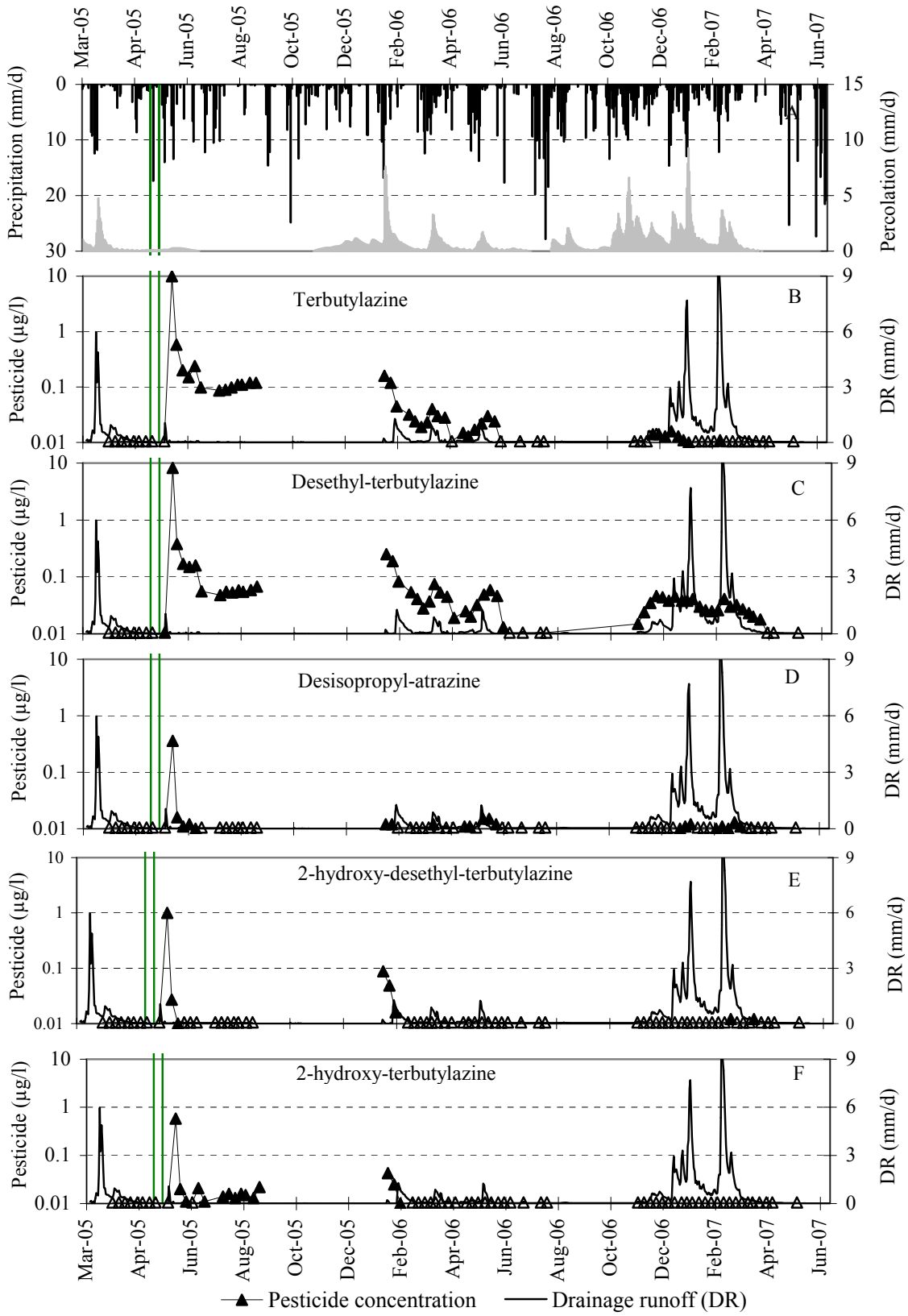

Figure 41. Precipitation and simulated percolation (A) together with concentration of terbutylazine (B), desethyl-terbutylazine (C), 2-hydroxy-terbutylazine (D), desisopropyl-atrazine (E) and 2-hydroxy-desethyl-terbutylazine (F) in the drainage runoff (DR on secondary axis) at Faardrup in 2005/2007. The green vertical lines indicate the dates of applications. Open triangles indicate values below the detection limit of 0.01 µg/l.

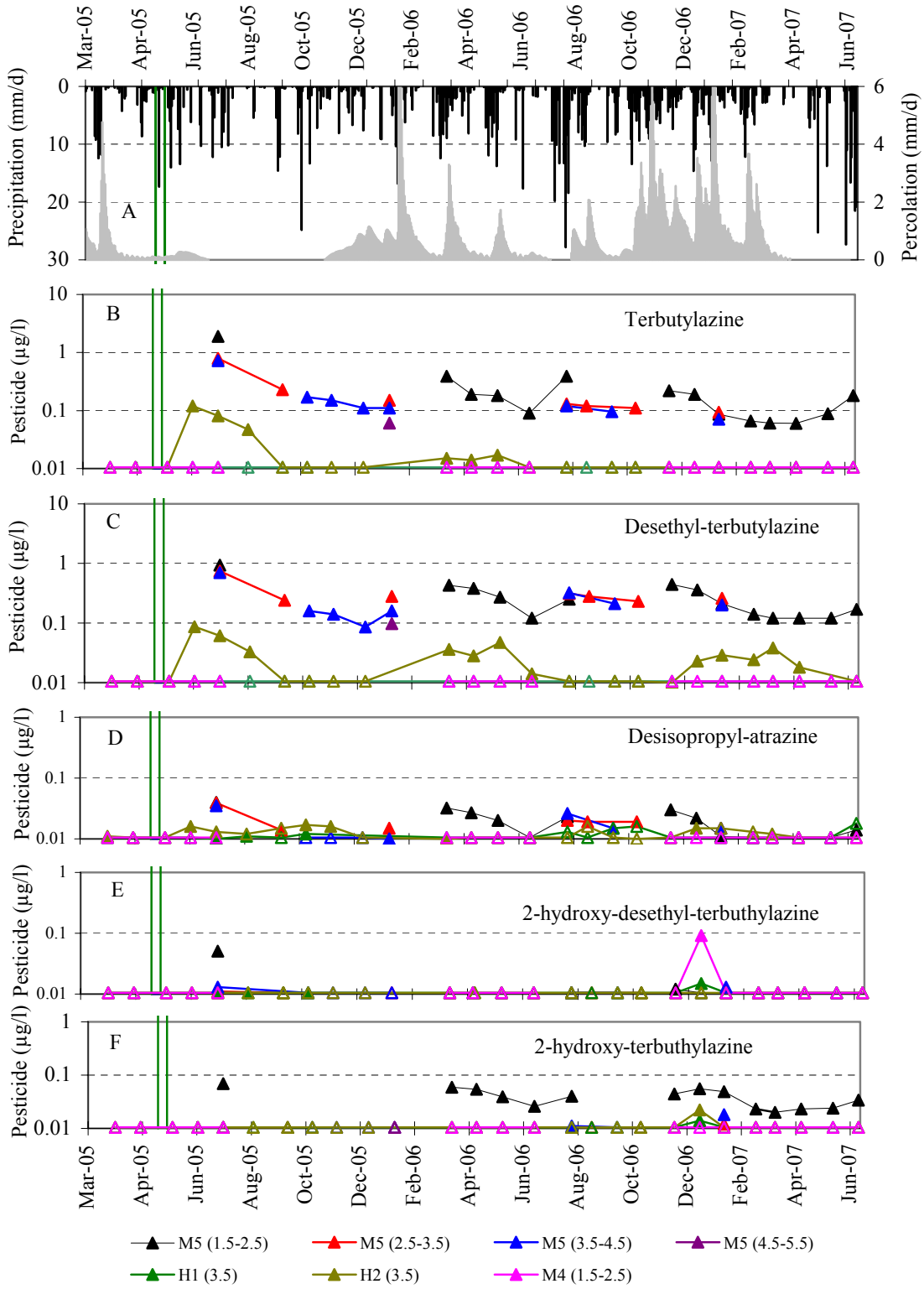

Figure 42. Precipitation and simulated percolation (A) together with concentration of terbutylazine (B), desethyl-terbutylazine (C), desisopropyl-atrazine (D), 2-hydroxy-desethyl-terbutylazine (E) and 2-hydroxy-terbutylazine in monitoring well H1, H2, M5 and the uppermost screen of M4 at Faardrup. None of these petsicides were detected in the lower screens of M4 (monitored mouthly) nor in M6 (monitored half-yearly). 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.

