

# The Danish Pesticide Leaching Assessment Programme

Monitoring results May 1999–June 2010

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*Cover photo:* Lasse Gudmundsson  
*Cover:* Henrik Klinge Pedersen  
*Layout and graphic production:* Authors  
*Printed:* September 2011  
*Price:* DKK 200

ISBN 978-87-7871-312-4

Available from:

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The report is also available as a pdf file at [www.pesticidvarsling.dk](http://www.pesticidvarsling.dk)

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# Table of contents

PREFACE

SUMMARY

DANSK SAMMENDRAG

<b>1</b>	<b>INTRODUCTION .....</b>	<b>13</b>
1.1	OBJECTIVE .....	13
1.2	STRUCTURE OF THE PLAP .....	14
<b>2</b>	<b>PESTICIDE LEACHING AT TYLSTRUP.....</b>	<b>17</b>
2.1	MATERIALS AND METHODS .....	17
2.1.1	<i>Site description and monitoring design .....</i>	<i>17</i>
2.1.2	<i>Agricultural management .....</i>	<i>18</i>
2.1.3	<i>Model setup and calibration.....</i>	<i>18</i>
2.2	RESULTS AND DISCUSSION .....	19
2.2.1	<i>Soil water dynamics and water balances.....</i>	<i>19</i>
2.2.2	<i>Bromide leaching.....</i>	<i>21</i>
2.2.3	<i>Pesticide leaching.....</i>	<i>23</i>
<b>3</b>	<b>PESTICIDE LEACHING AT JYNDEVAD.....</b>	<b>29</b>
3.1	MATERIALS AND METHODS .....	29
3.1.1	<i>Site description and monitoring design .....</i>	<i>29</i>
3.1.2	<i>Agricultural management .....</i>	<i>29</i>
3.1.3	<i>Model setup and calibration.....</i>	<i>31</i>
3.2	RESULTS AND DISCUSSION .....	33
3.2.1	<i>Soil water dynamics and water balances.....</i>	<i>33</i>
3.2.2	<i>Bromide leaching.....</i>	<i>34</i>
3.2.3	<i>Pesticide leaching.....</i>	<i>36</i>
<b>4</b>	<b>PESTICIDE LEACHING AT SILSTRUP .....</b>	<b>43</b>
4.1	MATERIALS AND METHODS .....	43
4.1.1	<i>Site description and monitoring design .....</i>	<i>43</i>
4.1.2	<i>Agricultural management .....</i>	<i>43</i>
4.1.3	<i>Model setup and calibration.....</i>	<i>45</i>
4.2	RESULTS AND DISCUSSION .....	46
4.2.1	<i>Soil water dynamics and water balances.....</i>	<i>46</i>
4.2.2	<i>Bromide leaching.....</i>	<i>49</i>
4.2.3	<i>Pesticide leaching.....</i>	<i>50</i>
<b>5</b>	<b>PESTICIDE LEACHING AT ESTRUP.....</b>	<b>61</b>
5.1	MATERIALS AND METHODS .....	61
5.1.1	<i>Site description and monitoring design .....</i>	<i>61</i>
5.1.2	<i>Agricultural management .....</i>	<i>61</i>
5.1.3	<i>Model setup and calibration.....</i>	<i>63</i>
5.2	RESULTS AND DISCUSSION .....	63
5.2.1	<i>Soil water dynamics and water balances.....</i>	<i>63</i>
5.2.2	<i>Bromide leaching.....</i>	<i>66</i>
5.2.3	<i>Pesticide leaching.....</i>	<i>67</i>
<b>6</b>	<b>PESTICIDE LEACHING AT FAARDRUP.....</b>	<b>77</b>
6.1	MATERIALS AND METHODS .....	77
6.1.1	<i>Site description and monitoring design .....</i>	<i>77</i>
6.1.2	<i>Agricultural management .....</i>	<i>80</i>
6.1.3	<i>Model setup and calibration.....</i>	<i>80</i>
6.2	RESULTS AND DISCUSSION .....	81
6.2.1	<i>Soil water dynamics and water balances.....</i>	<i>81</i>
6.2.2	<i>Bromide leaching.....</i>	<i>83</i>
6.2.3	<i>Pesticide leaching.....</i>	<i>85</i>

<b>7</b>	<b>PESTICIDE ANALYSIS QUALITY ASSURANCE .....</b>	<b>89</b>
7.1	MATERIALS AND METHODS .....	89
7.1.1	<i>Internal QA</i> .....	89
7.1.2	<i>External QA</i> .....	89
7.2	RESULTS AND DISCUSSION .....	90
7.2.1	<i>Internal QA</i> .....	90
7.2.2	<i>External QA</i> .....	92
7.3	SUMMARY AND CONCLUDING REMARKS .....	94
<b>8</b>	<b>SUMMARY OF MONITORING RESULTS .....</b>	<b>95</b>
<b>9</b>	<b>REFERENCES.....</b>	<b>107</b>

**APPENDIX 1.** CHEMICAL ABSTRACTS NOMENCLATURE FOR THE PESTICIDES ENCOMPASSED BY THE PLAP.

**APPENDIX 2.** PESTICIDE MONITORING PROGRAMME - SAMPLING PROCEDURE.

**APPENDIX 3.** AGRICULTURAL MANAGEMENT.

**APPENDIX 4.** PRECIPITATION DATA FOR THE PLAP SITES.

**APPENDIX 5.** PESTICIDE DETECTION IN SAMPLES FROM DRAINAGE SYSTEM, SUCTION CUPS AND MONITORING SCREENS.

**APPENDIX 6.** LABORATORY INTERNAL CONTROL CARDS.

# 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. The programme has now been prolonged twice, initially with funding from the Ministry of the Environment and the Ministry of Food, Agriculture and Fisheries for the period 2002 to 2009, and presently with funding from the Danish Environmental Protection Agency for the period 2010 to 2015.

The work was conducted by the Geological Survey of Denmark and Greenland (GEUS), the Department of Agroecology (DJF) at Aarhus University and the Department of Bioscience (NERI), Aarhus University under the direction of a management group comprising Jeanne Kjær (GEUS), Annette E. Rosenbom (GEUS), Walter Brüsich (GEUS), Lis Wollesen de Jonge (DJF), Preben Olsen (DJF), Ruth Grant (NERI) and Steen Marcher (Danish Environmental Protection Agency).

This report presents the results for the period May 1999–June 2010. Results covering part of the period May 1999–June 2009 have been reported previously (Kjær *et al.*, 2002, Kjær *et al.*, 2003, Kjær *et al.*, 2004, Kjær *et al.*, 2005c, Kjær *et al.*, 2007, Kjær *et al.*, 2008, Kjær *et al.*, 2009, and Rosenbom *et al.*, 2010b). 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 2008.

The report was prepared jointly by Annette E. Rosenbom, Walter Brüsich, René K. Juhler, Jeanne Kjær, and Lasse Gudmundsson (all GEUS), Preben Olsen, and Finn Plauborg (DJF), and Ruth Grant (NERI). While all authors contributed to the whole report, authors were responsible for separate aspects as follows:

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- Soil water dynamics and water balances: Annette E. Rosenbom, Finn Plauborg, and Ruth Grant.
- Pesticide analysis quality assurance: René K. Juhler.

Jeanne Kjær  
September 2011



## 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 regulation of pesticides. The specific aim is to analyse whether pesticides applied in accordance with current regulations leach to groundwater in unacceptable concentrations. The programme currently evaluates the leaching risk of 42 pesticides and 41 degradation products at five agricultural sites ranging in size from 1.1 to 2.4 ha. The evaluation is based upon monitoring results representing detections in 1 meters depth (water collected via drains and suction cups) and detections in groundwater monitoring screens (1.5-4.5 meter below ground surface, hereafter m b.g.s.). This report presents the results for the entire monitoring period May 1999–June 2010. Results covering part of the period May 1999–June 2009 have been reported previously.

Highlights from **monitoring period 2009-2010** where **6** pesticides were applied, show that:

- Bifenox acid (degradation product of bifenox) can on loamy soil leach through the root zone and enter both drainage water system and groundwater monitoring wells in concentrations exceeding 0.1 µg/l. Average concentration in the drainage water exceeded 0.1 µg/l and concentrations exceeding 0.1 µg/l were observed up to six months after application. Similar evidence of pronounced leaching was **not** observed on the coarse sandy soil as there was only a single detection of bifenox acid in soil water, whereas bifenox was detected very sporadically in soil and groundwater, concentrations always less than 0.1 µg/l.
- Ethofumesate, this year used in a new admissible dose that is five times lower than in past applications, was detected once in groundwater, concentrations at less than 0.1 µg/l. When, in the past (before the imposed regulation), ethofumesate was used at a much higher dose, leaching above 0.1 µg/l to both drains and groundwater monitoring wells was observed.
- Metamitron, this year used in a dose 33% lower than the permitted, did not cause leaching above 0.1 µg/l of either metamitron or its metabolite metamitron–desamino. When, in the past, metamitron was used at maximum allowed dose, leaching above 0.1 µg/l to both drainage system and groundwater monitoring wells was observed. It is not possible to say if the low leaching this year is related to the climatic conditions/timing or the reduced dose.
- The leaching pattern of the remaining three pesticides (bentazone, azoxystrobin, triasulfuron) was in line with the previous observations (outlined below).

The results of the **entire monitoring period 1999-2010** covering 42 pesticides, show that:

- Of the 42 pesticides applied, 11 pesticides and/or their degradation product(s) (clopyralid, chlormequat, desmedipham, fenpropimorph, florasulam, iodosulfuron-methyl-sodium, linuron, metsulfuron-methyl, thiamethoxam, tribenuron-methyl, and triasulfuron) did not leach during the entire monitoring period.
- The monitoring data indicate pronounced leaching of 14 of the applied pesticides and/or their degradation products. The following compounds leached through the soil entering drains and suction cups (placed 1 m b.g.s) in average concentrations exceeding 0.1 µg/l:
  - *azoxystrobin* and its degradation product *CyPM*,
  - *bentazone*
  - *CL153815* (degradation product of picolinafen)
  - *pirimicarb-desmethyl-formamido* (degradation product of pirimicarb)
  - *propyzamide*
  - *tebuconazole*
  - *glyphosate* and its degradation product *AMPA*
  - **PPU** (degradation products of rimsulfuron)
  - **Bifenox acid** (degradation product of bifenox)
  - **ethofumesate**
  - **TFMP** (degradation product of fluazifop-P-butyl)
  - *metamitron* and its degradation product **metamitron-desamino**
  - **metribuzin-desamino-diketo** and **metribuzin-diketo** (degradation products of metribuzin)
  - **terbuthylazine** and its degradation products: **desethyl-terbuthylazine**, *2-hydroxy-desethyl-terbuthylazine*, and *2-hydroxy-terbuthylazine*

For the pesticides and/or their degradation products *marked in Italics*, pronounced leaching is mainly confined to the depth of 1 meter, where pesticides were frequently found in samples collected from drains and suction cups, while a limited number of detections (fewer than 5 samples per field) exceeding 0.1 µg/l were found in groundwater monitoring wells. For the pesticides and/or their degradation products **marked in bold**, pronounced leaching below the depth of 1 m was observed. Apart from PPU, these were all frequently detected in concentrations exceeding 0.1 µg/l in groundwater monitoring wells, exceedance of 0.1 µg/l being observed more than six months after application. Although PPU was only detected in a few samples in concentrations exceeding 0.1 µg/l, elevated concentrations just below 0.1 µg/l were found in groundwater monitoring wells during a two-year period, thus confirming the pronounced leaching and high persistency of PPU in soil and groundwater. Repeated applications of PPU may thus pose a contamination risk of the shallow groundwater. Moreover, for the glyphosate being frequently applied on one loamy soil, detections in groundwater monitoring wells have gradually increased over time. On two occasions heavy rain events and snowmelt induced leaching to the groundwater monitoring wells in concentrations exceeding 0.1 µg/l more than two years after the application.



- The monitoring data also indicate leaching of an additional 17 pesticides, but in low concentrations. Although concentrations exceeded 0.1 µg/l in several samples collected from suction cups and drains (1 m b.g.s.), average leaching concentrations on a yearly basis did not. None of the compounds were found in groundwater monitoring wells in concentrations exceeding 0.1 µg/l.

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).

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 2010 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 2008.



## Dansk sammendrag

I 1998 vedtog Folketinget at iværksætte projektet ”Varslingssystem for udvaskning af Pesticider til grundvandet” (VAP). VAP er et omfattende monitoringsprogram, der undersøger udvaskning af pesticider anvendt i landbrug 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 (Miljøstyrelsen) procedurer for regulering af sprøjtemidler. Udvasningsrisikoen for 42 pesticider og 41 nedbrydningsprodukter er således op til i dag undersøgt på fem marker, der har en størrelse på mellem 1,1 og 2,4 ha. Undersøgelsen bygger på monitoringsresultater henholdsvis repræsenterende fund i en meters dybde (indhentet via dræn og sugeceller) og fund i grundvandsmoniteringsfiltre (1.5-4.5 meter under terræn, herefter m u.t.). Denne rapport opsummerer resultaterne for den samlede monitoringsperiode maj 1999 – juni 2010; resultater fra de foregående år maj 1999 – juni 2009 er blevet afrapporteret i de tidligere rapporter.

”Highlights” fra den seneste monitoringsperiode **2009-2010**, hvor **6** pesticider blev udbragt, viser følgende:

- Bifenox-syre (nedbrydningsprodukt af bifenox) blev på lerjorde udvasket fra rodzonen (1 m.u.t.) til både dræn og grundvandsfiltre i koncentrationer over 0,1 µg/l. I dræne oversteg den årlige middelkoncentration 0,1 µg/l, og i grundvandsfiltrene blev der på en ud af to testede lerjorde fundet koncentrationer over 0,1 µg/l op til seks måneder efter udbringning. Tilsvarende udvaskning blev ikke set på den grovsandede jord, hvor der kun var et enkelt fund af bifenox-syre (i jordvandet) samt sporadiske fund af bifenox i lave koncentrationer (under 0,1 µg/l).
- Ethofumesat, der som følge af Miljøstyrelsens restriktioner dette år blev udbragt i en dosis 5 gange lavere end tidligere, blev denne gang kun fundet i en enkelt prøve (<0,1 µg/l). Ved tidligere anvendelser med den høje dosering, blev ethofumesat udvasket til både dræn og grundvandsfiltre i koncentrationer over 0,1 µg/l.
- Metamitron, som dette år blev udbragt i den anbefalede dosis, hvilket var 33% mindre end den maksimalt tilladte mængde, blev ikke udvasket i koncentrationer, der oversteg 0,1 µg/l. Ved tidligere udbringninger (ved den maksimalt tilladte dosis) blev metamitron og dets nedbrydningsprodukt metamitron-desamino udvasket i koncentrationer der oversteg 0,1 µg/l i både dræn og grundvandsfiltre. Det er imidlertid ikke til at sige om den mindskede udvaskning dette år skyldes den lavere dosering eller de klimatiske forhold.
- For de øvrige 3 stoffer (bentazon, azoxystrobin, triasulfuron) var de observerede udvasningsforløb meget lig tidligere observationer (beskrevet nedenfor).

Resultater for hele **monitoringsperioden 1999-2010**, som omfatter **42** pesticider viser følgende:

- Af de 42 pesticider, der er blevet udbragt, blev 11 pesticider eller nedbrydningsprodukter heraf (clopyralid, chlormequat, desmedipham, fenpropimorph, florasulam, iodosulfuron-methyl-natrium, linuron, metsulfuron-methyl, thiamethoxam, tribenuronmethyl og triasulfuron) **ikke** fundet udvasket i løbet af den samlede monitoringsperiode.
- 14 af de udbragte stoffer eller nedbrydningsprodukter heraf gav anledning til en markant udvaskning. Følgende stoffer blev udvasket til dræn og sugeceller, beliggende i ca. 1 meters dybde i gennemsnitskoncentrationer over 0,1 µg/l:
  - *azoxystrobin* og dets nedbrydningsprodukt *CyPM*
  - *bentazon*
  - *CL153815* (nedbrydningsprodukt af picolinafen)
  - *pirimicarb-desmethyl-formamido* (nedbrydningsprodukt af pirimicarb)
  - *propyzamid*
  - *tebuconazol*
  - *glyphosat* og dets nedbrydningsprodukt *AMPA*
  - **PPU** (nedbrydningsprodukt af rimsulfuron)
  - **bifenox-syre** (nedbrydningsprodukt af bifenox)
  - **ethofumesat**
  - **TFMP** (nedbrydningsprodukt af fluazifop-P-butyl),
  - *metamitron* og dets nedbrydningsprodukt **metamitron-desamino**
  - **metribuzin-desamino-diketo** og **metribuzin-diketo** (nedbrydningsprodukter af metribuzin)
  - **terbuthylazin** og dets nedbrydningsprodukter **desethyl-terbuthylazin**, *2-hydroxy-desethyl-terbuthylazin*, and *2-hydroxy-terbuthylazin*

For de pesticider eller nedbrydningsprodukter heraf fremhævet med *kursiv* var udvaskningen primært begrænset til 1 m.u.t., hvor de blev fundet hyppigt i dræn og sugeceller. Selvom hovedparten af stofferne blev fundet i koncentrationer over 0,1 µg/l i grundvandsfiltrene, var antallet af overskridelser få (mindre end 5 pr. mark). Pesticider markeret med **fed** blev derimod udvasket til grundvandsfiltrene i en større grad. På nær PPU blev samtlige stoffer relativt hyppigt fundet i koncentrationer over 0,1 µg/l i grundvandsfiltrene, hvor koncentrationer over 0,1 µg/l blev fundet mere end seks måneder efter udbringning. Om end det kun var enkelte prøver som indeholdt mere end 0,1 µg/l PPU, blev der igennem en toårig periode fundet PPU i grundvandet i koncentrationer tæt på de 0,1 µg/l, hvilket bekræfter den høje persistens af PPU i jord og grundvand. Gentagne udbringninger af PPU kan potentielt forurene det allerøverste grundvand. Glyphosat er blevet udbragt flere gange på en af de lerede forsøgslokaliteter. På denne mark er der igennem de seneste år konstateret et stigende antal fund af glyphosat i grundvandsfiltrene. To gange har markante nedbørshændelse samt snesmeltning forårsaget udvaskning af glyphosat til grundvandsfiltrene i koncentrationer over 0,1 µg/l mere end to år efter udbringning.