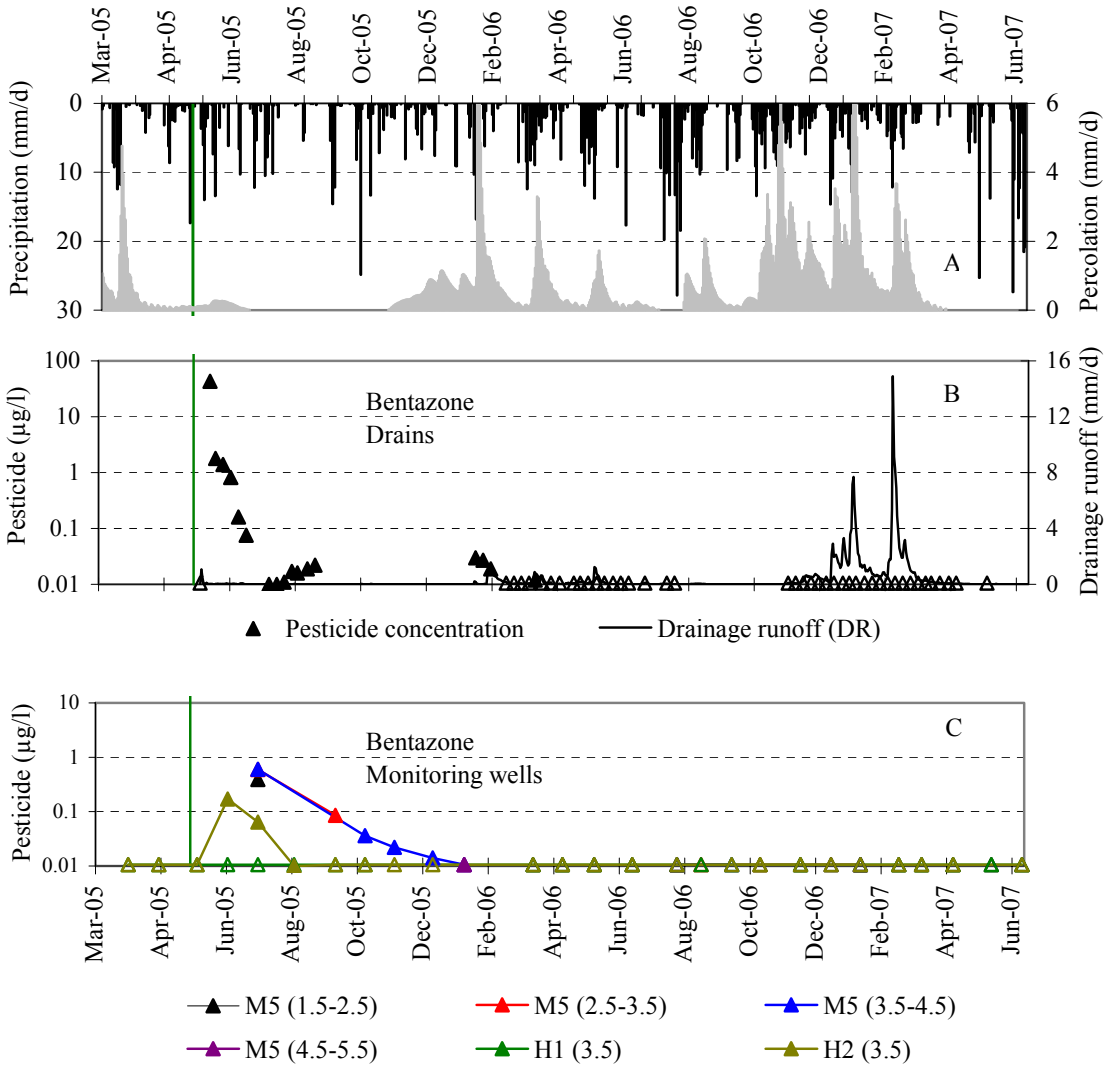

Figure 43. Precipitation and simulated percolation (A) together with concentration of bentazone in the drainage runoff (B) and in monitoring wells M5 and H (C) The green vertical lines indicate the dates of applications, numbers in parentheses screen depth and open triangles values below the detection limit of 0.01 µg/l.

Bentazone was found both in the drainage system and in groundwater, Figure 43. Initial concentrations were much higher than that of terbutylazine and its metabolites. However, concentrations fell rapidly below 0.1µg/l during the summer of 2005, and bentazone has not been found in high concentrations during 2006/2007. Unlike terbutylazine and desethylterbutylazine, which leached over a long period of time, marked leaching of bentazone was confined to a short period of time. This leaching pattern was similar to that observed at Silstrup, Jyndevad (Kjær *et al.* 2007) and Estrup (Section 5.2.3).

The leaching risk of pesticides applied in 2006 will not be evaluated until the 2008 monitoring results become available, i.e. when two years of monitoring data have been collected. But it should be noted, though, that propyzamide and one of its metabolites has been leached to the drainage system (Figure 44, Table 13, Appendix 5, Table A5.5) where four very high concentrations of propyzamide gave a calculated mean concentration of 0.138 µg/l. It should be noted that drainage runoff commenced more than two and a half months prior to the application and the weighted concentrations refer to a period of 4.5 months (17 February - 1 July 2007)

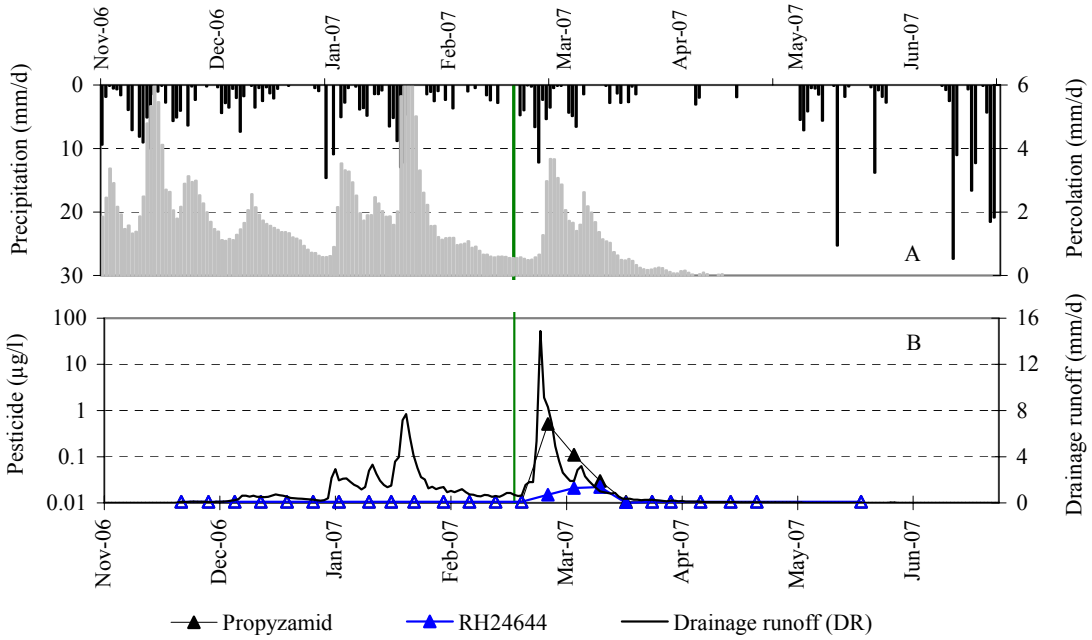

Figure 44. Precipitation and simulated percolation (A) together with concentration of propyzamide and RH24644 (B) in the drainage runoff (DR on secondary axis) at Faardrup in 2006/2007. The green vertical lines indicate the date of applications. Open triangles indicate values below the detection limit 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 2006 – June 2007 are presented below, while those for the preceding monitoring periods are given in Kjær *et al.* (2002, 2003, 2004, 2005c and 2007).

7.1 Materials and methods

The pesticide analyses were carried out at commercial laboratories selected on the basis of a competitive tender. In order to assure the quality of the analyses, the call for tenders included requirements as to the laboratory's quality assurance (QA) system comprising both an internal and an external control procedure. In addition to specific quality control under the PLAP, the laboratory 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 laboratory analysed one or two control samples prepared at each laboratory as part of their standard method of analysis. The pesticide concentration in the internal QA samples ranged between 0.05–0.06 µg/l. When using these data it was possible to calculate and separate the analytical standard deviation into within-day (S_w), between-day (S_b) and total standard deviation (S_t). Total standard deviation was calculated using the following formula (Wilson 1970, Danish EPA 1997):

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

7.1.2 External QA

Every four months, 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 14). Fresh ampoules were used for each set of standard solutions. For preparation of the controls 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 14. Blank samples consisting of HPLC water were also included in the external QA procedure every month. All samples included in the control were labelled with coded reference numbers so that the laboratories were unaware of which samples were controls and which were blanks.

Table 14. Pesticide concentrations in both the original ampoules and in the resulting high-level and low-level external control samples

Compound	Original ampoules (mg/l)	High-level control (µg/l)	Low-level control (µg/l)
AMPA	1	0.117	0.050
Azoxystrobin	1	0.117	0.050
Bentazone	1.3	0.152	0.065
Clopyralid	1.3	0.152	0.065
CYPM	1.3	0.152	0.065
Epoxiconazole	1	0.117	0.050
Florasulam	1.3	0.152	0.065
Fluroxypyr	1	0.117	0.050
Glyphosate	1	0.117	0.050
Metsulfuron-methyl	1	0.117	0.050
Pendimethalin	1	0.117	0.050
Pirimicarb-desmethyl-formamido	1	0.117	0.050
Propyzamide	1	0.117	0.050
Terbutylazine-desethyl	1	0.117	0.050
Thiamethoxam	1	0.117	0.050

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.

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 in 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 for pesticides where the requirement for normality is not fulfilled. Such data should obviously be interpreted with caution.

As a "rule of thumb", the between-day standard deviation should be no more than double the within-day standard deviation. From Table 15 it can be seen that S_b/S_w ratios greater than two were observed for several compounds. For three compounds, the results indicate that day-to-day variation makes a significant contribution. Among the compounds meeting the normality requirement, the S_b/S_w ratio is highest for triazinamin-methyl. When all compounds are considered, a relatively high S_b/S_w ratio is apparent for AMPA. This relatively high value is caused by a very low within-day standard deviation, i.e. within each laboratory day, the variation on the AMPA analysis is small compared to the other compounds, whereas the variation between days is comparable to the other compounds analysed. Thus, a low value of S_w rather than critical values of S_b caused the high ratios, as reflected by the low S_t. As reflected by the data in Table 15, the three compounds with significant between-day contribution were clopyralid, ioxynil, and metribuzin-desamino-diketo.

The total standard deviations (S_t) of the various analyses of pesticides and degradation products lie within the range 0.002–0.011 µg/l (only data with $n \geq 3$ are included in the analysis). The overall mean S_t was 0.006 µg/l. Analysing S_t with a *t*-test revealed that, in contrast to previous years, there were significant differences between the total standard deviation observed for pesticides and degradation products, with the highest S_t being observed for the analysis of degradation products (*t*-test, equal variances, α=0.05). The compounds with the poorest reproducibility were all degradation products: PPU, PPU-desamido, 2-hydroxy-desethyl-terbutylazine, 2-hydroxy-terbuhylazin, and triazinamin-methyl.