- Andre 17 stoffer gav anledning til udvaskning. Selv om flere af disse stoffer i én meters dybde ofte blev fundet i koncentrationer over 0,1 µg/l, var der ikke tale om, at udvaskningen som årsmiddel oversteg 0,1 µg/l. Stofferne blev heller ikke fundet i grundvandsfiltrene i koncentration over 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. Monitoring 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 monitoringsresultaterne for de fem områder for perioden maj 1999 - juni 2010 primært med fokus på pesticider udbragt i 2008. En del af stofferne har kun været inkluderet i monitoringsprogrammet 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) pesticides have so far been detected in 53% of all screens monitored and in 61% of the screens placed in the upper groundwater (Thorling, L. (red), 2010).

The increasing detection of pesticides in groundwater over the past 10 years has given rise to the desire 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 to the 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 leaching study results to be included in the risk assessments.

## 1.1 Objective

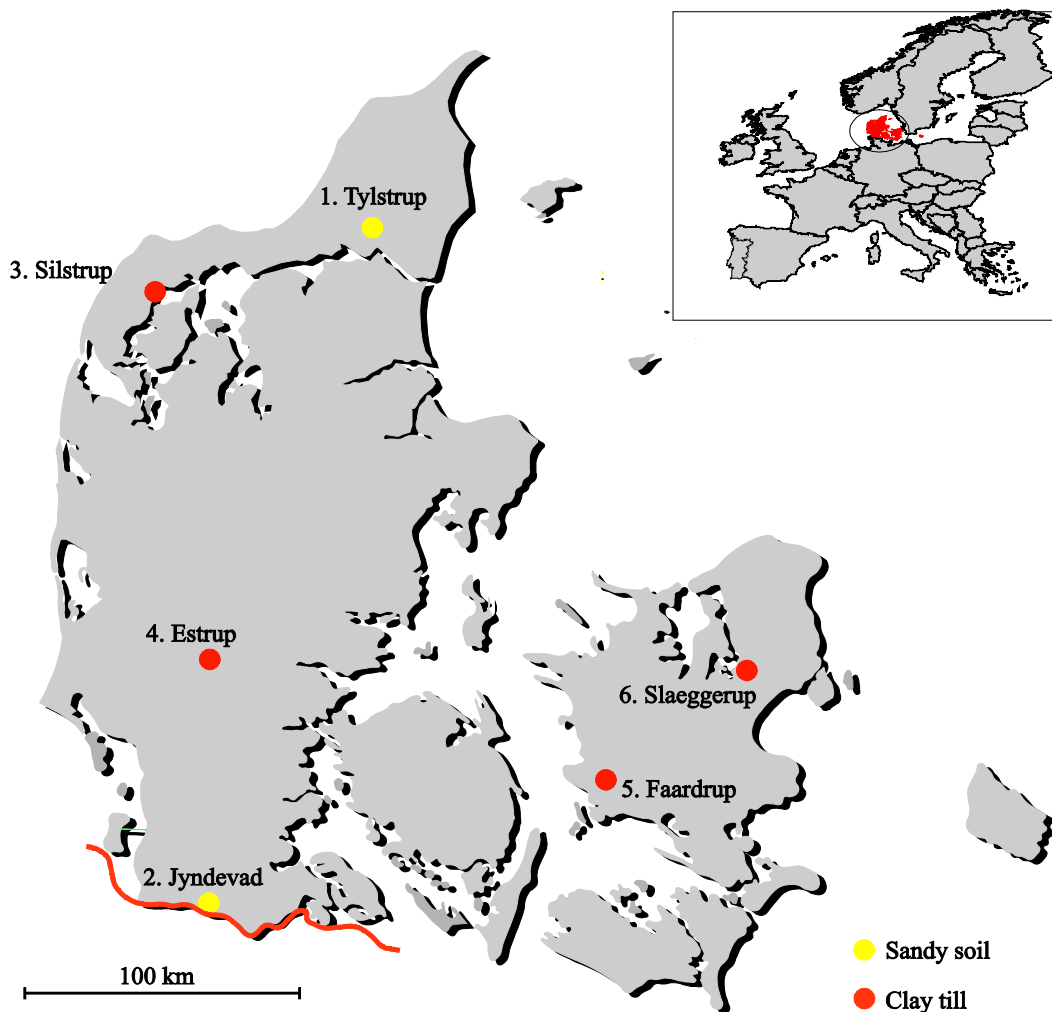
In 1998, the Danish Government initiated the Pesticide Leaching Assessment Programme (PLAP), an intensive monitoring programme with the purpose of evaluating the leaching risk of pesticides under field conditions. The PLAP is intended to serve as an early warning system providing decision-makers with 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, 42 pesticides and 41 degradation products are included in the PLAP. All the compounds analysed are listed in Appendix 1.



**Figure 1.** Location of the PLAP sites Tylstrup, Jydevad, 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 at maximum permitted doses and in the manner specified in the regulations. Hence any pesticides or degradation products appearing 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, Jyndeved 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	Jyndeved	Silstrup	Estrup	Faardrup
Location	Brønderslev	Tinglev	Thisted	Askov	Slagelse
Precipitation <sup>1)</sup> (mm/y)	668	858	866	862	558
Pot. evapotransp. <sup>1)</sup> (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
Depths to tile drain (m b.g.s.)			1.1	1.1	1.2
Monitoring initiated	May 1999	Sep 1999	Apr 2000	Apr 2000	Sep 1999
<b>Geological characteristics</b>					
– 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 <sup>2)</sup>	1.5
– Depth to the reduced matrix (m b.g.s.)	>12	10–12	5	>5 <sup>2)</sup>	4.2
– Max. fracture depth <sup>3)</sup> (m)	–	–	4	>6.5	8
– Fracture intensity 3–4 m depth (fractures/m)	–	–	<1	11	4
– Ks in C horizon (m/s)	2.0·10 <sup>-5</sup>	1.3·10 <sup>-4</sup>	3.4·10 <sup>-6</sup>	8.0·10 <sup>-8</sup>	7.2·10 <sup>-6</sup>
<b>Topsoil characteristics</b>					
– 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

<sup>1)</sup> Yearly normal based on a time series for the period 1961–90. The data refer to precipitation measured 1.5 m above ground.

<sup>2)</sup> Large variation within the field.

<sup>3)</sup> 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 2009. The main focus of this report is on the leaching risk of pesticides applied during 2007. For a detailed description of the earlier part of the monitoring period (May 1999–June 2009), see previous publications on [http://pesticidvarsling.dk/publ\\_result/index.html](http://pesticidvarsling.dk/publ_result/index.html).

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 entire monitoring period from May 1999–June 2010. The five site models have been calibrated for the monitoring period May 1999–June 2004 and validated for the monitoring period July 2004–June 2010.

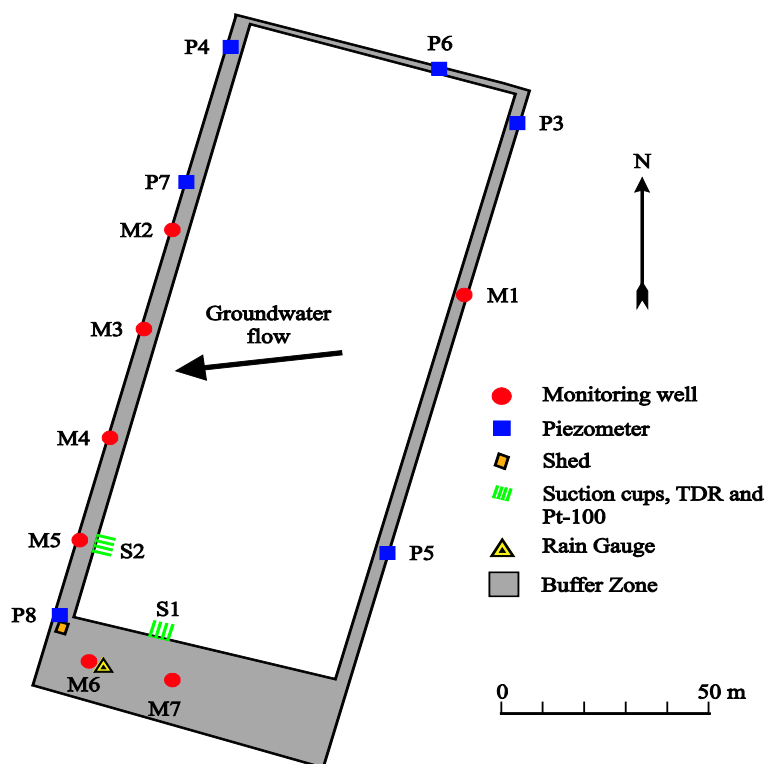
Scientifically valid methods of analysis are essential to ensure the integrity of the PLAP. The field monitoring work has therefore been supported by intensive quality assurance entailing continuous evaluation of the analyses employed. The quality assurance methodology and results are presented in Section 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 characterised as loamy sand with 6% clay and 2.0% total organic carbon (Table 1). The aquifer material consists of an approx. 20 m deep layer 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 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). Pesticide monitoring is conducted monthly and half-yearly from suction cups and selected monitoring wells as described in Table A2.1 in Appendix 2.

### 2.1.2 Agricultural management

Management practice during the 2009 and 2010 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 previous monitoring reports available on [http://pesticidvarsling.dk/publ\\_result/index.html](http://pesticidvarsling.dk/publ_result/index.html).

The field was ploughed on 10 April 2009 and on 14 April sown with spring barley (cv. Keops), which emerged on 21 April. On 15 May, when the barley had three detectable tillers, the herbicides MCPA and bentazone were applied, of which only the latter was monitored. Fungi were treated on 23 June at 80% inflorescence using azoxystrobin, and pests were treated on 8 July at late milk stage using tau-fluvalinate. Tau-fluvalinate and azoxystrobin were not included in the monitoring programme. The barley received 26 mm irrigation on 29 June at the end of flowering and 27 mm at late milk stage on 8 July. An amount of 53.4 hkg/ha of grain (85% dry matter (DM)) was harvested on 20 August, slightly above the average for the soil type this year (Plantedirektoratet, 2009). On 28 August, 17.4 hkg/ha of straw (100% DM) was removed from the field.

On 4 April 2010 the field was ploughed and on 6 May planted with potatoes (cv. Kuras). On 26 May, before emergence, the field was sprayed with the herbicides aclonifen and rimsulfuron. Rimsulfuron was applied again on 8 June, when the fifth leaf of the main stem had unfolded. Cyazofamid was used against fungi six times between 15 June and 2 August. On 9 July a fungicide containing mancozeb and metalaxyl was used, of which only metalaxyl was monitored. Between 9 August and 23 August the fungicide mancozeb was again applied, but not monitored. The crop was irrigated twice, with 29 mm on 6 July and 28 mm on 27 July. The yield of potatoes, harvested on 20 October, was 470.3 hkg/ha with 27.2% DM (128.0 hkg/ha at 100% DM), yields being below the average for the year and soil type (Plantedirektoratet 2010).

### 2.1.3 Model setup 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 2010 and to establish an annual water balance.

Compared to Rosenbom *et al.* (2010b), a year of validation was added to the MACRO-setup for the Tylstrup site. The setup was hereby calibrated for the monitoring period May 1999–June 2004 and validated for the monitoring period July 2004–June 2010. 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 setup and results related to simulated bromide transport are described in Barlebo *et al.* (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 <sup>2)</sup>	Precipitation	Irrigation	Actual evapotranspiration	Groundwater recharge <sup>3)</sup>
1.5.99–30.6.99 <sup>1)</sup>	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
1.7.07–30.6.08	773	913	126	572	467
1.7.08–30.6.09	773	1269	26	600	695
1.7.09–30.6.10	773	863	27	419	471

<sup>1)</sup> Accumulated for a two-month period.

<sup>2)</sup> Normal values based on time series for 1961–1990.

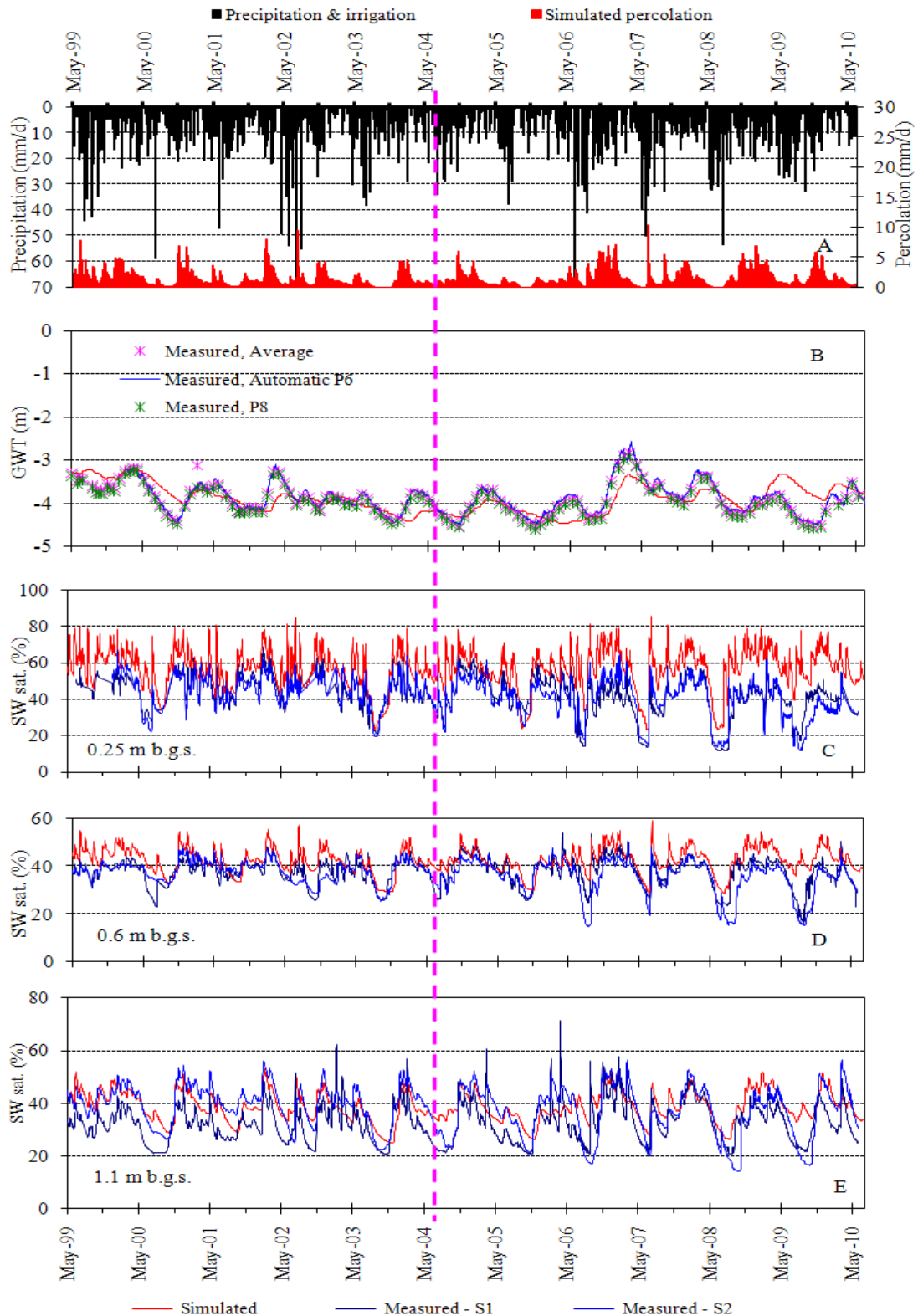
<sup>3)</sup> Groundwater recharge is calculated as precipitation + irrigation - actual evapotranspiration.

## 2.2 Results and discussion

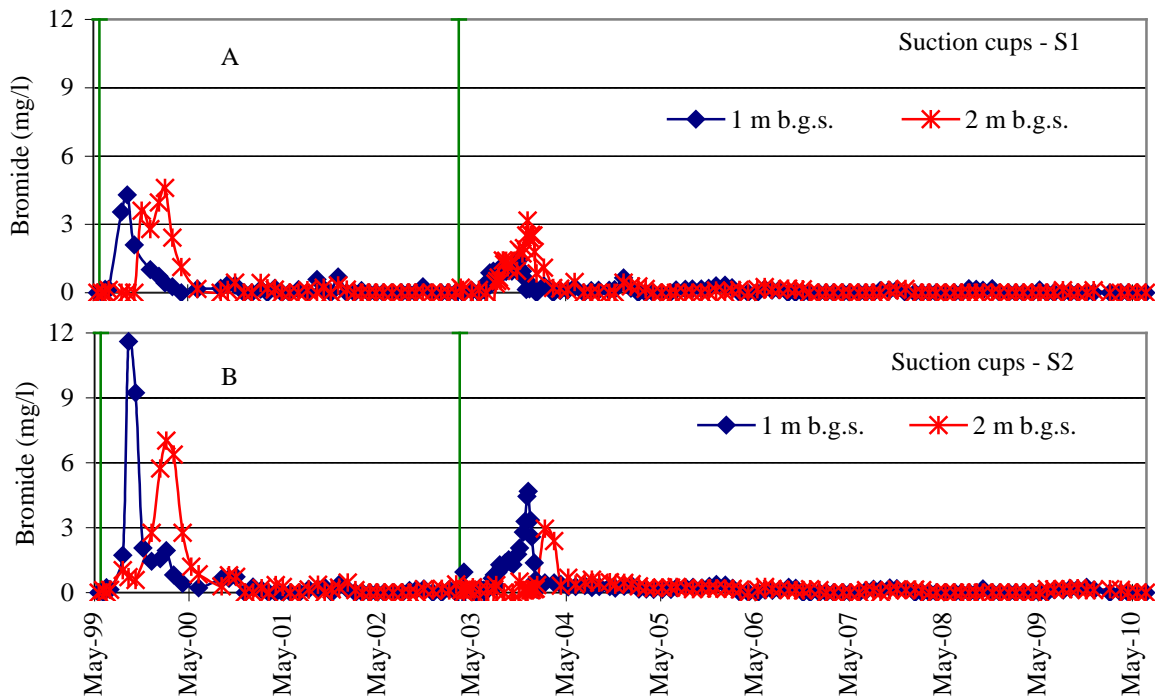
### 2.2.1 Soil water dynamics and water balances

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). During the last three hydraulic years the level in water saturation at 25 cm b.g.s. was, however, overestimated. Moreover the initial decrease in water saturation observed during the summer periods at 25, 60, and 110 cm b.g.s. was 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. Values for precipitation and actual evapotranspiration for the most recent hydraulic year, July 2009–June 2010, were among the lowest observed since monitoring began at the site, and the monthly precipitation pattern for this year was low to medium compared with earlier years, except for the wettest November monitored. Especially January was very dry (Appendix 4). Artificial irrigation was minimal, which could be the result of a wet July. The groundwater recharge/percolation was medium compared to the other hydraulic years, and continuous (Figure 3A).



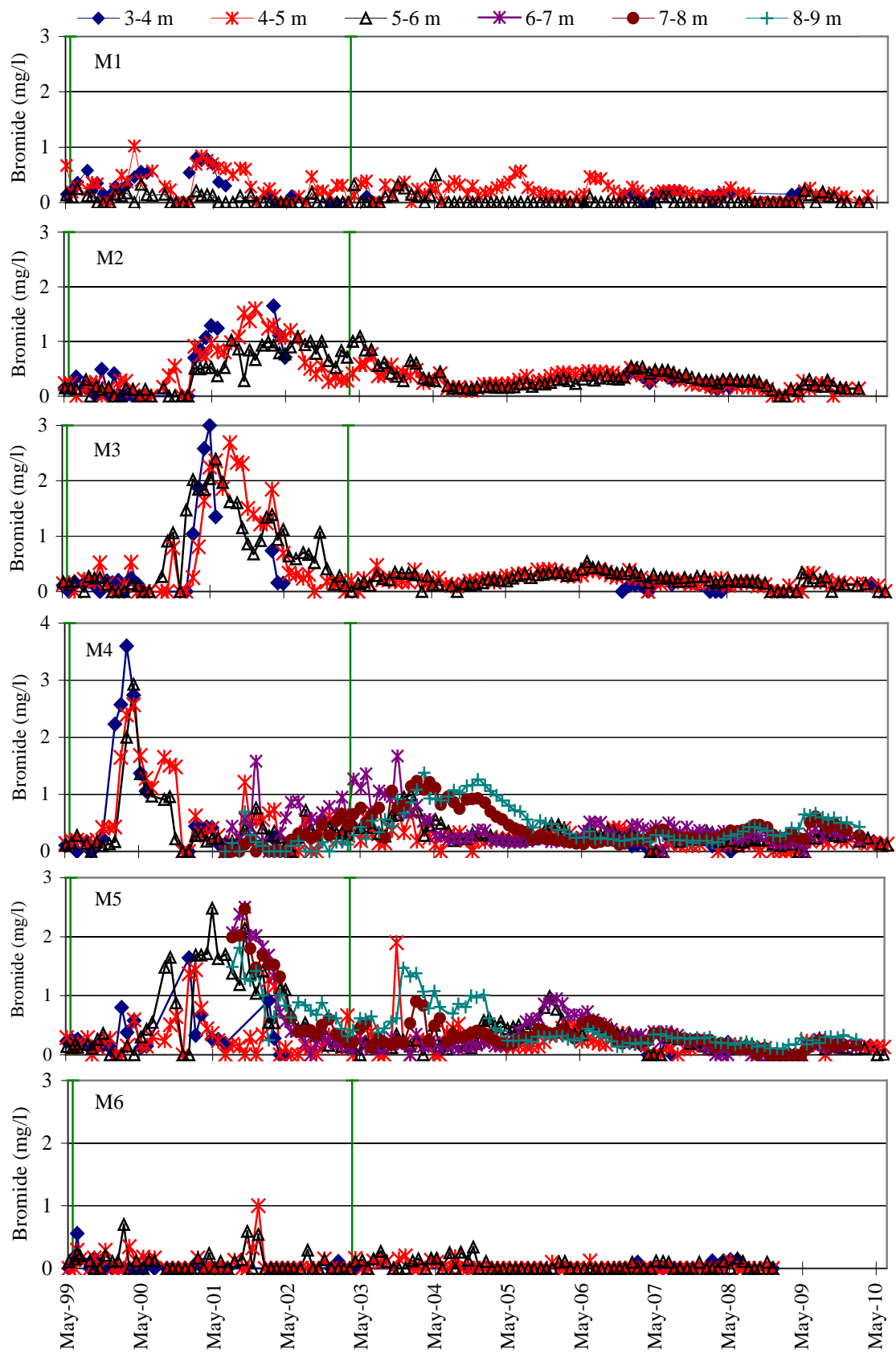
**Figure 3.** Soil water dynamics at Tylstrup: Measured precipitation, irrigation and simulated percolation 1 m b.g.s. (A), simulated and measured groundwater level GWT (B), and simulated and measured soil water saturation (SW sat.) at three different soil depths (C, D and E). The measured data in B 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 2010).



**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.

### 2.2.2 Bromide leaching

Bromide has now been applied twice at Tylstrup. The bromide concentrations measured until 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).



**Figure 5.** Bromide concentration in the groundwater at Tylstrup. The data derive from monitoring wells M1–M6. Monitoring at well M6 was suspended September 2008 (Appendix 2). Screen depth is indicated in m b.g.s. The green vertical lines indicate the dates of bromide applications.

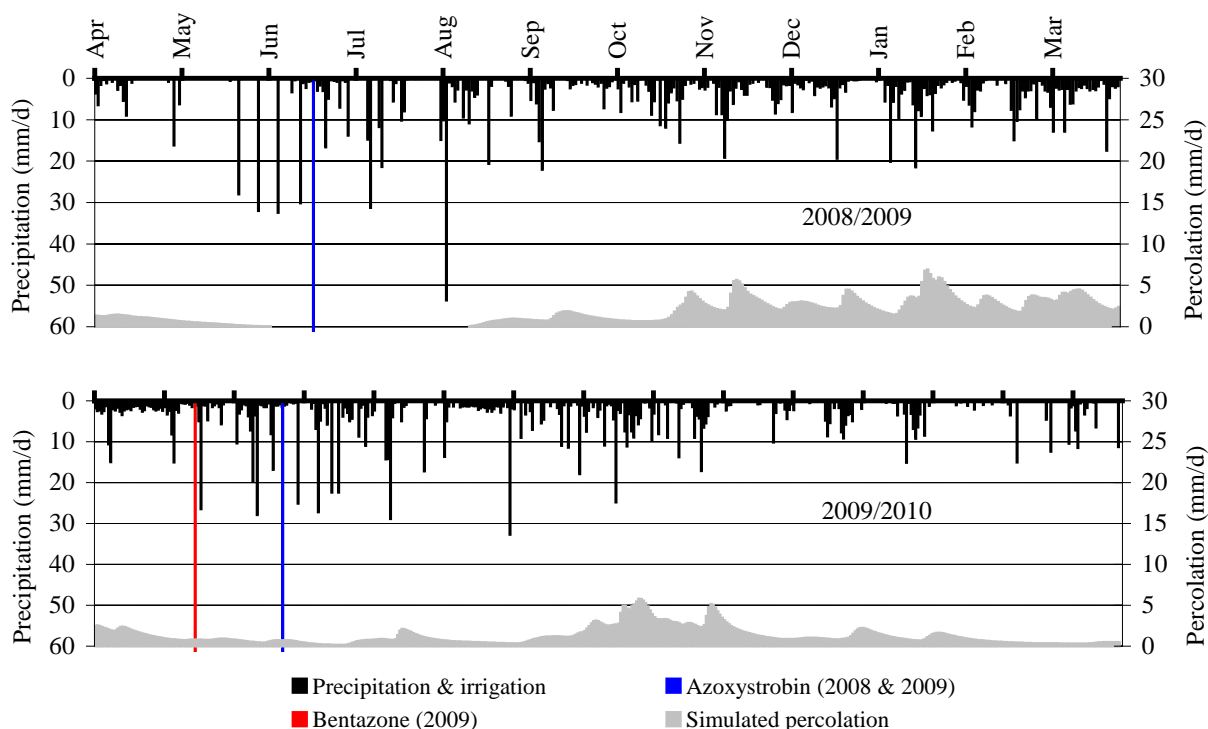


### 2.2.3 Pesticide leaching

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 latest two 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 some of the applied pesticides degrade rapidly, e.g. mancozeb (applied here as Dithane DG), tribenuron-methyl (applied here as Express ST) and rimsulfuron (applied here as Titus). The risk of leaching is therefore 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 PLAP (Table 3). Pesticides applied later than April 2010 are not evaluated in this report and hence are not included in Table 3 and Figure 6.

The current report focuses on the pesticide applied from 2008 and onwards, while leaching risk of pesticides applied before 2008 has been evaluated in previous monitoring reports (see [http://pesticidvarsling.dk/publ\\_result/index.html](http://pesticidvarsling.dk/publ_result/index.html)). The leaching of metribuzin is further detailed in Kjær *et al.* (2005b) and Rosenbom *et al.* (2009).



**Figure 6.** Application of pesticides included in the monitoring programme, precipitation and irrigation (primary axis) together with simulated percolation 1 m b.g.s. (secondary axis) at **Tylstrup** in 2008/2009 (upper) and 2009/2010 (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. 1<sup>st</sup> month perc. refers to accumulated percolation within the first month after the application. C<sub>mean</sub> refers to average leachate concentration at 1 m b.g.s. the first year after application (See Appendix 2 for calculation method).

Crop and analysed pesticides	Application Date	End of monitoring	Prec. (mm)	Perc. (mm)	1 <sup>st</sup> month perc. (mm)	C <sub>mean</sub> (µg/L)
<b>Potatoes 1999</b>						
Linuron (Afalon)	May 99	Jul 01	2550	1253	87	<0.01
- <i>ETU</i> <sup>1)</sup> (Dithane DG)	Jun 99	Oct 01	2381	1169	73	<0.01
Metribuzine (Sencor WG)	Jun 99	Jul 03	4223	2097	85	<0.01
- <i>metribuzine-diketo</i>		Jul 10 <sup>†</sup>	11142	5387	85	0.05–0.36
- <i>metribuzine-desamino</i>		Jul 03	4223	2097	85	<0.02
- <i>metribuzine-desamino-diketo</i>		Apr 08	8689	4192	85	0.14–0.97
<b>Spring barley 2000</b>						
Triasulfuron (Logran 20 WG)	May 00	Apr 03	2740	1283	13	<0.02
- <i>triazinamin</i>						<0.02
Propiconazole (Tilt Top)	Jun 00	Jul 03	2948	1341	11	<0.01
Fenpropimorph (Tilt Top)	Jun 00	Jul 03	2948	1341	11	<0.01
- <i>fenpropimorphic acid</i>						<0.02
Pirimicarb (Pirimor G)	Jun 00	Apr 03	2622	1263	17	<0.01
- <i>pirimicarb-desmethyl</i>						<0.02
- <i>pirimicarb-desmethyl-formamido</i>						<0.02
<b>Winter rye 2001</b>						
Pendimethalin (Stomp SC)	Nov 00	Apr 03	2271	1219	109	<0.01
<i>Triazinamin-methyl</i> <sup>2)</sup> (Express)	Nov 00	Apr 03	2271	1219	109	<0.02
Propiconazole (Tilt Top)	May 01	Jul 03	2948	1341	11	<0.01
Fenpropimorph (Tilt Top)	May 01	Jul 03	2948	1341	11	<0.01
- <i>fenpropimorphic acid</i>						<0.01
<b>Winter rape 2002</b>						
Clomazone (Command CS)	Sep 01	Jul 04	2534	1194	9	<0.01
- <i>FMC65317</i> ( <i>propanamide-clomazone</i> )						<0.02

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

<sup>1)</sup> Degradation product of mancozeb. The parent compound degrades too rapidly to be detected by monitoring.

<sup>2)</sup> 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 2009.

Degradation products of rimsulfuron, which was applied in June 2004, continued to leach also in 2009/2010, but now only in small concentrations. The results of this 2004 application are summarised below and in Rosenbom *et al.* (2010a).

Rimsulfuron degrades rapidly in the soil, and the leaching risk is therefore associated with the degradation products PPU and PPU-desamino. PPU has been found several times in suction cups situated 1 m and 2 m b.g.s. at both S1 and S2 (Figure 7). The first detection of PPU occurred 10 months after the application of rimsulfuron (Figure 7B), after which PPU was found in 122 out of 192 analysed samples with concentrations ranging between 0.017 and 0.150 µg/l. PPU-desamino has been found in 35 out of 192 analysed samples with concentrations ranging between 0.01 and 0.042 µg/l. A little more than two years after application, PPU was found at 1 m depth at S2, whereafter PPU was detected in 46 out of 99 analysed samples with concentrations ranging between 0.01 and 0.067 µg/l (Figure 7D). At S2, the number of detections and concentration levels of PPU-desamino were low (Figure 7D and 7E; Appendix 5). Small concentrations of PPU were seen in both S1 and S2 at the end of the monitoring period, indicating that although leaching had reduced, it had not yet ceased. After application of rimsulfuron, average concentrations did not exceed 0.1 µg/l in any of the five years for either of the degradation products (Table 4).

**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. 1<sup>st</sup> month perc. refers to accumulated percolation within the first month after the application. C<sub>mean</sub> refers to average leachate concentration at 1 m b.g.s. the first year after application (See Appendix 2 for calculation method).

Crop and analysed pesticides	Application date	End of monitoring	Prec. (mm)	Perc. (mm)	1 <sup>st</sup> month perc. (mm)	C <sub>mean</sub> (µg/l)
<b>Winter wheat 2003</b>						
Bromoxynil (Oxitril CM)	Oct 02	Apr 05	2082	995	53	<0.01
Ioxynil (Oxitril CM)	Oct 02	Apr 05	2082	995	53	<0.01
Fluroxypyr (Starane 180)	May 03	Jul 05	1867	787	50	<0.02
Flamprop-M-isopropyl (Barnon Plus 3)	May 03	Jul 05	2635	1031	42	<0.01
- <i>Flamprop-M (free acid)</i>						
Dimethoate (Perfekthion 500 S)	Jul 03	Jul 05	1629	722	14	<0.01
<b>Potatoes 2004</b>						
- <i>Fluazifop-P (free acid)</i> <sup>1)</sup> (Fusilade X-tra)	May 04	Jul 06	1754	704	16	<0.01
- PPU <sup>2)</sup> (Titus)	Jun 04	Jul 10 <sup>†</sup>	6211	3008	13	<0.01 <sup>3)</sup>
- PPU-desamino <sup>2)</sup> (Titus)	Jun 04	Jul 10 <sup>†</sup>	6211	3008	13	<0.01 <sup>3)</sup>
<b>Maize 2005</b>						
Terbutylazine (Inter-Terbutylazine)	May 05	Jul 07	2145	933	16	<0.01
- <i>desethyl-terbutylazine</i>						<0.01
- <i>2-hydroxy-terbutylazine</i>						<0.01
- <i>desisopropyl-atrazine</i>						<0.01 <sup>4)</sup>
- <i>2-hydroxy-desethyl-terbutylazine</i>						<0.01
Bentazone (Laddok TE)	Jun 05	Jul 07	2061	927	33	<0.01
- AIBA						<0.01
<b>Spring barley 2006</b>						
- <i>triazinamin-methyl</i> <sup>5)</sup> (Express ST)	Jun 06	Jul 08	2349	1184	43	<0.02
Epoxiconazole (Opus)	Jul 06	Jul 08	2233	1148	24	<0.01
<b>Winter rape 2007</b>						
Thiamethoxam (Cruiser RAPS) <sup>6)</sup>	Aug 06	Apr 08	2030	1123	57	<0.01
- CGA 322704						<0.02
Propyzamide (Kerb 500 SC)	Feb 07	Apr 09	2400	1172	40	<0.01
- RH-24644						<0.01
- RH-24580						<0.01
- RH-24655						<0.01
Clopyralid (Matrigon)	Mar 07	Apr 09	2317	1112	24	<0.01
<b>Winter wheat 2008</b>						
Pendimethalin (Stomp)	Oct 07	Dec 09	2595	1324	27	<0.01
Tebuconazole (Folicur EC250)	Nov 07	Mar 10	2696	1427	46	<0.01
Azoxystrobin (Amistar)	Jun 08	Jul 10 <sup>†</sup>	2265	1151	0	<0.01
- CyPM						<0.01
<b>Spring barley 2009</b>						
Bentazone (Basagran M75)	May 09	Jul 10 <sup>†</sup>	1084	512	22	<0.01
Azoxystrobin (Amistar)	Jun 09	Jul 10 <sup>†</sup>	920	485	11	<0.01
- CyPM						<0.01

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

<sup>1)</sup> Degradation product of fluazifop-P-butyl. The parent compound degrades too rapidly to be detected by monitoring.