Table 15. Internal QA of pesticide analyses carried out in the period 01.07.06 – 30.06.07. Results of the test for normality, one-way analysis of variance (ANOVA), the estimated values of standard deviations (w: within-day, b: between-day, t: total – see text for details), pesticide concentration in internal QA sample (Conc.) and number of duplicate samples (n) are 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 Sb Between day contribution ANOVA α=0.05	Sw (µg/l)	Sb (µg/l)	St (µg/l)	Ratio Sb/Sw	n	Conc (µg/l)
2-hydroxy-desethyl-terbutylazine (D)			0.004	0.008	0.009	1.86	51	0.050
2-hydroxy-terbutylazin (D)			0.004	0.008	0.009	2.35	52	0.052
AMPA (D)			0.001	0.003	0.003	4.22	11	0.053
PPU (D)			0.006	0.007	0.009	1.14	25	0.053
PPU-desamino (D)			0.002	0.008	0.008	3.52	25	0.053
Azoxystrobin	Yes		0.002	0.005	0.005	2.31	23	0.053
Azoxystrobin	Yes		0.002	0.005	0.005	2.31	30	0.056
Bentazone			0.002	0.005	0.006	3.34	52	0.050
Bromoxynil			0.001	0.003	0.003	2.42	10	0.051
Clopyralid	Yes	yes	0.004	0.001	0.004	0.22	22	0.050
Desethylterbutylazine (D)			0.002	0.005	0.005	2.65	53	0.053
Desisopropylatrazin (D)	Yes		0.002	0.005	0.006	2.30	23	0.053
Desisopropylatrazin (D)	Yes		0.002	0.005	0.006	2.30	29	0.054
Florasulam	Yes		0.002	0.002	0.003	1.09	37	0.050
Glyphosat			0.002	0.003	0.004	1.22	11	0.055
Ioxynil	Yes	yes	0.002	0.001	0.002	0.36	10	0.051
Metribuzine-desamino-diketo (D)	Yes	yes	0.004	0.004	0.006	0.90	11	0.050
Metribuzine-diketo (D)	Yes		0.003	0.004	0.005	1.24	11	0.050
Pendimethalin			0.002	0.006	0.006	3.30	46	0.050
Pirimicarb			0.001	0.004	0.004	3.74	33	0.053
Pirimicarb-desmethyl-formamido (D)	Yes		0.002	0.004	0.004	2.20	33	0.052
Propyzamide			0.001	0.005	0.005	3.73	28	0.052
Propyzamide			0.001	0.005	0.005	3.73	24	0.053
Terbutylazine			0.002	0.005	0.005	2.56	53	0.051
Triazinamin-methyl (D)	Yes		0.003	0.011	0.011	3.56	12	0.054

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, averages ranging from 70% - 111%. Exceptions are glyphosate and mesosulfuron for which recovery are low in some of the spiked samples. A possible explanation for a low recovery could be degradation of the spiked compound during transport, storage or analysis. As the results for each field site in Table 16 are based on only one to three observations, this should not be interpreted too rigorously. However, the data may indicate possible recovery problems for mesosulfuron.

The low recovery of glyphosate is due to glyphosate not being detected in 1 of 6 spiked samples. While glyphosate was not detected in one of the spiked samples, the recovery in the remaining five samples ranged from 60 – 86%. It should be noted that it was the first time that glyphosate had not been detected in any of the 78 samples that since 2003 have been spiked with glyphosate.

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

	Jyndevad		Silstrup		Tylstrup		Estrup		Faardrup		Average
	Low	High	Low	High	Low	High	Low	High	Low	High	
AMPA							84	68			76
Azoxystrobin		102		103			99	103	73	94	95
Bentazone	95	97	94	94			93	92	73	99	92
Clopyralid					68	91					80
CyPM		89		90	75	96	84	90	60	75	82
Desethylterbutylazin	96	108	97	111			108	108*	87	111	103
Fluroxypyr		134		123	95	110			109	94	111
Glyphosate							49	66			57
Metsulfuron methyl					94	98					96
Pendimethalin		76		80	77	87	81	80			80
Pirimicarb-desmethyl-formamido		98		94*	89	97					95
Epoxiconazole	94	101	96	103	94	98	92	98	69	87	93
Florasulam		74		79			79	81			78
Propyzamide	90		91		75	94			99	93	90
Thiamethoxam	94		94						80	105	93

** Indicates that a degradation product of the compound was detected even if it was not included in the spiking solution.*

Contamination of samples during collection, storage and analysis is not likely to occur. In a total of 74 blank samples, only three pesticide degradation products were detected in two samples. Samples found to contain pesticides and their degradation products are thus regarded as true positive findings. Apart from mesosulfuron (not detected in 3 of out 4 spiked samples) as well as glyphosate/AMPA (not being detected in 1 out of 6 spiked samples), all the pesticides in the spiked samples were detected in all samples.

During the 2004/2006 monitoring period a total of six pesticides and 13 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 6.

7.3 Summary and concluding remarks

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

- Reproducibility of the pesticide analyses was good, total standard deviation being in the range 0.002-0.011 µg/l.
- In contrast to previous years, a difference in reproducibility was observed between pesticides and degradation products, the total error being lowest for the parent compounds.
- Recovery was generally good (average recovery ranging between 70–111%) in external spiked samples. Low recovery of glyphosate was, however, observed in some samples.
- Contamination of samples during collection, storage and analysis is not likely to occur. In a total of 74 blank samples, only three pesticide degradation products were detected in two samples.

8 Summary of monitoring results

This section summarizes the monitoring data from the entire monitoring period, i.e. both data from the two most recent monitoring years (detailed in this report) and data from the previous monitoring years (detailed in previous reports Kjær *et al.,* 2002, 2003, 2004, 2005c and 2007). Pesticide detections in samples from drainage system, suction cups and monitoring wells are detailed in Appendix 5. The monitoring data reveal that the applied pesticides exhibit three different leaching patterns – no leaching, slight leaching and pronounced leaching (see Table 17). 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 17. 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 in 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 in the coarse, sandy soil 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.,* 2005a for details).

Table 17. 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 2007 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)					
Metribuzine (H)		1)			
Pirimicarb (I)					
Propyzamide (H)	*		*		*
Rimsulfuron (H)					
Terbutylazine (H)					
Amidosulfuron (H)		2)		2)	
Bromoxynil (H)					
Clomazone (H)	*				
Dimethoate (I)					
Epoxiconazole (F)	*	*	*	*	*
Mancozeb (F)					
Mesosulfuronmethyl (H)		*		*	
Fenpropimorph (F)					
Flamprop-M-isopropyl (H)					
Fluazifop-P-butyl (H)					
Fluroxypyr (H)			*		
Ioxynil (H)					
MCPA (H)					
Pendimethalin (H)					
Phenmedipham (H)					
Propiconazole (F)					
Prosulfocarb (H)					
Pyridate (H)					
Clopyralid (H)	*		*		
Desmedipham (H)					
Florasulam (H)		*		*	
Linuron (H)					
Metsulfuron-methyl (H)					
Thiamethoxam (I)	*				*
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 18. 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)	61(1.4)	0
-CyPM		0	62(0.34)	95(0.77)	4(0.059)
Bentazone	1(0.012)	30(1.6)	52(6.4)	125(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)	232(31)	8(0.093)
- AMPA		3(0.022)	137(0.35)	283(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)
Metribuzine	3(0.024)				
- metribuzin-desamino-diketo	317(2.1)	20(1.831)			
- metribuzin-diketo	630(0.69)	29(1.372)			
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)
Propyzamide	0		32(1.6)		4(0.51)
- RH-24644	0		17(0.051)		4(0.022)
- RH-24580	0		2(0.016)		0
- RH-24655	0		0		0
- PPU[4]	40(0.15)	204(0.29)			
- PPU-desamido[4]	14(0.042)	109(0.13)			
Terbutylazine	0	0	96(1.55)	77(11)	74(10)
- desethyl-terbutylazine	2(0.012)	42(0.056)	269(1.08)	83(8.2)	96(8.3)
- desisopropyl-atrazine	18(0.042)		47(0.047)*	84(0.44)	72(0.36)
- 2hydroxy- desethyl -terbutylazine	6(0.026)		29(0.11)*	70(6.3)	16(1)
- 2-hydroxy-terbutylazine	1(0.04)		26(0.039)*	67(0.99)	35(0.58)
Amidosulfuron		3(0.11)		0	
Bromoxynil	0	0		3(0.6)	0
Clomazon	0				1(0.28)
-propanamide-clomazone	0				1(0.3)
Dimethoate	0	0	2(1.417)	0	0
- ETU[1]	9(0.038)				
Epoxiconazole	0	0	0	1(0.39)	0
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	0	13(0.109)	20(0.069)	1(0.037)
- flamprop (free acid)	0	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		4(0.058)	2(0.19)
Ioxynil	0	0		20(0.25)	2(0.011)
Mesosulfuron-methyl		0		13(0.059)	
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)
Pendimethalin	0	0	14(0.064)		
- 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.

- Terbutylazine as well as its degradation products leached through the root zone at high average concentrations on loamy soils. At the three loamy soil sites Silstrup, Estrup and Faardrup, desethylterbutylazine leached from the root zone entering the drainage water in average concentrations exceeding 0.1 µg/l. At the Silstrup (Kjær *et al.,* 2007) and Faardrup sites desethylterbutylazine was frequently detected in the monitoring screens situated beneath the drainage system, concentrations exceeding 0.1 g/L being detected during a 2- and 24-month period, respectively. Leaching at Estrup (Kjær *et al.,* 2007) was confined to the drainage depth, however. Minor leaching of desethylterbutylazine was also seen at the two sandy sites Jyndevad and Tylstrup, where desethylterbutylazine was detected in low concentrations (<0.1 µg/l) in the soil water sampled 1 m b.g.s. While desethylterbutylazine was not detected in the groundwater monitoring screens at Tylstrup, it was frequently detected in low concentration (< 0.1 µg/l) at Jyndevad (see Kjær *et al.,* 2004 and section 2.2.3 for details). Marked leaching of terbutylazine was also seen at two of the three loamy sites (Estrup and Faardrup), the leaching pattern being similar to that of desethylterbutylazine. 2-hydroxy-desethyl-terbutylazine and 2-hydroxy terbutylazine leached at both Faardrup and Estrup and at the latter site the average drainage concentration exceeded 0.1 µg/L. Leaching of these two metabolites was at both sites confined to the drainage system. These two metabolites were not detected in groundwater monitoring screen at Estrup, whereas at Faardrup they were found, however, frequency of detection as well as concentration level being very low.

- One 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 four years PPU also reached the downstream monitoring screens. Although the concentration decreased during the last year of monitoring, elevated concentrations in both suction cups and monitoring wells could be found towards the end of the current monitoring period (i.e. five years after application). Minor leaching of PPU was also seen at the sandy site Tylstrup, where low concentrations (0.021 - 0.11 µg/l) were detected in the soil water sampled 1 and 2 m b.g.s., but only in one groundwater sample from a monitoring well (Appendix 5). 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 (see Kjær *et al.* 2007 for details).