<sup>2)</sup> Degradation product of rimsulfuron. The parent compound degrades too rapidly to be detected by monitoring.

<sup>3)</sup> Leaching increased the second and third year after application (see Figure 7 and Table 4).

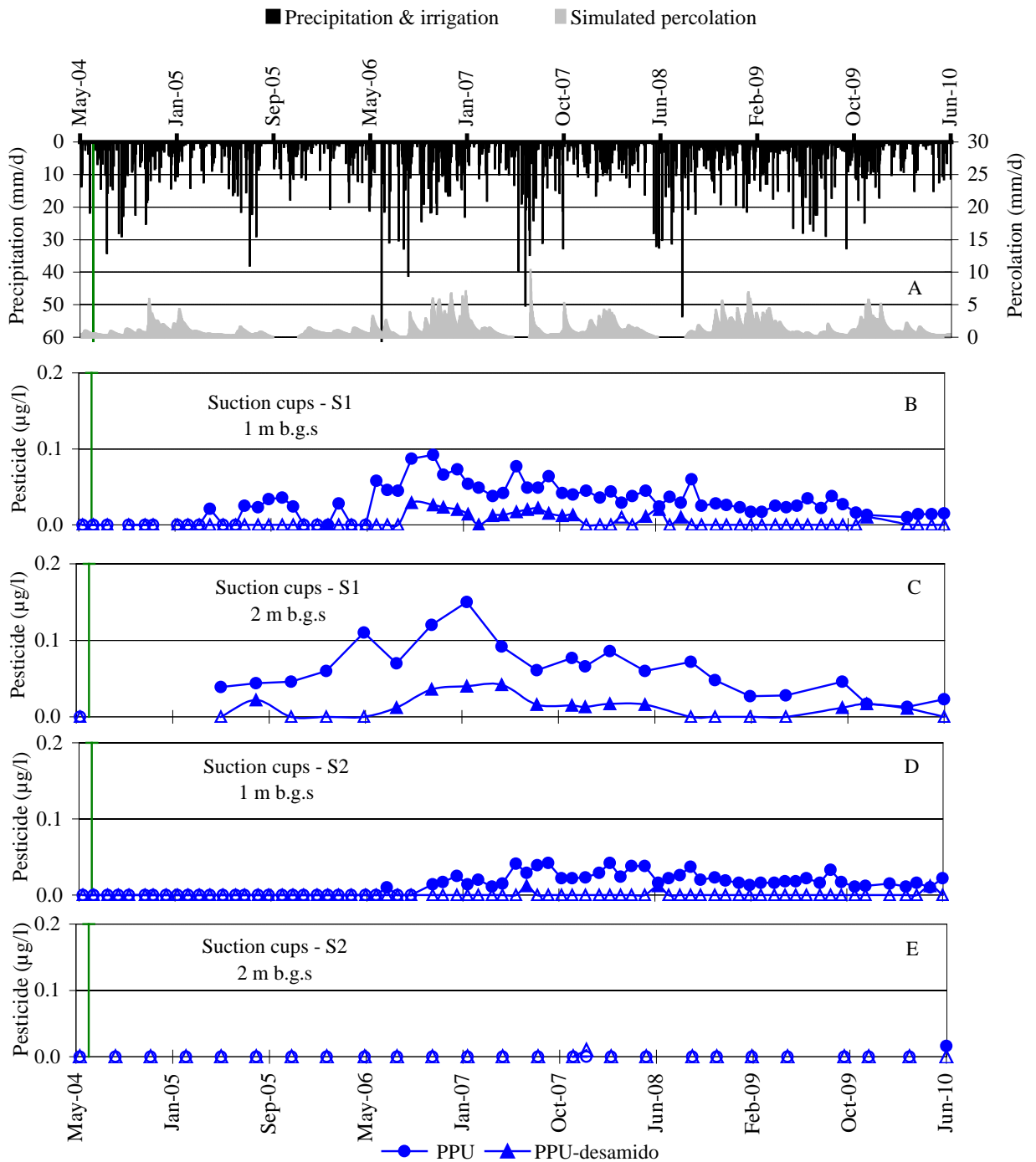
<sup>4)</sup> Leaching increased during the second year after application but measured concentrations did not exceed 0.042 µg/l (see Kjær et al., 2008).

<sup>5)</sup> Degradation product of tribenuron-methyl. The parent compound degrades too rapidly to be detected by monitoring.

<sup>6)</sup> Unlike the other pesticide applied via surface spray application, thiamethoxam was directly applied in the soil as the rape seeds (cv. Lioness) were dressed with thiamethoxam.

<sup>†</sup> Monitoring will continue during the following year. The values for prec. and perc. are accumulated up to July 2009.

PPU was found in two groundwater samples (0.045 µg/l on 7 December 2005 in the monitoring screen of M4 located 4.4-5.4 m b.g.s. and 0.011 µg/l on 11 February 2009 in M5.5). PPU-desamino has not been detected 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 ( $\mu\text{g/l}$ ) in suction cups installed at location S1 at 1 m b.g.s. (B) and 2 m b.g.s. (C) and location S2 at 1 m b.g.s. (D) and 2 m b.g.s. (E) at **Tylstrup**. The green vertical line indicates the date of pesticide application. Open symbols indicate concentrations below the limit of detection ( $0.02 \mu\text{g/l}$  prior to July 2006 and  $0.01 \mu\text{g/l}$  thereafter). While *PPU*-desamino has not been detected in the groundwater, *PPU* was detected in two groundwater samples (see text).

**Table 4.** Percolation together with estimated average concentration ( $\mu\text{g/l}$ ) of PPU and PPU-desamino 1 m b.g.s. at Tylstrup.

	Percolation (mm/y)	PPU		PPU-desamino	
		Suction cup – S1	Suction cup – S2	Suction cup – S1	Suction cup – S2
1.7.04–30.6.05	528	<0.02	<0.02	<0.02	<0.02
1.7.05–30.6.06	257	0.01-0.03	<0.02	<0.02	<0.02
1.7.06–30.6.07	529	0.07	0.01-0.02	0.02	<0.01
1.7.07–30.6.08	529	0.04	0.03	0.01	<0.01
1.7.08–30.6.09	672	0.02	0.02	<0.01	<0.01
1.7.09–30.6.10	476	0.01	0.01	<0.01	<0.01

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 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 28-47%. Results from the field-spiked samples revealed that PPU is degraded slightly during analysis (see Rosenbom *et al.*, 2010b; section 7.2.2.). Thus, the observed PPU-desamino probably derives from degradation in the sample during analysis rather than from degradation occurring in the soil. As a consequence, the concentration of PPU is likely to be underestimated, while that of PPU-desamino is likely to be overestimated.

The pesticides applied on winter wheat in 2008 and spring barley in 2009 and their degradation products (Table 3) have not been found in any of the analysed water samples, the exception being tebuconazole detected once in a groundwater sample (0.011  $\mu\text{g/l}$  on 4 April 2008 in M4, 2.5–3.5 m b.g.s.). Moreover, bentazone has been found in one sample (10 April 2006, at S1 1 m b.g.s.) originating from the application in 2005, indicating that no leaching occurred from the 2009 application.



## 3 Pesticide leaching at Jyndevad

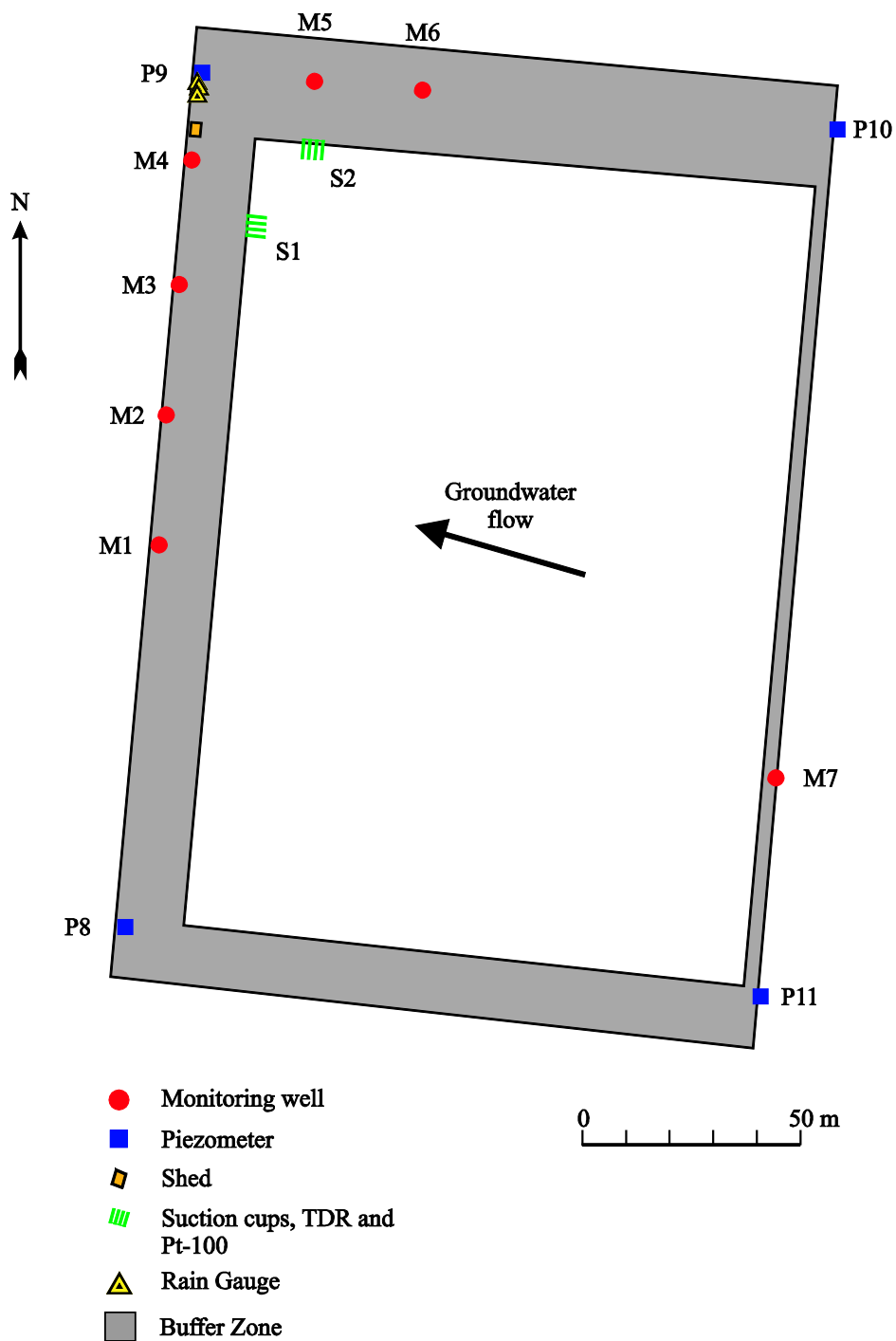
### 3.1 Materials and methods

#### 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 9B) The overall direction of groundwater flow is towards the northwest (Figure 8). The soil can be classified as Arenic Eutrudept and Humic Psammentic Dystrudept (Soil Survey Staff, 1999) with coarse sand as the dominant texture class and topsoil containing 5% clay and 1.8% total organic carbon (Table 1). The geological description points to a rather homogeneous aquifer of meltwater sand, with local 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 2008-2009 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 previous monitoring reports available on [http://pesticidvarsling.dk/publ\\_result/index.html](http://pesticidvarsling.dk/publ_result/index.html).



**Figure 8.** Overview of the Jynde vad 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). Pesticide monitoring is conducted monthly and half-yearly from selected monitoring wells and suction cups as described in Table A2.1 in Appendix 2.



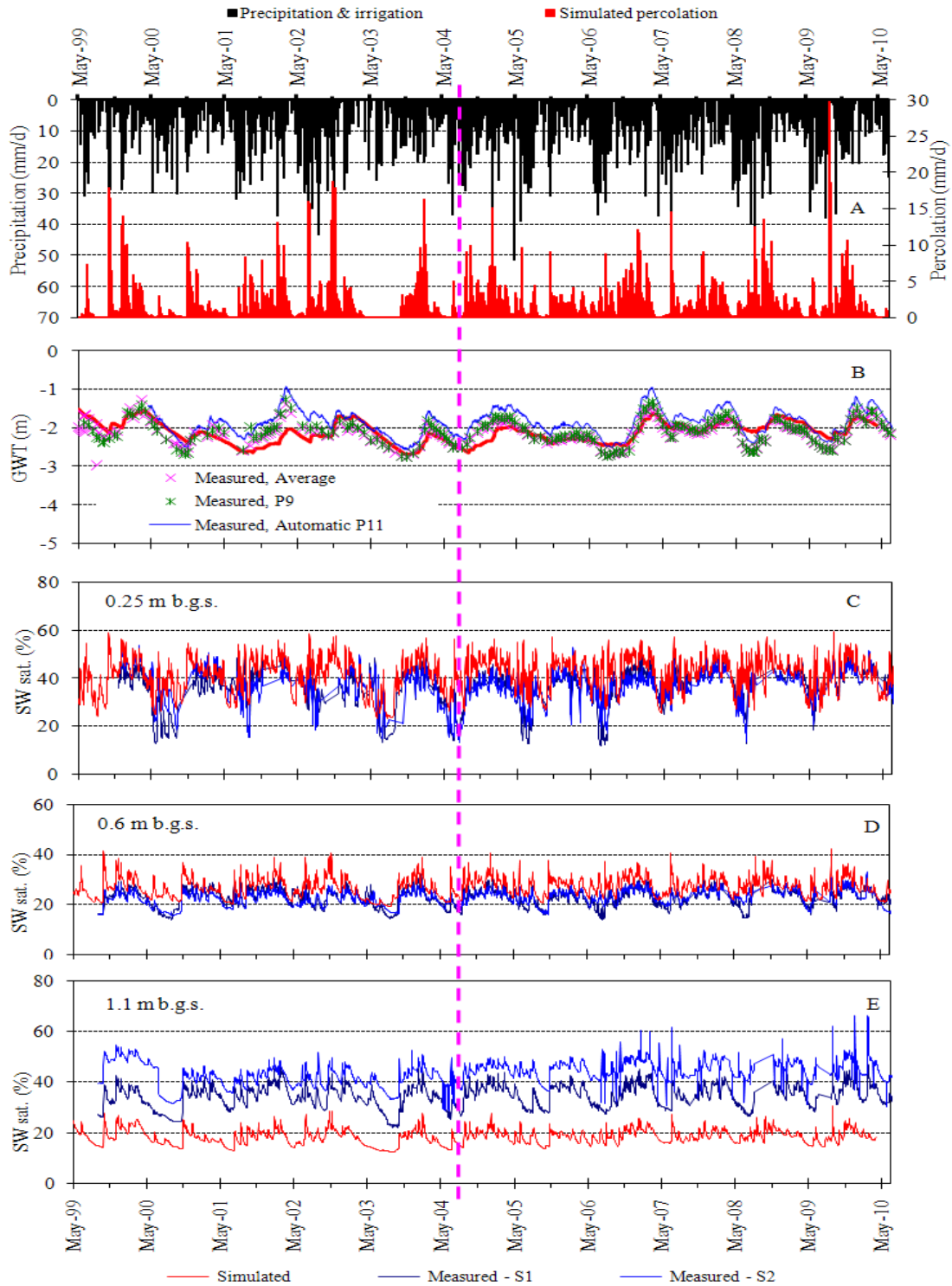
The field was ploughed on 17 March 2009 and the following day sown with spring barley (cv. Simba). The herbicide bifenox was applied on 27 April before the start of tillering. The herbicides bentazone and MCPA were applied two weeks later, at the beginning of stem elongation, although MCPA was not included in the monitoring. Fungicides were applied around late boot stage on 26 May, using boscalide and epoxiconazole, of which only the latter was monitored. The field was irrigated on three occasions: 30 mm on 26 May, at the late boot stage; 27 mm on 5 June at the beginning of heading and finally 27 mm on 29 June, at the beginning of flowering. The crop was harvested on 7 August, yielding 64.0 hkg/ha of grain and 19.5 hkg of straw (85 and 100% DM, respectively), grain yield being nearly 30% above the average for the soil type and year (Plantedirektoratet, 2009).