- In the loamy soil of Estrup ethofumesate, metamitron and its degradation product metamitron-desamino leached through the root zone into the drainage water, average concentrations. exceeding 0.1 µg/l. 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 the drainage system and groundwater monitoring screens. Average concentrations in drainage water were not as high as at Estrup, although concentrations exceeding 0.1 µg/l were observed in both drainage water and groundwater monitoring screens during a 1–6 month period (see Kjær *et al.,* 2002 and Kjær *et al.,* 2004 for details).

- Pirimicarb-desmethyl-formamido (degradation product of pirimicarb) leached through the root zone in high average concentrations from the loamy soil of Estrup into the drainage water, average concentrations exceeding 0.1 µg/l. Pirimicarb-desmethyl-formamido has not been detected in deeper monitoring screens. Comparable high levels of leaching of pirimicarb-desmethyl-formamido have not been observed with any of the previous applications of pirimicarb at the five other PLAP sites (Table 17 and Kjær *et al.*, 2004).

- Bentazone leached through the root zone in average concentrations exceeding 0.1 µg/l at the loamy sites of Silstrup, Estrup and Faardrup. Moreover, bentazone was frequently detected in the monitoring screens situated beneath the drainage system of the Silstrup and Faardrup sites. Apart from a few samples, however, concentrations detected were all below 0.1 µg/l. At Estrup leaching was mostly confined to the depth of the drainage system and rarely detected in deeper monitoring screens (Appendix 5). On the sandy soils bentazone leached at Jyndevad but not at Tylstrup. At Jyndevad, 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 after application. Thereafter, leaching diminished and bentazone was not subsequently detected in the monitoring wells (Table 18). Although leached in high average concentrations (>0.1 µg/l) at four sites, the leaching of bentazone was generally observed within a short period of time. Initial concentrations of bentazone were usually very high, but then decreased rapidly. In general, concentrations exceeding 0.1 were only found within a period of one to four months following the application.

- Propyzamide leached from the root zone at the loamy Silstrup and Faardrup site, entering the drainage water at average concentrations exceeding 0.1 µg/l Propyzamide was also detected in the monitoring screen situated beneath the drainage system. Apart from a few samples, the concentrations in the screens were always less than 0.1 µg/l, however (Appendix 6). The leaching risk at Faardrup and Silstrup cannot be fully evaluated until the 2008 monitoring data become available, i.e. when two years of monitoring data have been collated.

- Azoxystrobin, and in particular its degradation product CyPM, leached through the root zone in high average concentrations at the loamy sites Silstrup and Estrup. CyPM leached into the drainage water in 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. Neither the loamy Faardrup site nor the sandy Jyndevad site had similar high levels of leaching (Appendix 6).

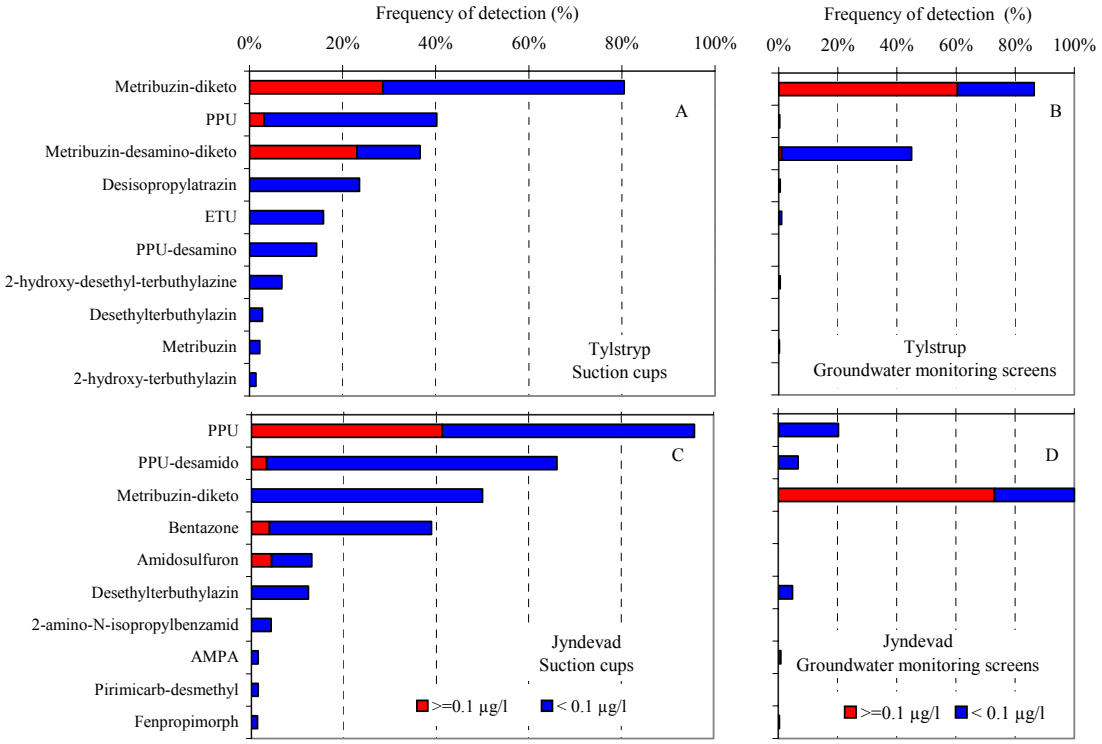

Figure 45. Frequency of detection in samples from the suction cups (left) and groundwater monitoring screens located deeper than the suction cups (right) at the sandy soil sites at Jyndevad (C, D). Frequency is estimated for the entire monitoring period and the time that the different pesticides have 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.

The monitoring data also indicate leaching of a further 17 pesticides, but not in such high concentrations. Although the concentrations exceeded 0.1 µg/l in several samples, the average leaching concentration (1 m b.g.s.) did not. This is summarized in Table 18, showing the number of samples in which the various pesticides were detected on each site as well as 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 it 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.

Eight of the 36 pesticides applied – about 22% – did not leach during the monitoring period. This group includes the three different sulfonylureas – metsulfuronmethyl, triasulfuron and tribenuron-methyl applied at several sites. For example, tribenuron-methyl was applied at four different sites under different hydrological conditions, percolation (1 m b.g.s.) during the first month after application ranging from 0 to 114 mm. The monitoring results give no indication of leaching for any of the compounds or their degradation products, including triazinamin and triazinamin-methyl. It should, however, be noted, that the leaching risk associated with a late autumn application of tribenuron-methyl has not yet been evaluated for the loamy soils.

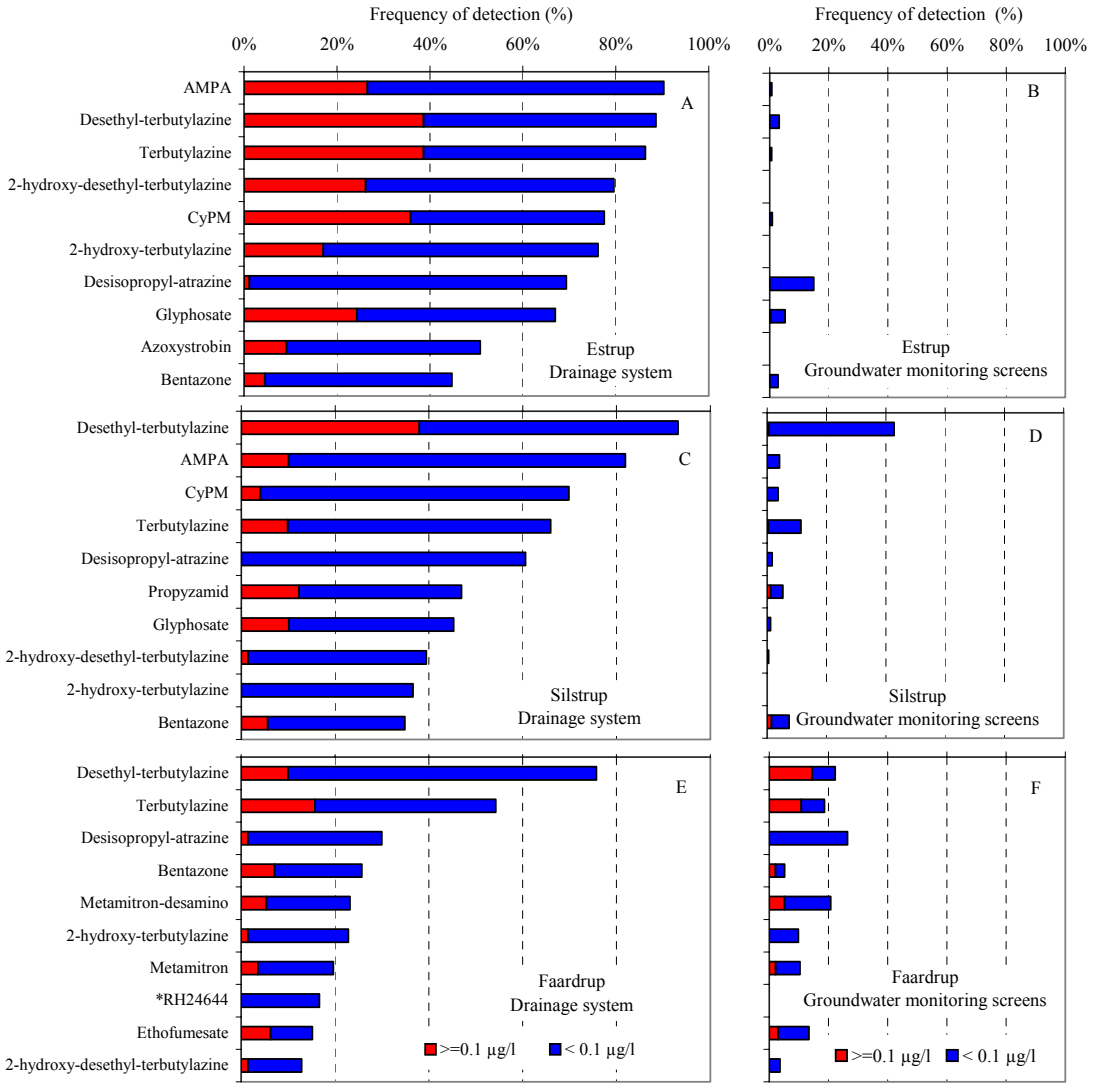

Figure 46. Frequency of detection in samples from the drainage system (left) and groundwater monitoring screens located deeper than the drainage system (right) at the loamy soil sites Silstrup (A, B), Estrup (C, D) and Faardrup (E, F). Frequency is estimated for the entire monitoring period and the time 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.

As reported in Kjær *et al.* 2007, pendimethalin also leached from the root zone at Estrup in high concentrations. When evaluating the results presented in Kjær *et al.* 2007, it should, however, be noted that the pesticide application of pendimethalin was not done in accordance with current regulation. The results are therefore omitted from the PLAP report.

The leaching patterns of the sandy and loamy sites are further illustrated in Figure 45 and 46, showing the frequency of detection in samples collected 1 m b.g.s. (suction cups on sandy soils and drainage systems on loamy soils) and the deeper located groundwater monitoring screens.

On the sandy soils, as compared to the loamy, the number of leached pesticides as well as the frequency of detection was much lower (Figure 45 and 46), the exceptions being the mobile and persistent degradation products of rimsulfuron and metribuzin frequently

found in both suction cups and groundwater monitoring wells. This difference was mainly due to the different flow patterns characterising the two different soil types. On the sandy soils infiltrating water mainly passed through the matrix, thereby providing good conditions for sorption and degradation. Pesticides being leached in the sandy soils were thus restricted to mobile as well as persistent pesticides. On the loamy soils pronounced macropore transport resulted in the pesticides moving very rapidly through the unsaturated zone. Compared to the sandy soils residence time was much lower on the structured, loamy soils. As a result of this, various types of pesticides, even those being strongly sorbed, were prone to leaching on that type of soil.

At the loamy sites pronounced leaching was generally confined to the depth of the drainage system. Several pesticides were often detected in the drainage system, whereas the amount of pesticide reaching the monitoring screens situated beneath the drainage system was limited and varied considerably within the three sites (Figure 46). These differences should be seen in relation to the different sampling procedures applied. Frequent, integrated water samples can be provided from a drainage system that continuously capture water infiltrating throughout the drainage runoff season. However, although the monitoring screens situated beneath the drainage systems were sampled less frequently (on a monthly basis from a limited number of the monitoring screens (Appendix 2), pesticides were frequently found in selected screens at Faardrup and Silstrup. Hitherto, at the Estrup site leaching of pesticides has mainly been confined to the depth of the drainage system. Apart from 25 samples containing glyphosate, pesticides have only sporadically been detected in the screens beneath the drainage system (Appendix 5). The differences are, however, 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 is less permeable with less preferential flow through macropores (se Kjær *et al.* 2005c for details). The movement of water and solute may therefore be slower at Estrup, allowing for dispersion, dilution, sorption and degradation and thereby reducing risk of a deeper transport.

Comparing the loamy sites, the number of drainage water samples containing pesticides/degradation products was markedly higher at Silstrup and Estrup than at Faardrup, largely attributable to the differences in the hydrological conditions; precipitation and subsequent percolation occurring within the first month after application were, generally, higher at Silstrup and Estrup than at Faardrup (Table 9, Table 11 and Table 12).

9 References

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

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

Barlebo H.C., Rosenbom, A. and Kjær, J. (2007): Evaluation of Pesticide Scenarios for the Registration Procedure; no. 1178; Danish Environmental Protection Agency. Available on http://www2.mst.dk/common/Udgivramme/Frame.asp? http://www2.mst.dk/Udgiv/publications/2007/978-87-7052-540-/html/default_eng.htm.

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

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

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

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

Guzzella, L., Rullo, S., Pozzoni, F. and Giuliano, G. (2003): Studies on mobility and degradation pathways of terbutylazine using lysimeters on a field scale, *J. Environ. Qual.* 32, 1089-1098.

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

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

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

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

Kjær, J., Olsen, P., Barlebo, H. C., Juhler, R. K., Plauborg, F., Grant, R., Gudmundsson, L. and Brüsch, W. (2004): The Danish Pesticide Leaching Assessment Programme: Monitoring results, May 1999–June 2003, Geological Survey of Denmark and Greenland, 2004.

Kjær, J., Olsen, P., Ullum, M. and Grant, R. (2005a): Leaching of glyphosate and amino-methylphosphonic acid from Danish agricultural field sites, *J. Environ. Qual.*, 34, 608–630.

Kjær, J., Olsen, P., Henriksen, T. and Ullum, M. (2005b): Leaching of metribuzin metabolites and the associated contamination of a sandy Danish aquifer, *Environ. Sci. Technol*. 39, 8374-8381.

Kjær, J., Olsen, P., Barlebo, H. C., Juhler, R. K., Henriksen T., Plauborg, F., Grant, R., Nygaard P. and Gudmundsson L. (2005c): The Danish Pesticide Leaching Assessment Programme: Monitoring results, May 1999–June 2004, Geological Survey of Denmark and Greenland, 2005.

Kjær, J., Olsen, P., Barlebo, H. C., Henriksen T., Plauborg, F., Grant, R., Nygaard P. Gudmundsson, L. and Rosenbom, A. (2007): The Danish Pesticide Leaching Assessment Programme: Monitoring results, May 1999–June 2006, Geological Survey of Denmark and Greenland, 2007.

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

Larsbo, M., Roulier, S., Stenemo, F., Kasteel, R. and Jarvis, N. (2005): An improved dual-permeability model of water flow and solute transport in the vadose zone. *Vadose Zone Journal* 4(2), 398-406.

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

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

Pedersen, C. Aa. (ed) (2005): Oversigt over Landsforsøgene: Forsøg og undersøgelser i de landøkonomiske foreninger. Dansk Landbrugsrådgivning, Landscentret, Planteavl. 412 pp.

Plantedirektoratet (2006): Vejledning om gødsknings- og harmoniregler. Ministeriet fo Fødevare, Landbrug og Fiskeri. Revideret udgave 29. september 2006. 104 pp.

Rosenbom, A. E., van der Keur, P., Barlebo, H.C., Grant, R. and Plauborg, F., (2007): Predicting bromide transport in unsaturated soils (In prep.)

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

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

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

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
CGA 322704 *	N-(2-chloro-thiazol-5-yl-methyl)-N'-methyl-N''-nitro-guanidine
Clomazone	2-[(2-chlorphenyl)methyl]-4,4-dimethyl-3-isoxazolidione
Clopyralid	3,6-Dichloropyridine-2-carboxylic acid
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
Epoxiconazole*	(2RS, 3SR)-1-(2-(2-chlorophenyl)-2,3-epoxy-2-(4-fluorophenyl)propyl)-1H-1,2,4-triazol
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
Florasulam	2',6',8-Trifluoro-5-methoxy-s-triazolo [1,5-c]pyrimidine-2-sulfonanilide
Florasulam-desmethyl *	N-(2,6-difluorophenyl)-8-fluro-5-hydroxy[1,2,4]triazolo[1,5-c]pyrimidine-2-sulfonamide
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
Mesosulfuron	2-[(4,6-dimethoxypyrimidin-2-ylcarbamoyl)sulfamoyl]-α-(methanesulfonamido)-p-toluic acid
Mesosulfuronmethyl *	Methyl 2-[3-(4,6-dimethoxypyrimidin-2-yl)ureidosulfonyl]-4-methanesulfonamidomethylbenzoate
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
Metribuzine	4-amino-6-tert-butyl-4,5-dihydro-3-methylthio-1,2,4-triazine-5-one
Metribuzine-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
Metribuzine-desamino	6-(1,1-dimethylethyl)-3-(methylthio)-1,2,4-triazin-5(4H)-one
Metribuzine-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
Pendimethaline	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
Propyzamide	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
Thiamethoxam*	3-(2-cholro-thiazol-5-ylmethyl)-5-methyl[1,3,5]oxadiazinan-4ylidene-N-nitroamine
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 Kjær *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 months (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 events additional samples (sampled flow-proportionally during 1 – 2 days) were also analysed for pesticides. In June 2004 the drainage monitoring programme was revised. From July 2004 and onwards pesticide analyses were done weekly on water sampled flow-proportionally from the drainage water system. See Kjær *et al.* 2003 for further details on the methods of flow-proportional 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 flow-proportional sampling was applied the numbers were:

$M_i = Ct_i \cdot V_i$ *If no flow event occurs within the i'te week*

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

(*I'te* – hvad står det for? Og skulle det være *i'th* ?)

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)

Table 9, 10 and 11 report the weighted average leachate concentration in the drainage water within the first drainage season after application. In these tables this calculation period is defined as the period from the date of application until 1 July the following year.

On the sandy soils the weighted average concentration of pesticides 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 2005 to 2006 growing seasons. The active ingredients of the various pesticides are indicated in parentheses.

Date	Management practice
05.10.04	Potatoes harvested (tuber yield 119.9hkg/ha, 100% dry matter, 512 hkg/ha of potatoes)
01.04.05	Rotary cultivated – 8 cm depth
07.04.05	Ploughed – 20 cm depth
20.04.05	Seed bed preparation – 4 cm depth
26.04.05	Seed bed preparation – 7 cm depth
28.04.05	Maize Sown – cultivar 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)
05.11.05	Rotary cultivated - 8 cm depth
21.04.06	Ploughed - 22 cm depth
21.04.06	Rolled with a concrete roller
23.04.06	Seed bed preparation - 7 cm depth
23.04.06	Spring barley sown (cultivare Cabaret)
06.06.06	Express ST (tribenuron-methyl) - weeds - 4.25 tablets/ha
03.07.06	Opus (epoxiconazole) - fungi - 1.0 l/ha
19.06.05	Irrigation - 29 mm
24.08.06	Spring barley harvested (grain yield 55,6 hkg/ha; 85% dry matter)
24.08.06	Straw shredded, amount 33.2 hkg/ha
25.08.06	Rotary cultivated - depth 5.0 cm (straw incorporation)
26.08.06	Ploughed - depth 23 cm.
26.08.06	Winter rape sown (Cultivare Lioness)
26.08.06	Herbicide - 0.33 l/ha Command CS (clomazone)
06.09.06	Seedbed preparation – 7 cm depth
06.09.06	Winter rape resown (cultivare Castille)
09.02.07	Herbicide - 1.0 l/ha Kerb 500 SC (propyzamide)

Table A3.2 Management practice at Jyndevad during the 2005 to 2006 growing seasons. The active ingredients of the various pesticides are indicated in parentheses.