Having been ploughed on 14 April 2010, the field was planted with potatoes (cv. Kuras) on 4 May. Before the potatoes emerged the field was sprayed with the herbicides aclonifen and rimsulfuron on 27 May. Rimsulfuron was applied again on 8 June. The fungicide cyazofamid was used five times between 28 June and 9 August, whereas azoxystrobin was applied on 6 July and a combination of mancozeb and metalaxyl on 25 July. Aphids were sprayed once using lambda-cyhalothrin on 16 July. The field was irrigated three times with 25, 25, and 30 mm on 24 June, 30 June and 8 July, respectively. Neither mancozeb, azoxystrobin nor lambda-cyhalothrin was included in the monitoring. The potatoes were harvested on 19 October yielding 450 hkg/ha with 26.8% DM (120.6 hkg/ha at 100% DM), yields being below the average for the soil type and year (Plantedirektoratet, 2010).

### **3.1.3 Model setup 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 2010 and to establish an annual water balance.

Compared with the setup in Rosenbom *et al.* (2010b), a year of validation was added to the MACRO-setup for the Jyndevad site. The setup was hereby calibrated for the monitoring period May 1999–June 2004 and validated for the monitoring period July 2004–June 2010. 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 setup as well as results related to simulated bromide transport are described in Barlebo *et al.* (2007).



**Figure 9.** Soil water dynamics at **Jynde vad**: Measured precipitation, irrigation and simulated percolation 1 m b.g.s. (A), simulated and measured groundwater level (B), and simulated and measured soil water saturation (SW sat.) at three different soil depths (C, D and E). The measured data in B derive from piezometers located in the buffer zone. The measured data in C, D and E derive from TDR probes installed at S1 and S2 (Figure 8). The broken vertical line indicates the beginning of the validation period (July 2004-June 2010).

## 3.2 Results and discussion

### 3.2.1 Soil water dynamics and water balances

The model simulations were generally consistent with the observed data, thus indicating a good model description of the overall soil water dynamics in the unsaturated zone (Figure 9). The dynamics of the simulated groundwater table were well described with MACRO 5.1 (Figure 9B). For the recent hydraulic year, no measurements of the water saturation were obtained during the following two periods: 1 June – 25 August 2009 (given a breakdown in the TDR measuring system) and 7 February – 6 March 2010 (given a sensor error). However, as noted earlier in Rosenbom *et al.* (2010b), the model still had some difficulty in capturing the degree of soil water saturation 1.1 m b.g.s. (Figure 9E) and also the decrease in water saturation observed during summer periods at 25 and 60 cm b.g.s.

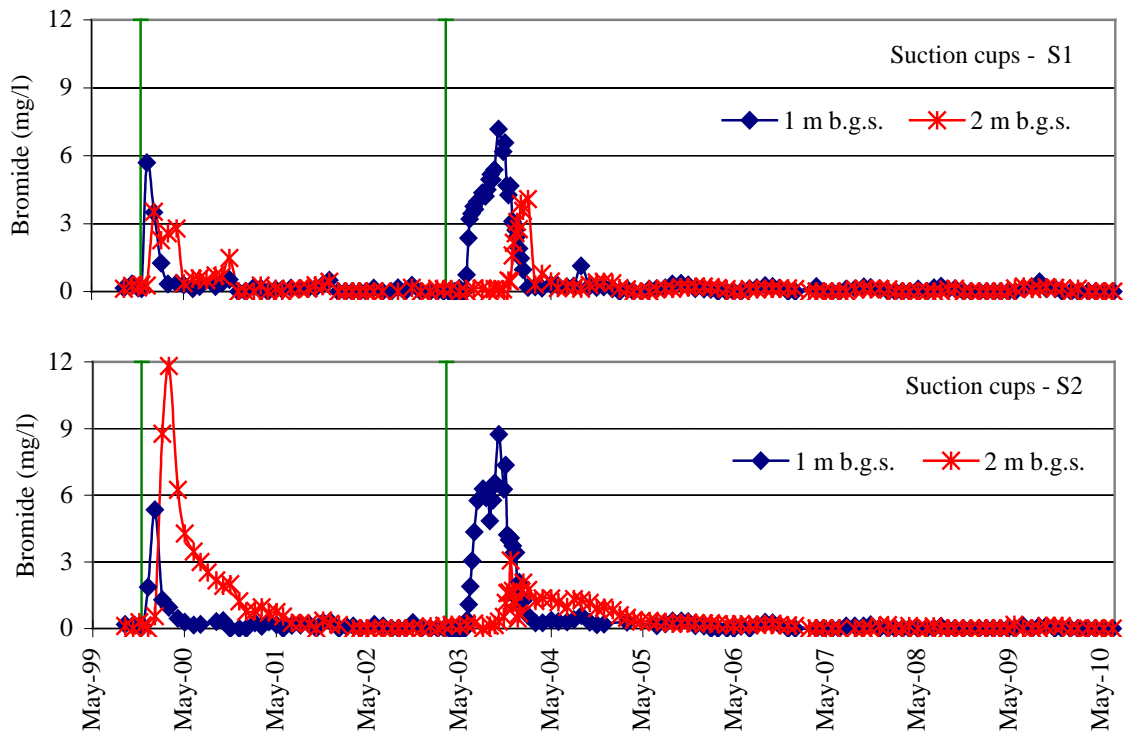
The resulting water balance for Jyndevad for the 11 monitoring periods is shown in Table 5. Compared with the previous ten years, the latest hydraulic year July 2009-June 2010 was characterised by having medium precipitation, simulated actual evapotranspiration and irrigation values. Precipitation in the latest hydraulic year was characterised by November being very wet, and January to June being very dry (Appendix 4). Periods without continuous percolation 1 m b.g.s. were therefore simulated in the spring of 2010.

**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 <sup>1)</sup>	Precipitation	Irrigation	Actual Evapotranspiration	Groundwater Recharge <sup>2)</sup>
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	857	117	490	484
1.7.06–30.6.07	995	1304	114	571	847
1.7.07–30.6.08	995	1023	196	613	605
1.7.08–30.6.09	995	1048	114	547	615
1.7.09–30.6.10	995	1034	80	516	599

<sup>1)</sup> Normal values based on time series for 1961–1990.

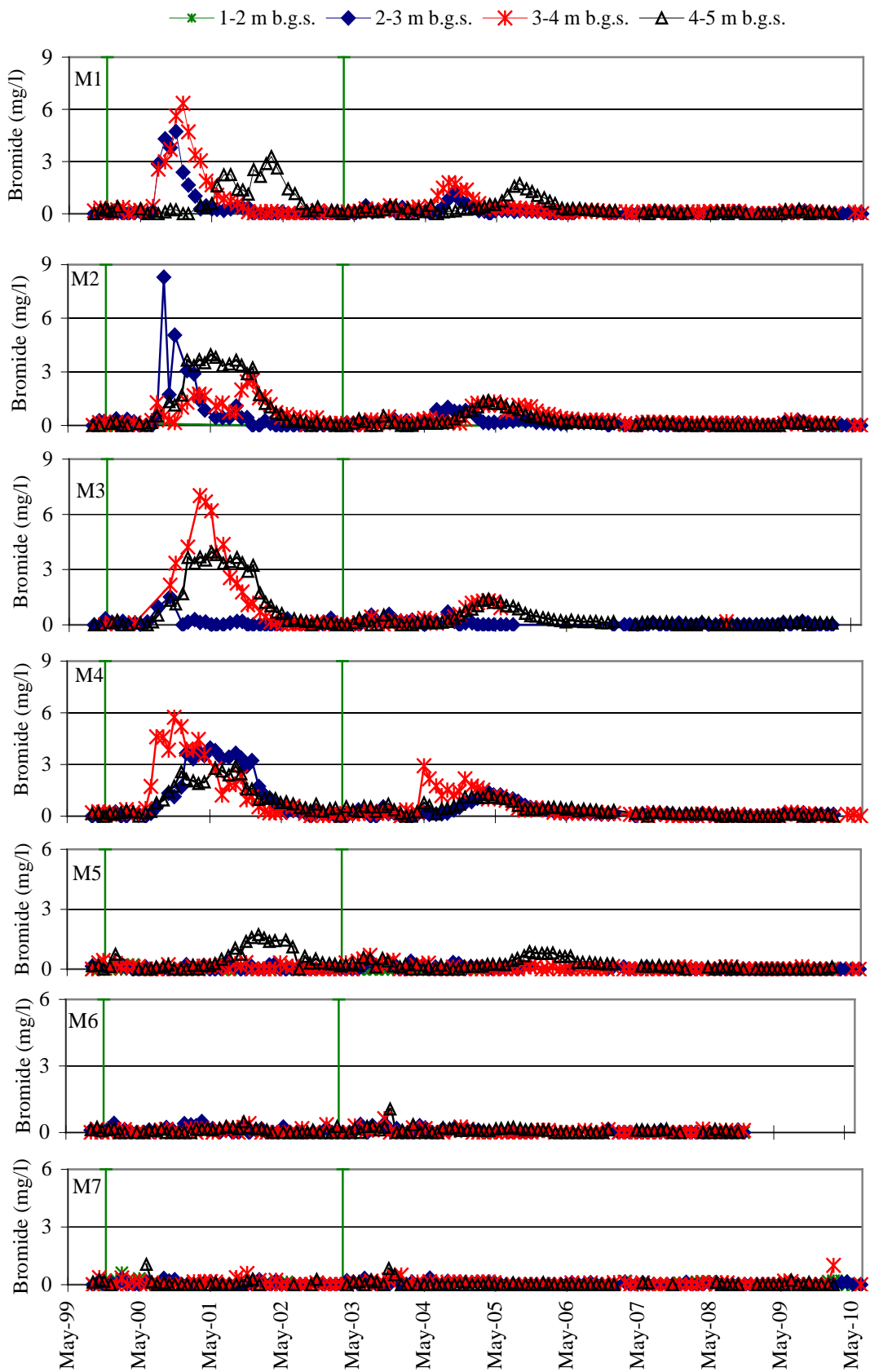
<sup>2)</sup> Groundwater recharge is calculated as precipitation + irrigation - actual evapotranspiration.



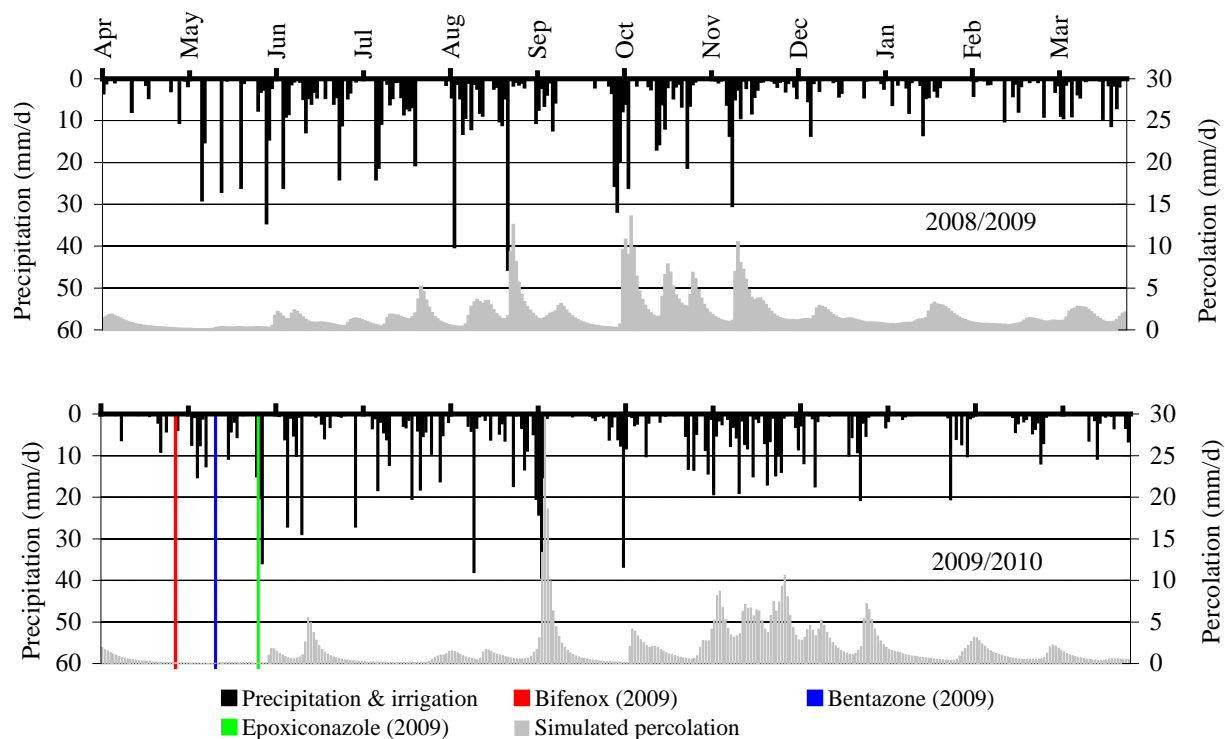
**Figure 10.** Bromide concentration in the unsaturated zone at **Jynde vad**. The measured data derive from suction cups installed 1 m b.g.s. (upper) and 2 m b.g.s. (lower) at locations S1 and S2 (Figure 8). The green vertical lines indicate the dates of bromide applications.

### 3.2.2 Bromide leaching

Bromide has now been applied twice at Jynde vad. The bromide concentrations measured until April 2003 (Figure 10 and Figure 11) relate to the bromide applied in autumn 1999, as described further in Kjær *et al.* (2003). Leaching of the bromide applied in March 2003 is evaluated in Barlebo *et al.* (2007).



**Figure 11.** Bromide concentration in the groundwater at **Jydevad**. The data derive from monitoring wells M1–M7. Monitoring at well M6 was suspended September 2008 (Appendix 2). Screen depth is indicated in m b.g.s. The green vertical lines indicate the dates of bromide applications.



**Figure 12.** Application of pesticides included in the monitoring programme, precipitation and irrigation (primary axis) together with simulated percolation 1 m b.g.s. (secondary axis) at **Jynde vad** in 2008/2009 (upper) and 2009/2010 (lower).

### 3.2.3 Pesticide leaching

Monitoring at Jynde vad 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 12. It should be noted that precipitation is corrected to the soil surface according to Allerup and Madsen (1979), whereas percolation (1 m b.g.s.) refers to accumulated percolation as simulated with the MACRO model. It should also be noted that as tribenuron-methyl (applied here as Express), pyridate (applied here as Lido) and rimsulfuron (applied here as Titus) degrade rapidly. The leaching risk is therefore associated with their respective degradation products: triazinamin-methyl, PHCP, PPU, and PPU-desamino rather than the parent compounds. For the same reasons the degradation products and not the parent compounds are monitored in PLAP (Table 6). The product Basagran M75 contains two active substances, bentazone and MCPA, but only bentazone is monitored. Pesticides applied later than April 2010 are not evaluated in this report and hence not included in Table 6 and Figure 12.

**Table 6.** Pesticides analysed at **Jynde vad** with the product used shown in parentheses. Degradation products are in italics. Precipitation (prec.) and percolation (perc.) are accumulated from date of first application until end of monitoring. 1<sup>st</sup> month perc. refers to accumulated percolation within the first month after application. C<sub>mean</sub> refers to average leachate concentration 1 m b.g.s the first year after application (See Appendix 2 for calculation method).