Date	Management practice
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)
29.03.06	Rotary cultivated - 5 cm depth
30.03.06	Ploughed - 20 cm depth
04.04.06	Rolled with a concrete roller
11.04.06	Spring barley sown - Cultivare Simba
26.05.06	Herbicide - 0.1 l/ha Primus (florasulam)
06.06.06	Irrigation - 27 mm/ha
08.06.06	Opus (epoxiconazole) - weeds - 1.0 l/ha
12.06.06	Irrigation - 30 mm/ha
26.06.06	Irrigation - 27 mm/ha
02.07.06	Irrigation - 30 mm/ha
07.07.06	Irrigation - 30 mm/ha
07.08.06	Spring barley harvested (Seed yield 60.49 kgh/ha; 85% dry matter. Straw yield 26.75 hkg/ha 100% dry matter)
20.09.06	Ploughed - 22 cm depth
20.09.06	Rolled with a concrete roller
21.09.06	Seed bed preparation - 6 cm depth
21.09.06	Sowing triticale - cultivare Dinaro
10.10.06	Herbicide - 250 g/ha Atlantis WG (mesosulfuron-methyl/iodosulfuron)

Table A3.3 Management practice at Silstrup during the 2005 to 2006 growing seasons. The active ingredients of the various pesticides are indicated in parentheses.

Date	Management practice
24.04.05	Spring barley sown – cultivare Cabaret
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	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 (Propyzamide)
17.11.05	Kerb 500 SC (propyzamide) - weeds - 1.0 l/ha
20.04.06	Herbicide –0.8 l/ha Matrigon (clopyralid)
05.05.06	Insecticide - 0.25 l/ha Fastac (alpha-cypermethin, not analyzed)
24.07.06	Windrowing - Stublehight 13 cm
07.08.06	Threshed (seed yield 37.3 hkg/ha 91% dry matter)
20.09.06	Ploughed - 22 cm depth
22.09.06	Sowing winter wheat sown - cultivare Skalmeje
22.09.06	Herbicide - 5.0 l/ha Stomp Pentagon (pendimethalin)

Table A3.4 Management practice at Estrup during the 2005 to 2006 growing seasons. The active ingredients of the various pesticides are indicated in parentheses.

Date	Management practice
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)
12.04.06	Ploughed – depth 18 cm - packed with a ring roller
07.04.06	Spring barley sown – cukltivare Simba
01.05.06	Rolled with a cam roller
17.05.06	Herbicide – 0.25 l/ha Starane 180 (fluroxypyr, not analyzed)
02.06.06	Herbicide – 0.25 l/ha Starane 180 (fluroxypyr, not analyzed)
06.06.06	Herbicide – 0.10 l/ha Primus (florasulam)
29.06.06	Fungicide - 1.0 l/ha Amistar (azoxystrobin)
17.08.06	Harvest of spring barley harvested (grain yield 59.2 hkg/ha; 85% dry matter)
11.09.06	Straw removed (straw yield 26.79 hkg/ha)
13.09.06	Ploughed - 18 cm depth - packed with a ring roller
14.09.06	Rotory cultivated - 4 cm depth
14.09.06	Winter wheat sown – cultivare Smuggler

Table A3.5 Management practice at Faardrup during the 2005 to 2006 growing seasons. The active ingredients of the various pesticides are indicated in parentheses.

Date	Management practice
26.04.05	Maize sown – cultivare Nescio
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
28.04.06	Spring barley sown - cultivare Scandium
26.05.06	Herbicide - 0.8 l/ha Starane 180 S (fluroxypur)
29.06.06	Fungicide - 1.0 l/ha Opus (epoxiconazole)
11.08.06	Harvest of spring barley harvested (grain yield 67.3 hkg; 85% dry matter. Straw yield 51.1 hkg/ha 100% dry matter)
17.08.06	Ploughed - 22 cm depth
17.08.06	Winter rape sown – cultivare Labrador
18.08.06	Herbicide - 0.33 l/ha Command CS (clomazone – not analysed)
19.02.07	Fungicide - 1.0 l/ha Kerb 500 SC (propyzamide)

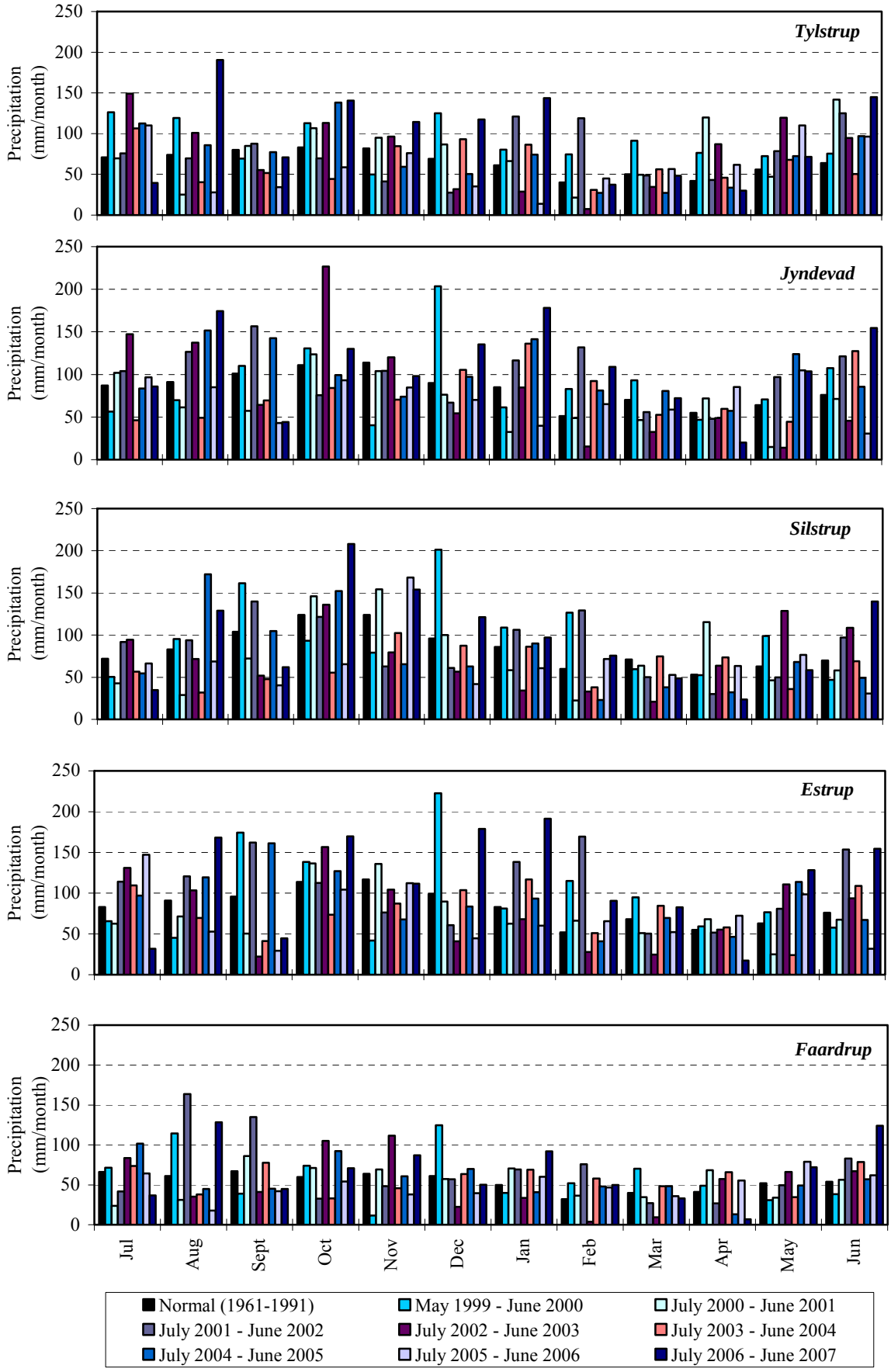

Figure A4.1. Monthly precipitation at all localities for the monitoring period July 2000–June 2006. Normal values (1961–1990) are included for comparison.

Table A5.1 Number of samples where pesticides were either not detected (n.d.), detected in concentrations below 0.1 µg/l (det<0.1 µg/l) or detected in concentrations 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 are 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
2-amino-N-isopropylbenzamid	191			72		
2-hydroxy-desethyl-terbutylazine	190	1		67	5	
2-hydroxy-terbutylazine	191			71	1	
Bentazone	191			71	1	
Bromoxynil	192			72		
CGA 322704	83			30		
Clomazone	224			82		
Clopyralid	6			10		
Desethylterbutylazine	191			70	2	
Desisopropylatrazine	190	1		55	17	
Dimethoate	176			65		
Epoxiconazole	107			40		
ETU	198	2		37	7	
Fenpropimorph	307			89		
Fenpropimorphic-acid	276			73		
Flamprop (free acid)	176			65		
Flamprop-M-isopropyl	176			65		
Fluazifop-P (free acid)	178			65		
Fluroxypyr	194			70		
FMC65317	208			74		
IN70941	266	1		58	36	3
IN70942	267			83	14	
Ioxynil	198			72		
Linuron	270			67		
Metribuzine	386	1		89	2	
Metribuzine-desamino	365			85		
Metribuzine-desamino-diketo	289	231	5	140	30	51
Metribuzine-diketo	71	136	317	43	114	63
Pendimethalin	242			70		
Pirimicarb	295			82		
Pirimicarb-desmethyl	295			81		
Pirimicarb-desmethyl-formamido	167			52		
Propiconazole	307			89		
Propyzamide	65			24		
RH24580	65			24		
RH24644	65			24		
RH24655	65			24		
Rimsulfuron	178			65		
Terbutylazine	179			72		
Thiamethoxam	83			30		
Triasulfuron	295			82		
Triazinamin	285			75		
Triazinamin-methyl	348			103		

Table A5.2 Number of samples where pesticides were either not detected (n.d), detected in concentrations below 0.1 µg/l (det<0.1 µg/l) or detected in concentrations 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 are 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
2-amino-N-isopropylbenzamid	178			45	2	
4-chlor-2-methylphenol	189			52		
Amidosulfuron	88			20	2	1
AMPA	221	2		68	1	
Azoxystrobin	193			55		
Bentazone	277			47	27	3
Bromoxynil	218			61		
CyPM	193			55		
Desethylterbutylazin	472	24		128	18	
Desmethyl-amidosulfuron	88			23		
Dimethoate	169			48		
Epoxiconazole	105			32		
Fenpropimorph	246	1		76	1	
Fenpropimorphic-acid	259			79		
Flamprop (free acid)	12			4		
Flamprop-M-isopropyl	12			4		
Florasulam	105			32		
Florasulam-desmethyl				12		
Fluazifop-P (free acid)	190			51		
Fluroxypyr	193			55		
Glyphosate	223			69		
IN70941	345	87	1	5	66	50
IN70942	404	29		41	76	4
Ioxynil	218			61		
MCPA	189			52		
Mesosulfuron				9		
Mesosulfuron-methyl	67			20		
Metribuzine	26			6		
Metribuzine-desamino	26			4		
Metribuzine-desamino-diketo	6	7	13	6		
Metribuzine-diketo		7	19	3	3	
Pendimethalin	257			71		
PHCP	184			59		
Pirimicarb	251			69		
Pirimicarb-desmethyl	251			68	1	
Pirimicarb-desmethyl-formamido	251			69		
Propiconazole	236			75		
Pyridate	116			39		
Rimsulfuron	168			48		
Terbutylazine	239			75		
Triazinamin-methyl	247			77		

Table A5.3 Number of samples where pesticides were either not detected (n.d), detected in concentrations below 0.1 µg/l (det<0.1 µg/l) or detected in concentrations 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 are 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
2-amino-N-isopropylbenzamid	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			
Clomazone	19			17			32					
Clopyralid	59	1	3	81			148	1				
CyPM	22	48	3	101	2		187	9				
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		
Epoxiconazole				10			22					
Ethofumesate	86	14	1	107	1		237	3		54	3	2
Fenpropimorph	82			74			148			27		
Fenpropimorphic- 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	50			74			142					
FMC65317	19			17			32					
Glyphosate	81	52	15	128			233	4		8		
Iodosulfuron-methyl-natrium				10			22					
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
Metsulfuron-methyl				10			22					
MHPC	100			106			234			55		
Pendimethalin	73	14		102			186					
PHCP	62		4	66	2		109	8	4			
Phenmedipham	101			108			240			59		
Pirimicarb	160	14		210			433	3		59		
Pirimicarb-desmethyl	173	1		210			436			59		
Pirimicarb-desmethyl-formamido	141			160			308			20		
Propiconazol	76	6		74			148			27		
Propyzamide	26	17	6	55	2	1	107	5	1			
Prosulfocarb	69	4	1	79	1		147					
RH24580	47	2		58			113					
RH24644	34	15		57	1		112	1				
RH24655	49			58			113					
Terbutylazine	31	51	9	108	5		173	30	1			
Triazinamin				10			22					
Triazinamin-methyl	82			74			148			27		

Table A5.4 Number of samples where pesticides were either not detected (n.d), detected in concentrations below 0.1 µg/l (det<0.1 µg/l) or detected in concentrations 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 are 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
2-amino-N-isopropylbenzamid	235	1		79	1		271			5		
2-hydroxy-desethyl-terbutylazine	18	47	23	34			120					
2-hydroxy-terbutylazine	21	52	15	34			120					
4-chlor-2-methylphenol	101	1		34			112					
Amidosulfuron	99			34			109					
AMPA	30	197	82	111			406	4		23		
Azoxystrobin	59	50	11	48			171					
Bentazone	136	99	11	77	10		299	1		3	2	2
Bromoxynil	135	1	2	41			125			3		
Clopyralid	1											
CyPM	27	50	43	46	2		171					
Desethylterbutylazine	10	44	34	29	5		120					
Desisopropylatrazine	27	60	1	33	1		98	22				
Dimethoate	88			42			160			23		
Epoxiconazole	5		1	3			9					
Ethofumesate	91	27	8	46			158					
Fenpropimorph	82	1		39			152			23		
Fenpropimorphic- acid	82			34			125			17		
Flamprop (free acid)	118	13		55			210			23		
Flamprop-M-isopropyl	111	20		55			210			23		
Florasulam	49			19			65					
Florasulam-desmethyl	39			17			56					
Fluroxypyr	87	1	2	34			120	1				
Glyphosate	102	132	75	108	2		383	23	2	23		
Ioxynil	118	14	6	41			125			3		
MCPA	91	9	2	34			111	1				
Mesosulfuron	32			11			39					
Mesosulfuron-methyl	19	13		11			39					
Metamitron	83	27	15	46			158					
Metamitron-desamino	76	38	11	46			157					
Metsulfuron-methyl	130			55			210			22	1	
Pirimicarb	159	39		67			225	1		6		
Pirimicarb-desmethyl	191			66			223			6		
Pirimicarb-desmethyl-formamido	198	13	13	76			261			5		
Propiconazol	192	22	3	86			311	2		23		
Terbutylazine	12	42	34	34			119	1				
Triazinamin	125			52			197	1		22		
Triazinamin-methyl	1											

Table A5.5 Number of samples where pesticides were either not detected (n.d), detected in concentrations below 0.1 µg/l (det<0.1 µg/l) or detected in concentrations above 0.1 µg/l (det>=0.1µg/l) at Faardrup. Numbers are accumulated for the entire monitoring periode, and pesticides monitored for less than one year are 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
2-amino-N-isopropylbenzamid	69	1		61			132					
2-hydroxy-desethyl-terbutylazine	61	8	1	60	1		126	6				
2-hydroxy-terbutylazine	54	15	1	59	2		115	17				
4-chlor-2-methylphenol	144		1	109			254					
AMPA	141	11	1	110			282	2		57	5	
Azoxystrobin	100			85			178					
Bentazone	52	13	5	58	2	1	125	4	3			
Bromoxynil	113			81			226			73		
CGA 322704	26			30			64					
Clomazone	84		1	69			166					
Clopyralid	31	1		24			72					
CyPM	96	4		85			178					
Desethylterbutylazine	17	46	7	48	13		102	2	28			
Desisopropylatrazine	49	20	1	36	25		106	26				
Desmedipham	111			66			165			29		
Dimethoate	77			58			148					
EHPC	86			52			123			16		
Epoxiconazole	39			38			81					
Ethofumesate	95	10	7	66			134	24	7	27	2	
Fenpropimorph	82			58	1		157			54		
Fenpropimorphic-acid	82			59			157			54		
Flamprop (free acid)	76	1		58			148					
Flamprop-M-isopropyl	70	1		56			142					
Fluazifop-P (free acid)	101	5	5	66			159	5	1	26	3	
Fluazifop-P-butyl	111			66			165			29		
Fluroxypyr	125		1	100	1		244			55		
FMC65317	84		1	69			166					
Glyphosate	149	4		109	1		282	2		61	1	
Ioxynil	111	1		81			225	1		73		
MCPA	143	1	1	109			255					
Metamitron	90	18	4	66			141	19	5	29		
Metamitron-desamino	86	20	6	66			117	36	12	29		
MHPC	108	2	1	66			163	1		29		
Phenmedipham	110	1		66			163	2		29		
Pirimicarb	123	9		90			244	2		52		
Pirimicarb-desmethyl	106	6		66			162	3		29		
Pirimicarb-desmethyl-formamido	109	3		66			163	2		29		
Propiconazol	159			116			304	1		54		
Propyzamide	21	1	2	22	1		48					
Prosulfocarb	80			61			126					
RH24580	24			23			48					
RH24644	20	4		23			48					
RH24655	24			23			48					
Terbutylazine	32	27	11	55	5	1	102	10	20			
Thiamethoxam	26			30			64					
Triazinamin-methyl	77			57			147					