Crop and analysed pesticides	Application Date	End of Monitoring	Prec. (mm)	Perc. (mm)	1 <sup>st</sup> month perc. (mm)	C <sub>mean</sub> (µg/l)
<b>Winter rye 2000</b>						
Glyphosate (Roundup 2000)	Sep 99	Apr 02	2759	1607	139	<0.01
- <i>AMPA</i>						<0.01
<i>Triazinamin-methyl</i> <sup>1)</sup> (Express)	Nov 99	Apr 02	2534	1451	86	<0.02
Propiconazole (Tilt Top)	Apr 00	Jul 02	2301	1061	3	<0.01
Fenpropimorph (Tilt Top)	Apr 00	Apr 02	2015	1029	3	<0.01
- <i>fenpropimorphic acid</i>						<0.01
<b>Maize 2001</b>						
Terbuthylazine (Lido 410 SC)	May 01	Apr 04	3118	1809	4	<0.01
- <i>desethyl-terbuthylazine</i>	May 01	Apr 07	6742	3826	4	<0.01–0.02
PHCP <sup>2)</sup> (Lido 410 SC)	May 01	Jul 03	2413	1366	4	<0.02
<b>Potatoes 2002</b>						
- <i>PPU</i> (Titus) <sup>3)</sup>	May 02	Jul 10 <sup>†</sup>	9389	5126	11	0.06 <sup>4)</sup> –0.13
- <i>PPU-desamino</i> (Titus) <sup>3)</sup>		Jul 10 <sup>†</sup>	9389	5126	11	0.01–0.03
<b>Spring barley 2003</b>						
MCPA (Metaxon)	Jun 03	Jul 05	2340	1233	0	<0.01
- <i>4-chlor,2-methylphenol</i>						<0.01
Dimethoate (Perfekthion 500 S)	Jun 03	Jul 05	2278	1232	1	<0.01
<b>Pea 2004</b>						
Bentazone (Basagran 480)	May 04	Jul 07	3888	2044	4	0.02 – 0.13
- <i>AIBA</i>						<0.01
Pendimethalin (Stomp SC)	May 04	Apr 07	3557	1996	4	<0.01
Pirimicarb (Pirimor G)	Jun 04	Apr 07	3493	1993	27	<0.01
- <i>Pirimicarb-desmethyl</i>						<0.01
- <i>Pirimicarb-desmethyl-formamido</i>						<0.02
- <i>fluazifop-P(free acid)</i> <sup>5)</sup>	Jun 04	Jul 06	2395	1233	27	<0.01
(Fusilade X-tra)						
<b>Winter wheat 2005</b>						
Ioxynil (Oxitril CM)	Oct 04	Apr 07	2955	1791	81	<0.01
Bromoxynil (Oxitril CM)	Oct 04	Apr 07	2955	1791	81	<0.01
Amidosulfuron (Gratil 75 WG)	Apr 05	Jul 07	1070	515	33	<0.01
Fluroxypyr (Starane 180 S)	May 05	Jul 07	2683	1360	37	<0.02
Azoxystrobin (Amistar)	May 05	Apr 07	2274	1283	49	<0.01
- <i>CyPM</i>						<0.02
<b>Spring barley 2006</b>						
Florasulam (Primus)	May 06	Jul 08	2779	1487	34	<0.01
- <i>florasulam-desmethyl</i>						<0.03
Epoxiconazole (Opus)	Jun 06	Dec 09	4698	2592	31	<0.01
<b>Triticale 2007</b>						
Mesosulfuron-methyl (Atlantis WG)	Oct 06	Dec 09	4177	2418	73	<0.01
- <i>mesosulfuron</i>						<0.01
Chlormequat (Cycocel 750)	Apr 07	Jul 08	1548	689	1	<0.01
Epoxiconazole (Opus)	May 07	Dec 09	3465	1815	6	<0.01
<b>Winter wheat 2008</b>						
Picolinafen (Pico 750 WG)	Oct 07	Mar 10	2934	1685	55	<0.01
- <i>CL153815</i>						<0.01
Tebuconazole (Folicur EC 250)	Dec 07	Mar 10	2807	1626	97	<0.01
<b>Spring barley 2009</b>						
Bifenox (Fox 480 SC)	Apr 09	Jul 10 <sup>†</sup>	1376	647	3	<0.02
- <i>bifenox acid</i>						<0.05
- <i>nitrofen</i>						<0.01
Bentazone (Basagran M75)	May 09	Jul 10 <sup>†</sup>	1328	646	14	0.06
Epoxiconazole (Bell)	May 09	Dec 09	972	518	43	<0.01

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

<sup>1)</sup> Degradation product of tribenuron-methyl. The parent compound degrades too rapidly to be detected by monitoring.

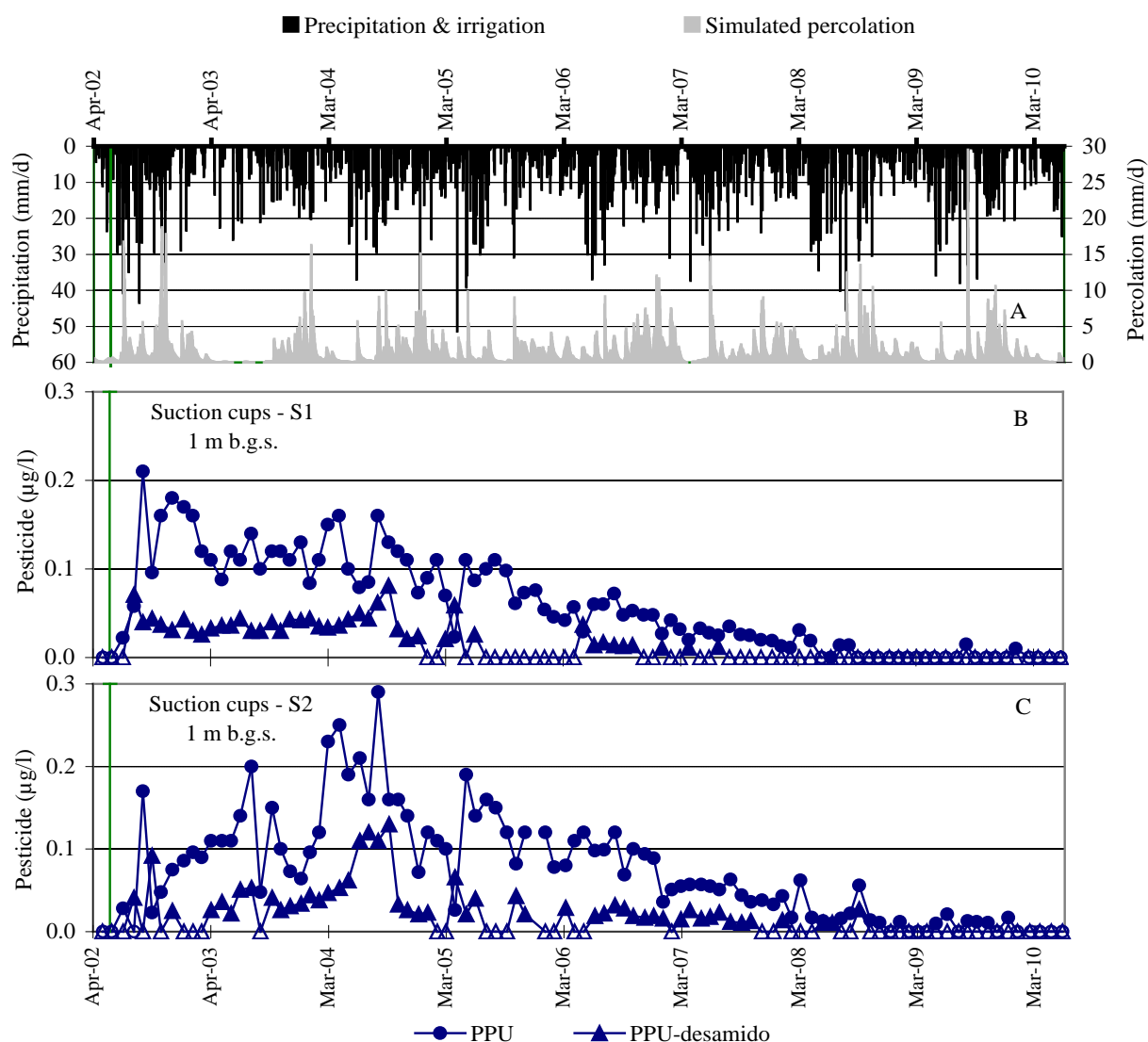
<sup>2)</sup> Degradation product of pyridate. The parent compound degrades too rapidly to be detected by monitoring.

<sup>3)</sup> Degradation product of rimsulfuron. The parent compound degrades too rapidly to be detected by monitoring.

<sup>4)</sup> Leaching increased the second year after application (see Figure 13).

<sup>5)</sup> Degradation product of fluazifop-P-butyl. The parent compound degrades too rapidly to be detected by monitoring.

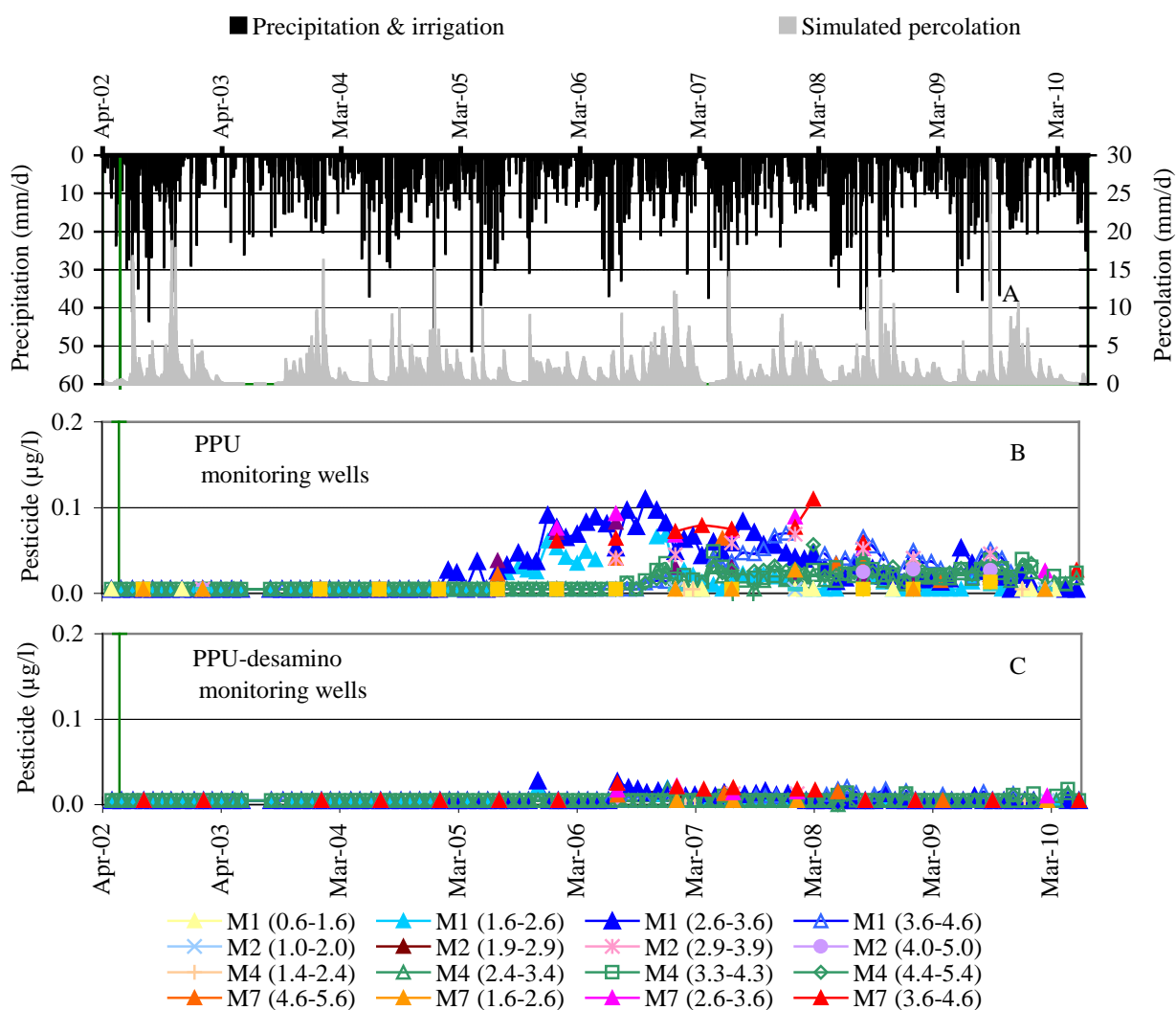
<sup>†</sup> Monitoring will continue for an additional year. The values for prec. and perc. are accumulated up to July 2009.



**Figure 13.** Precipitation, irrigation and simulated percolation 1 m b.g.s. (A) together with measured concentrations of PPU and PPU-desamino ( $\mu\text{g/l}$ ) in suction cups installed 1 m b.g.s. at location S1 (B) and S2 (C) at Jyndeved. The green vertical line indicates the date of pesticide application. Open symbols indicate concentrations below the limit of detection ( $0.02 \mu\text{g/l}$  prior to July 2006 and  $0.01 \mu\text{g/l}$  thereafter).

The current report focuses on the pesticides applied from 2008 and onwards, while leaching risk of pesticides applied before 2008 has been evaluated in previous monitoring reports (see [http://pesticidvarsling.dk/publ\\_result/index.html](http://pesticidvarsling.dk/publ_result/index.html)). Since PPU and PPU-desamino (degradation products of rimsulfuron applied in 2003) were still included in the current monitoring period, the results of these applications are, however, summarised below and in Rosenbom *et al.* (2010a). For a detailed description of the leaching pattern, including primary data and climatic conditions characterising the monitoring periods, see Kjær *et al.* (2005c).





**Figure 14.** Precipitation, irrigation and simulated percolation 1 m b.g.s. (A) together with measured concentrations ( $\mu\text{g/l}$ ) in downstream (M1, M2, M4) and upstream monitoring wells (M7) of PPU (B) and PPU-desamino (C) at Jynde vad. The numbers in parentheses indicate the depths of the analysed screens. The green vertical line indicates the date of pesticide application. Open symbols indicate concentrations below the limit of detection ( $0.02 \mu\text{g/l}$  prior to July 2006 and  $0.01 \mu\text{g/l}$  thereafter).

Two degradation products of rimsulfuron, PPU and PPU-desamino, were detected at 1 m depth in the suction cups at S1 and S2 (Figure 13). Both compounds were characterised by continuous leaching over a long period of time. Although the concentration decreased during the last monitoring year, PPU could still be found in low concentrations towards the end of 2009/2010, i.e. eight years after application. Average yearly concentrations of PPU reaching  $0.1 \mu\text{g/l}$  were seen as long as three years after application (Figure 13 and Table 7). With an overall travel time of about four years, PPU also reached the downstream monitoring screens (Figure 14). The most recent detection of PPU in monitoring screens of M1 (sampled monthly) was  $0.011 \mu\text{g/l}$  on 3 February 2010. In M2 (sampled half-yearly) the most recent detections were from 30 September 2009 ( $0.022$ -  $0.046 \mu\text{g/l}$ ). PPU showed up in M4 (sampled monthly) for the first time in September 2006. From then and until April 2010 PPU has been detected in 119 of a total of 129 samples, concentrations ranging between  $0.011$  and  $0.049 \mu\text{g/l}$ . In M7, PPU was still present on 17 March 2010 at  $0.026 \mu\text{g/l}$  (Figure 9 and Figure 15).

**Table 7.** Percolation together with estimated average concentrations ( $\mu\text{g/l}$ ) of PPU and PPU-desamino 1 m b.g.s. at **Jyndevad**. Leached mass refers to the total mass (% of applied rimsulfuron) leached during the monitoring period 1.7.02–30.6.10.

	Percolation (mm/y)	PPU		PPU-desamino	
		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	0.01-0.03
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	0.03-0.04	0.05
1.7.05–30.6.06	465	0.07	0.09	<0.02	0.01-0.02
1.7.06–30.6.07	815	0.05	0.08	0.01	0.02
1.7.07–30.6.08	643	0.02	0.04	<0.01	0.01
1.7.08–30.6.09	623	<0.01	0.02	<0.01	<0.01
1.7.09–30.6.10	619	<0.01	0.01	<0.01	<0.01

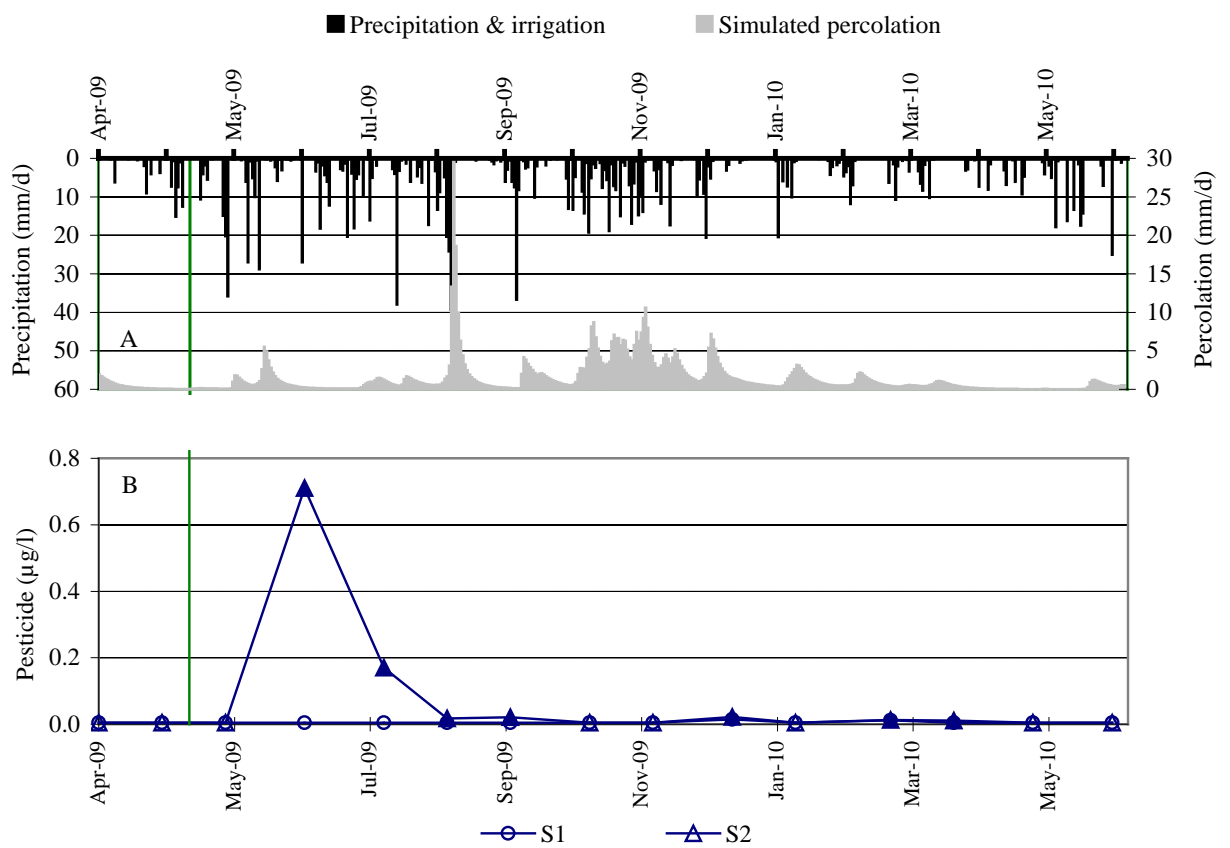
<sup>1)</sup> Expressed as rimsulfuron equivalent

The tracer test suggested that water sampled in M7 had not infiltrated at the PLAP site, but originated from the upstream neighbouring fields, where rimsulfuron had also been applied (Kjær *et al.*, 2007).

Furthermore, PPU-desamino was detected in monitoring wells, although the number of detections and concentration levels were lower than those of PPU-desamino (Figure 14C and Table A5.2 in Appendix 5). Finally, it should be noted that the concentration of PPU is likely to be underestimated by up to 22-44% due to stability problems, as described in Rosenbom *et al.* 2010a and section 7.2.2.

Four pesticides (tebuconazole, chlormequat, epoxiconazole and picolinafen, which can degrade to CL153815) were applied during the 2007/08 growing season. Picolinafen was detected in a monitoring well just once, at a concentration of 0.015  $\mu\text{g/l}$ , whereas its metabolite CL153815 was not found. Tebuconazole was detected once at 0.014  $\mu\text{g/l}$  in suction cups. Juhler *et al.* (2010) conducted a detailed analysis on the fate and transport of chlormequat at the site. This analysis was financially supported by Copenhagen Energy (Københavns Energi A/S). Chlormequat was not detected at all and epoxiconazole just once. None of the detections exceeded 0.1  $\mu\text{g/l}$  (Table A5.2, Appendix 5).

The herbicides bifenoxy and bentazone were used in the spring barley sown in 2009. Bifenoxy was found twice in suction cups, in concentrations of 0.034 and 0.036  $\mu\text{g/l}$ , four to six months after the application as well as in two monitoring wells five months after application, in concentrations of 0.05 and 0.033  $\mu\text{g/l}$  (Table A5.2). The metabolite bifenoxy acid was found once, 0.1  $\mu\text{g/l}$ , in a monitoring well four months after application. Bentazone was absent in all the samples from the monitoring wells (Table 20). It was, however, found frequently in samples from suction cups (Figure 15B and Table 18), reaching a maximum of 0.71  $\mu\text{g/l}$ . None of the substances were leached in yearly average concentrations exceeding 0.1  $\mu\text{g/l}$  (Table 6).



**Figure 15.** Precipitation, irrigation and simulated percolation 1 m b.g.s. (A) together with measured concentrations of bentazone in suction cups installed 1 m b.g.s. at location S and S2 (B) at **Jydevad**. The green vertical line indicates the date of pesticide application. Open symbols indicate concentrations below the limit of detection. Bentazone has not been detected in any water samples from the groundwater monitoring wells.



## 4 Pesticide leaching at Silstrup

### 4.1 Materials and methods

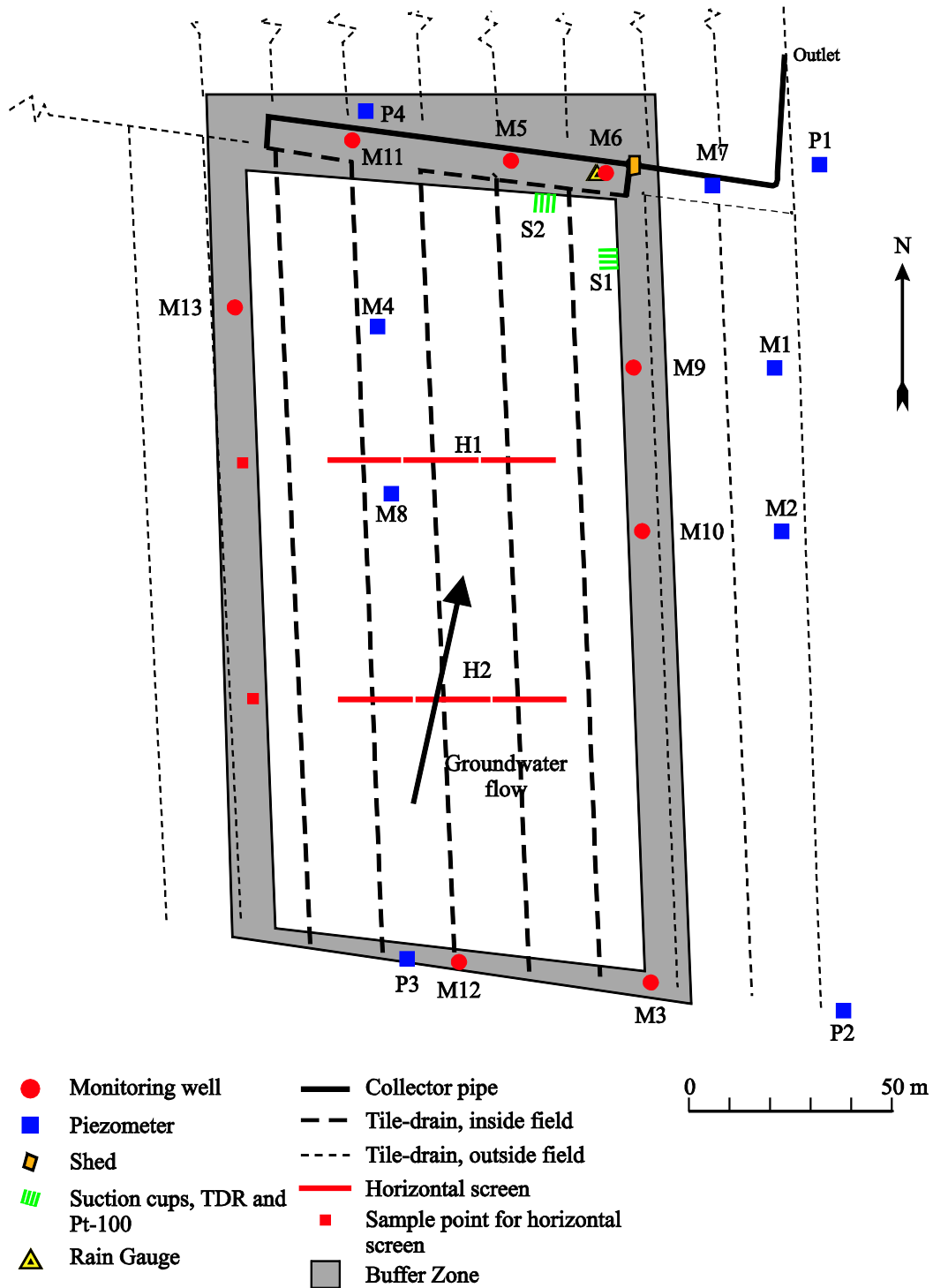
#### 4.1.1 Site description and monitoring design

The test field at Silstrup is located south of Thisted in north-western Jutland (Figure 1). The cultivated area is 1.69 ha (91 x 185 m) and slopes gently 1–2° to the north (Figure 15). Based on two profiles excavated in the buffer zone bordering the field the soil was classified as Alfic Argiudoll and Typic Hapludoll (Soil Survey Staff, 1999). The topsoil content of clay in the two profiles was 18 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 2008-2009 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 previous reports available on [http://pesticidvarsling.dk/publ\\_result/index.html](http://pesticidvarsling.dk/publ_result/index.html).

Having been harrowed, levelled and rolled between 21 April and 5 May 2008 the field was sown with fodder beat (cv. Kyros) on 7 May, which emerged on 15 May. A first spraying of weeds was done on 22 May when the first leaf was visible (pinhead-size) and the cotyledons horizontally unfurled, using triflusaluron, metamilon, and phenmedipham. A second spraying of weeds took place on 30 May, the crop having three leaves unfurled, using triflusaluron, metamilon, ethofumesate, and phenmedipham.



**Figure 16.** 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). Pesticide monitoring is conducted weekly from the drainage system (during period of continuous drainage runoff) and monthly and half-yearly from selected groundwater monitoring wells as described in Table A2.1 in Appendix 2.

A third spraying of weeds took place on 17 June, at the stage of five unfurled leaves, using triflurosulfuron, metamitron, ethofumesate, and phenmedipham. All of these herbicides except phenmedipham were included in the monitoring programme. On 26 June pests were treated with pirimicarb (not monitored) at the stage of six leaves. On 1 July weeds were sprayed a fourth time using fluazifop-P-butyl, at seven leaves. When the crop had eight unfurled leaves on 4 July a fifth and final treatment of weeds was done using triflurosulfuron, metamitron, and phenmedipham. A last spraying with pirimicarb (not monitored) against pests took place on 9 July where the crop covered 20% of the area. Beets were harvested on 27 October, yielding 17.3 t/ha of 100% DM. All beet tops (5.2 t/ha) were shredded and ploughed into the soil on 15 December.

Having been harrowed twice on 30 March 2009, pig slurry was injected and potassium bromide applied as a tracer on 2 April. Sowing of spring barley (cv. Keops), undersown with red fescue (cv. Jasperina), took place on 11 April 2009. The herbicide bentazone was sprayed on 19 May, when the barley had four detectable tillers. The fungicide azoxystrobin was applied on 24 June, but not included in the monitoring. On 16 July the spring barley was harvested as wholecrop, yielding 94.6 hkg/ha (100% DM). The red fescue was later sprayed with the herbicides iodosulfuron on 24 August, four tillers detectable, and with bifenoxy on 9 September, five tillers detectable. On 2 May 2010 weeds were sprayed with fluazifop-p-butyl and on 5 May with iodosulfuron and MCPA, the latter two were, however, not included in the monitoring. Harvest of grass seeds took place on 20 July, yielding 16.5 hkg/ha of seeds (87% DM). An amount of 69.3 hkg/ha of straw (100% DM) was burned in the field on 21 July 2010.

#### **4.1.3 Model setup and calibration**

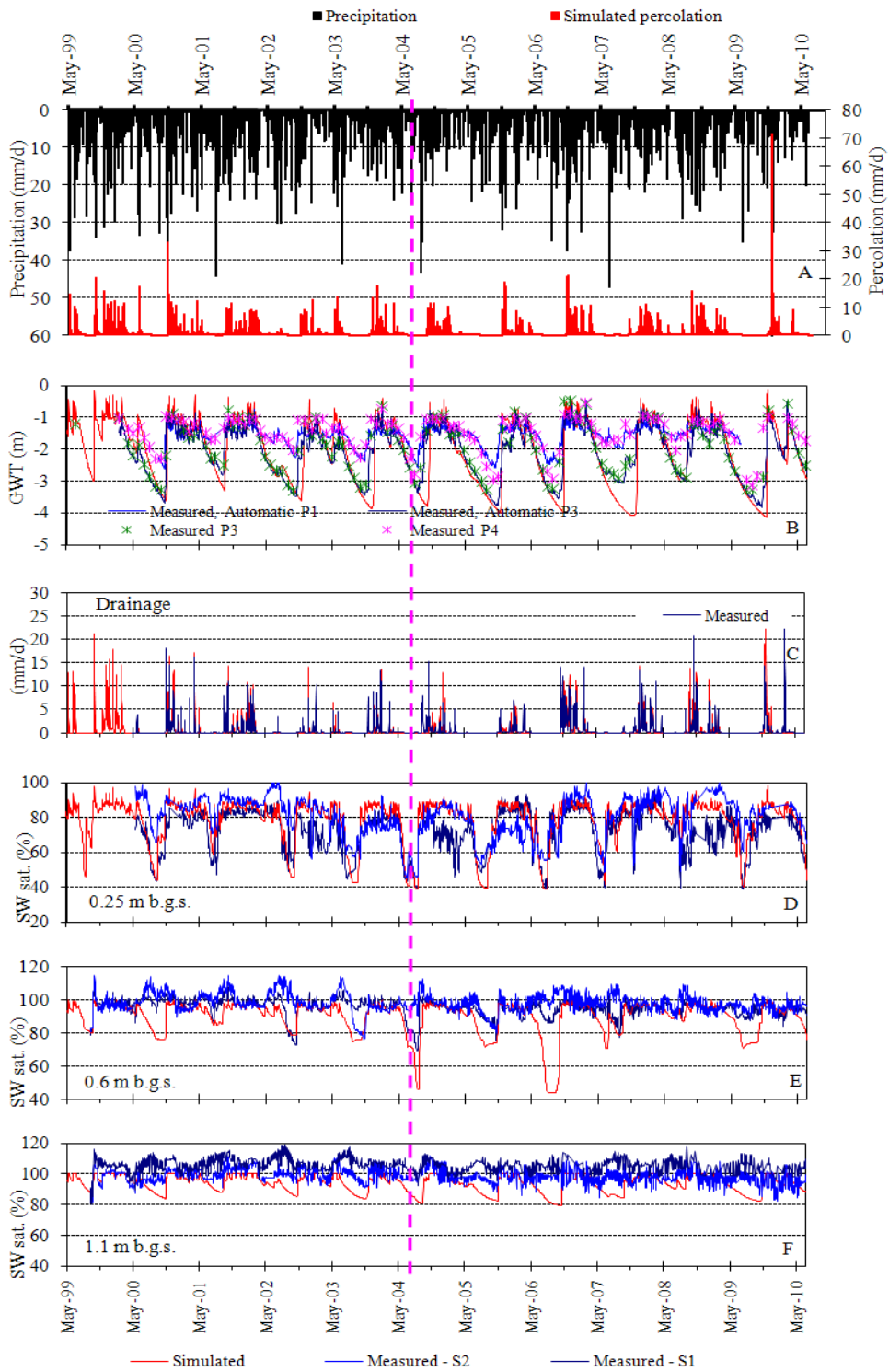
Compared with the setup in Rosenbom *et al.* (2010b), a year of validation was added to the MACRO setup for the Silstrup site. The setup was hereby calibrated for the monitoring period May 1999-June 2004 and validated for the monitoring period July 2004-June 2010. For this purpose, the following time series have been used: the observed groundwater table measured in the piezometers located in the buffer zone, soil water content measured at three depths (25, 60, and 110 cm b.g.s.) from the two profiles S1 and S2 (Figure 15), and the measured drainage flow. Data acquisition, model setup and results related to simulated bromide transport are described in Barlebo *et al.* (2007). Given impounding of water in the drainage water monitoring well, estimates for the measured drainage on 11 December 2006, 13-14 December 2006, and 28 February 2007 were based on expert judgment. Additionally, TDR-measurements at 25 cm b.g.s. in the period 15 December 2009 – 20 March 2010 were discarded given freezing soils (soil temperatures at or below zero degrees Celsius). The soil water content is measured with TDR based on Topp calibration (Topp *et al.*, 1980), which will underestimate the total soil water content at the soil water freezing point as the permittivity of frozen water is much less than that of liquid water (Flerchinger *et al.*, 2006).

## 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 17). As in Rosenbom *et al.* (2010b), 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 17B and 17C). The first drainage flow period of the past year was well captured by the model, whereas the magnitude of the second drainage flow period was not captured (Figure 17C). The last period can be characterised by frozen soil and precipitation in the form of snow – a situation, which MACRO has difficulties in describing. Additionally, drainage flow ( $q$ ) is calculated by means of continuous measurements of the water height ( $h$ ) at a V-notch in the drainage well and a  $q/h$  relationship. At events with extreme water flow it may happen that the discharge pipe has inadequate capacity to discharge the water, so that water will rise above the V-notch plate in the drainage well. This was the case during the snowmelt occurring on 12 March 2010, why adequate water sampling was not possible. At these events the  $q/h$  relationship is not valid, and the drainage flow is estimated at a water height ( $h$ ) corresponding to the maximum height ( $h$ ) of the V-notch plate, which could have resulted in an overestimation of the measured drainage flow. As in the previous monitoring periods, the overall trends in soil water content were described reasonably well (Figure 17D, 17E, and 17F), although the model still tended to describe the subsoil as being much drier during the summer period than measured by the deeper TDR probes (Figure 17E and 17F).





**Figure 17.** 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 (Figure 16). The broken vertical line indicates the beginning of the validation period (July 2004-June 2010).