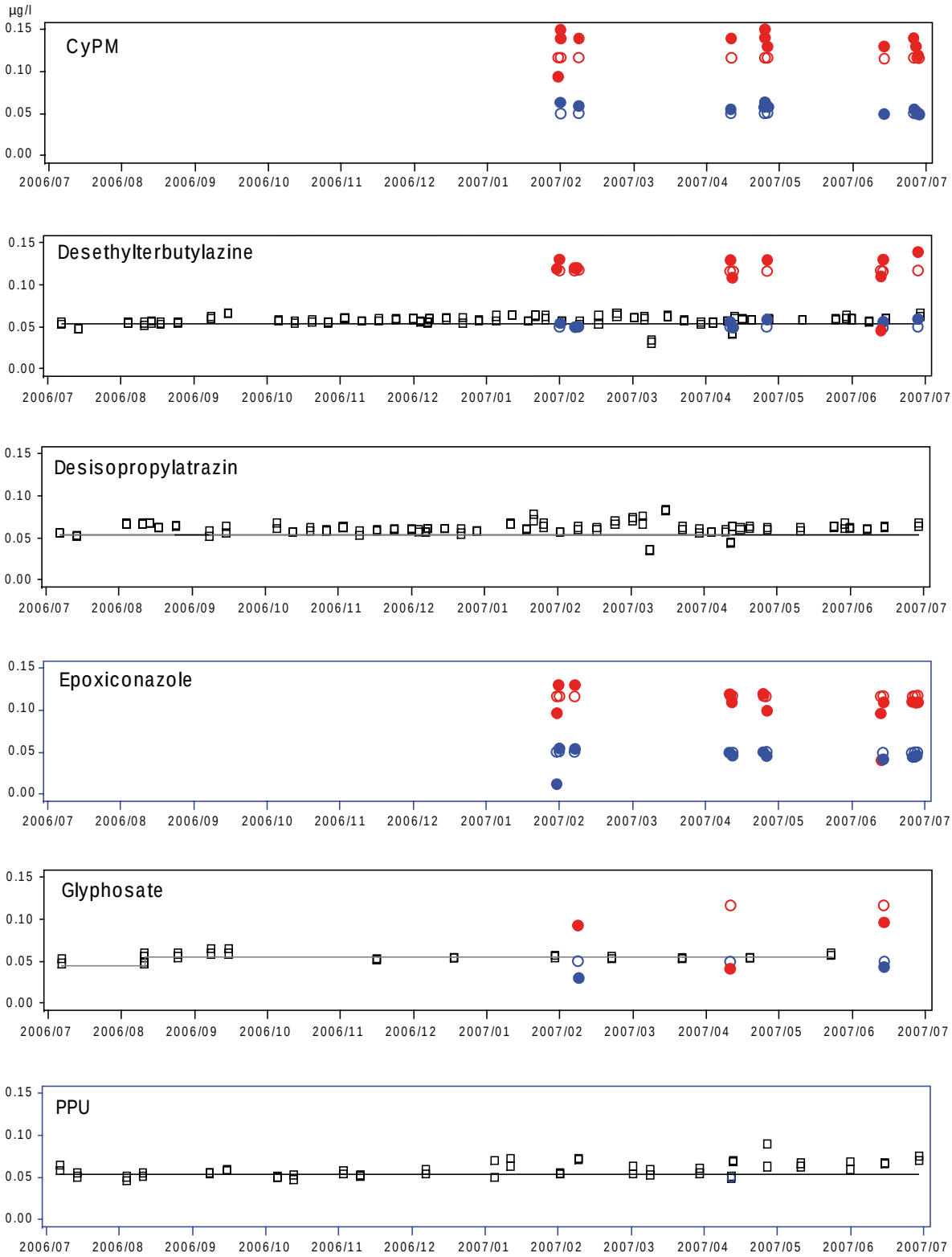

Figure A6.1 Quality control data for pesticide analysis by laboratory 1. Internal laboratory control samples are indicated by square symbols and the nominal level is indicated by the solid grey line (□ IQ measured, — IQ nominal concentration). External control samples are indicated by circles. Open circles indicate the nominal level (○ EQ nominal low, ○ EQ nominal high), and closed circles the observed concentration (● EQ measured low, ● EQ measured high).

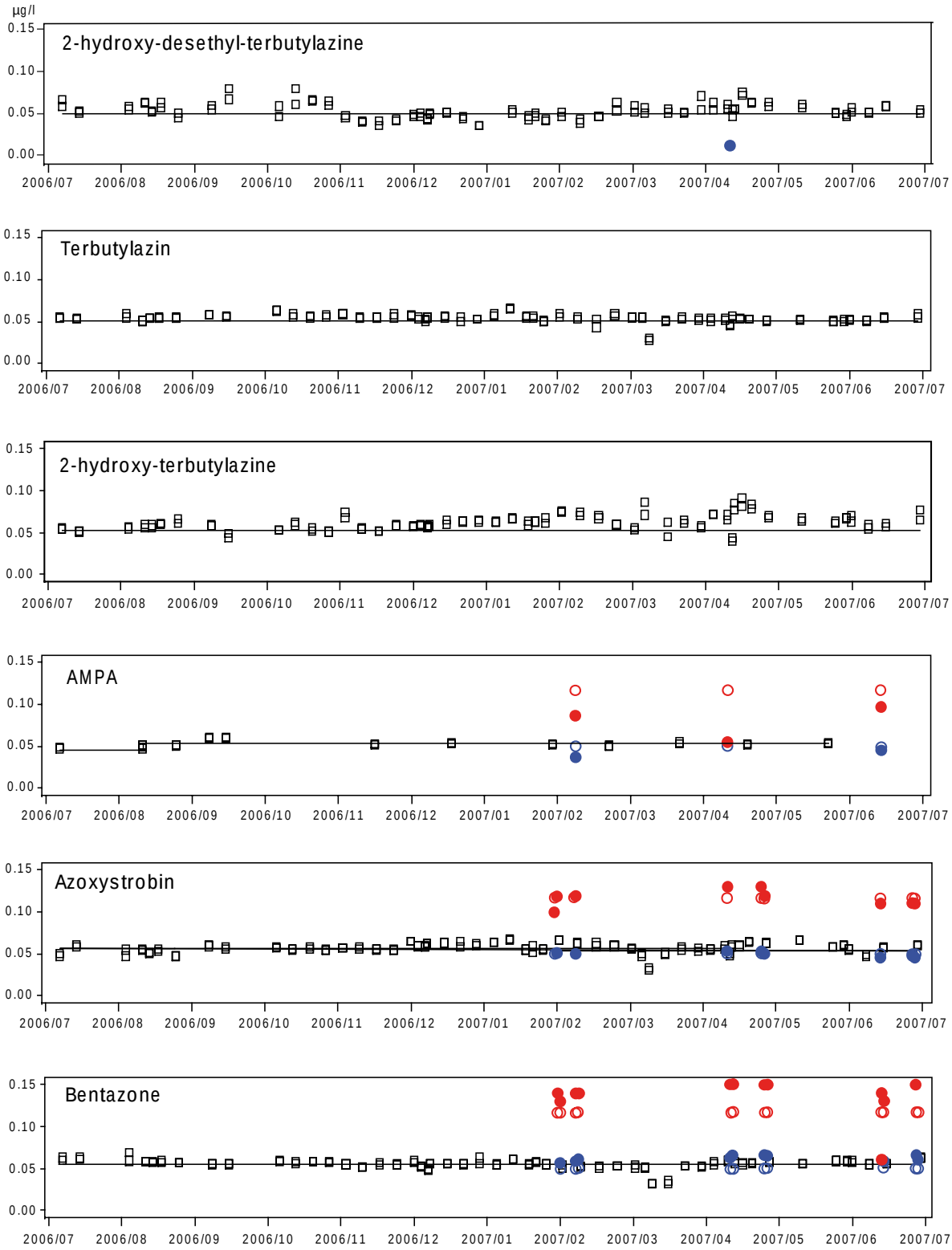

Figure A6.1 (Continued) Quality control data for pesticide analysis by laboratory 1. Internal laboratory control samples are indicated by square symbols and the nominal level is indicated by the solid grey line (¤ IQ measured, — IQ nominal concentration). External control samples are indicated by circles. Open circles indicate the nominal level (○ EQ nominal low, ○ EQ nominal high), and closed circles the observed concentration (● EQ measured low, ● EQ measured high).

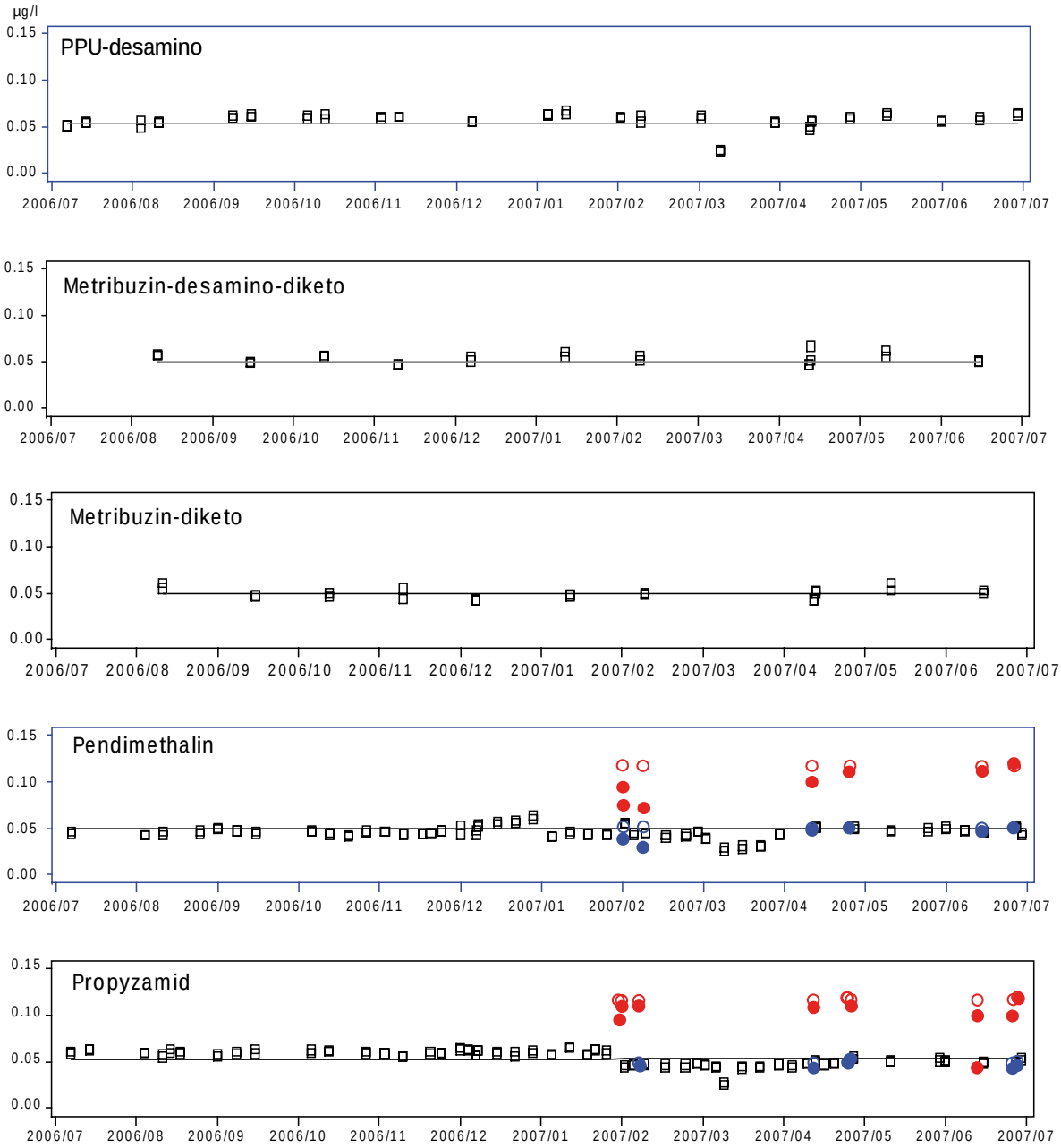

Figure A6.1 (Continued) Quality control data for pesticide analysis by laboratory 1. Internal laboratory control samples are indicated by square symbols and the nominal level is indicated by the solid grey line (¤ IQ measured, — IQ nominal concentration). External control samples are indicated by circles. Open circles indicate the nominal level (○ EQ nominal low, ○ EQ nominal high), and closed circles the observed concentration (● EQ measured low, ● EQ measured high).