**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 <sup>2)</sup>	Precipitation	Actual evapotranspiration	Measured drainage	Simulated drainage	Groundwater recharge <sup>3)</sup>
1.7.99–30.6.00 <sup>1)</sup>	976	1175	457	–	443	275 <sup>4)</sup>
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
1.7.07–30.6.08	976	877	434	200	184	242
1.7.08–30.6.09	976	985	527	161	260	296
1.7.09–30.6.10	976	835	398	203	222	234

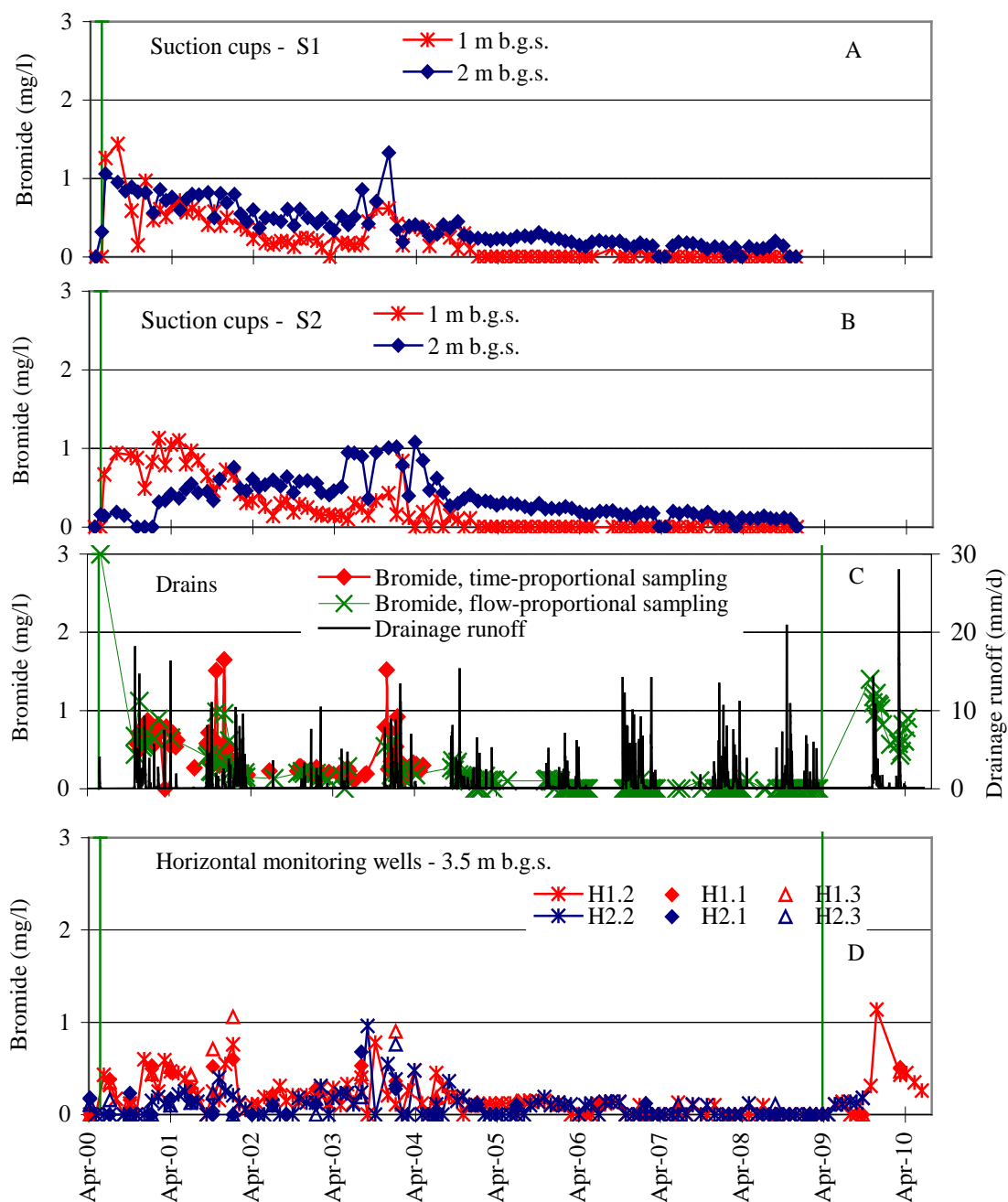
<sup>1)</sup> The monitoring started in April 2000.

<sup>2)</sup> Normal values based on time series for 1961–1990 corrected to soil surface.

<sup>3)</sup> Groundwater recharge calculated as precipitation - actual evapotranspiration - measured drainage.

<sup>4)</sup> Where drainage flow measurements were lacking, simulated drainage flow was used to calculate groundwater recharge.

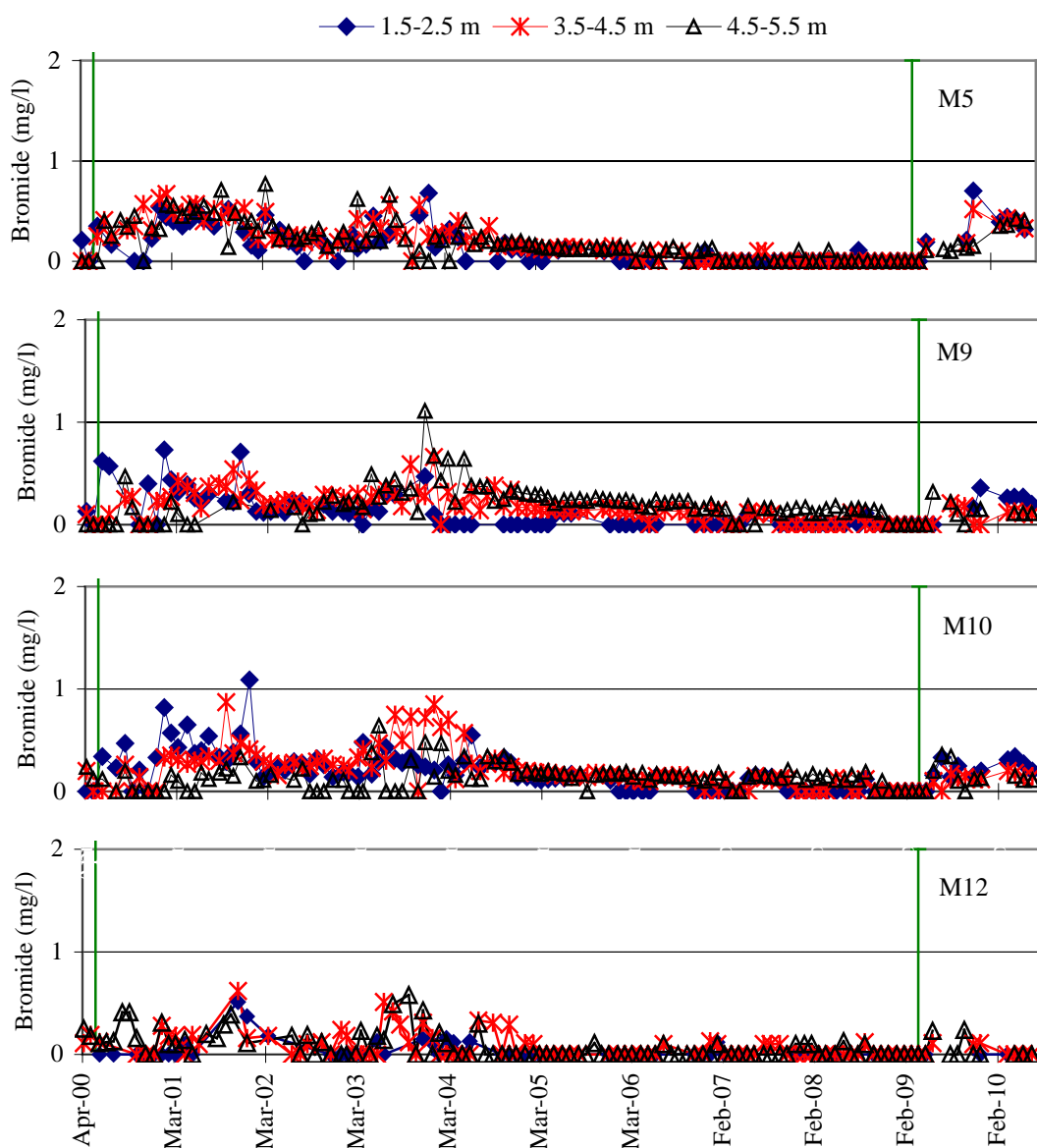
The resulting water balance for Silstrup for the entire monitoring period is shown in Table 8. Compared with the previous 11 years, the recent hydraulic year July 2009-June 2010 was characterised by having the third lowest precipitation, the lowest simulated actual evapotranspiration, and the fourth-highest measured drainage. Precipitation of this year was characterised by having the wettest month ever monitored at Silstrup in November with more than 300 mm, and August, September, March, April and June being very dry (Appendix 4). Due to this precipitation pattern, the simulated percolation pattern of the year July 2009-June 2010 was not represented by continuous percolation (Figure 17A). The climatic setting of this year gave rise to short periods with the groundwater table above the drainage level, causing the fourth-largest measured drainage since monitoring started in July 2000 (Figure 17B and 17C).



**Figure 18.** Bromide concentration at **Silstrup**. A and B refer to suction cups located at S1 and S2 (see Figure 16). The bromide concentration is also shown for drainage runoff (C) and the horizontal monitoring wells H1 and H2 (D). In March 2009, bromide measurements in the suction cups were suspended (Appendix 2). The green vertical lines indicate the dates of bromide applications.

#### 4.2.2 Bromide leaching

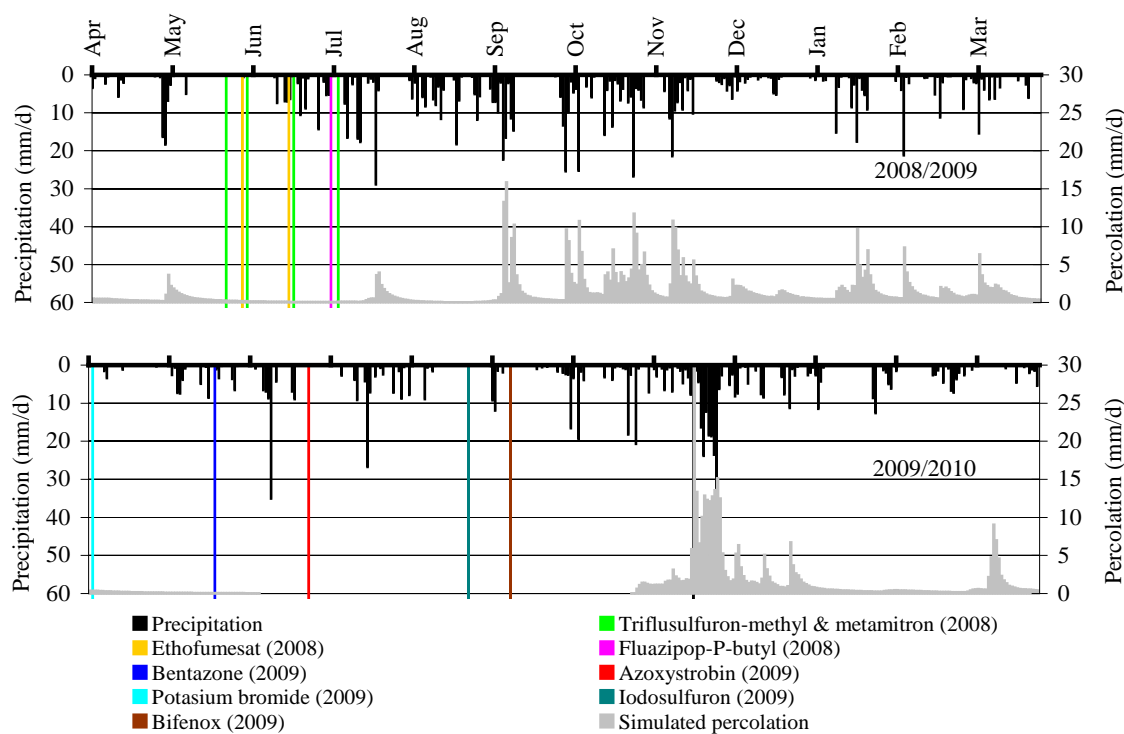
The bromide concentrations shown in Figure 18 and Figure 19 relate to the bromide applied in May 2000, as described in previous reports (Kjær *et al.* 2003 and Kjær *et al.* 2004) and further evaluated in Barlebo *et al.* (2007). In Marts 2009, bromide measurements in the suction cups and monitoring wells M6 and M11 were suspended. In April 2009, 31.5 kg/ha potassium bromide was applied for the second time.



**Figure 19.** Bromide concentration at **Silstrup**. The data derive from the vertical monitoring wells (M5–M12). In September 2008, monitoring wells M6 and M11 were suspended (Appendix 2). Screen depth is indicated in m b.g.s. The green vertical lines indicate the date of bromide applications.

### 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 percolation in Figure 19. 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. Moreover, pesticides applied later than April 2010 are not evaluated in this report and hence not included in Table 9.



**Figure 20.** Application of pesticides included in the monitoring programme, precipitation, and irrigation (primary axis) and simulated percolation 1 m b.g.s. (secondary axis) at **Silstrup** in 2008/2009 (upper) and 2009/2010 (lower).

It should also be noted that as tribenuronmethyl (applied here as Express), pyridate (applied here as Lido), and fluazifop-P-butyl (Fusilade Max) degrade rapidly, the leaching risk is associated with their respective degradation products: triazinamin-methyl, PHCP, fluazifop-P, and TFMP rather than the parent products. For the same reasons the degradation products and not the parent compounds are monitored in the PLAP (Table 9).

**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. 1<sup>st</sup> month perc. refers to accumulated percolation within the first month after application. C<sub>mean</sub> refers to average leachate concentration in the drainage water within the first drainage season after application (See Appendix 2 for calculation methods).

Crop and analysed pesticides	Application date	End of monitoring	Prec. (mm)	Perc. (mm)	1 <sup>st</sup> month perc. (mm)	C <sub>mean</sub> (µg/l)
<b>Fodder beet 2000</b>						
Metamitron (Goltix WG)	May 00	Apr 03	2634	1328	53	0.05
- <i>metamitron-desamino</i>						0.06
Ethofumesate (Betanal Optima)	May 00	Apr 03	2634	1328	53	0.03
Desmedipham (Betanal Optima)	May 00	Apr 03	2634	1328	53	<0.01
- <i>EHPC</i>						<0.02
Phenmedipham (Betanal Optima)	May 00	Apr 03	2634	1328	53	<0.01
- <i>MHPC</i>						<0.02
- <i>3-aminophenol</i>						<0.02
Fluazifop-P-butyl (Fusilade X-tra)	Jun 00	Jul 02	1953	1019	5	<0.01
- <i>fluazifop (free acid)</i>						<0.02
Pirimicarb (Pirimor G)	Jul 00	Jul 07	6452	2825	1	<0.01
- <i>pirimicarb-desmethyl</i>						<0.01
- <i>pirimicarb-desmethyl-formamido</i>						<0.02
<b>Spring barley 2001</b>						
<i>Triazinamin-methyl</i> <sup>1)</sup> (Express)	May 01	Jul 03	1941	951	10	<0.02
Flamprop-M-isopropyl (Barnon Plus 3)	Jun 01	Jul 03	1928	944	3	<0.01
- <i>flamprop (free acid)</i>						<0.01
Propiconazole (Tilt Top)	Jun 01	Jul 03	1928	944	3	<0.01
Fenpropimorph (Tilt Top)	Jun 01	Jul 03	1928	944	3	<0.01
- <i>fenpropimorphic acid</i>						<0.01
Dimethoate (Perfekthion 500 S)	Jul 01	Jul 03	1882	937	3	0.02
<b>Maize 2002</b>						
Glyphosate (Roundup Bio)	Oct 01	Apr 06	3802	1694	44	0.13
- <i>AMPA</i>						0.06
<i>PHCP</i> <sup>2)</sup> (Lido 410 SC)	May 02	Jul 04	1764	738	6	0.06
Terbuthylazine (Lido 410 SC)	May 02	Apr 06	3320	1327	6	0.07
- <i>desethyl-terbuthylazine</i>		Apr 05				0.15
- <i>2-hydroxy-terbuthylazine</i>		Apr 05				<sup>3)</sup>
- <i>2-hydroxy-desethyl-terbuthylazine</i>		Apr 05				<sup>3)</sup>
- <i>desisopropyl-atrazine</i>		Apr 05				<sup>3)</sup>
<b>Peas 2003</b>						
Bentazone (Basagran 480)	May 03	Jul 06	2634	1055	44	0.26
- <i>AIBA</i>						<0.01
Pendimethalin (Storm SC)	May 03	Apr 06	2634	1055	44	<0.01
Glyphosate (Roundup Bio)	Sep 03	Apr 06	2207	971	0	<0.01
- <i>AMBA</i>						0.02
<b>Winter wheat 2004</b>						
Prosulfocarb (Boxer EC)	Oct 03	Apr 06	2125	974	37	0.01
MCPA (Metaxon)	May 04	Jul 06	1797	710	4	<0.01
- <i>4-chlor,2-methylphenol</i>						<0.01
Azoxystrobin (Amistar)	Jun 04	Jul 06	1781	706	0	0.01
- <i>CyPM</i>		Jul 07	2931	1202	0	0.09
Pirimicarb (Pirimor G)	Jul 04	Jul 07	2818	1205	0	<0.01
- <i>Pirimicarb-desmethyl</i>						<0.01
- <i>Pirimicarb-desmethyl-formamido</i>						<0.02

<sup>1)</sup> Degradation product of tribenuron-methyl. The parent compound degrades too rapidly to be detected by monitoring.

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

<sup>3)</sup> Average leachate concentration within the first drainage season after application could not be calculated, as monitoring started January 2003 (7 month after application). See Kjær et al.(2007) for further information.

The current report focuses on the pesticides applied from 2008 and onwards, while the leaching risk of pesticides applied before 2008 has been evaluated in previous monitoring reports (see [http://pesticidvarsling.dk/publ\\_result/index.html](http://pesticidvarsling.dk/publ_result/index.html)).

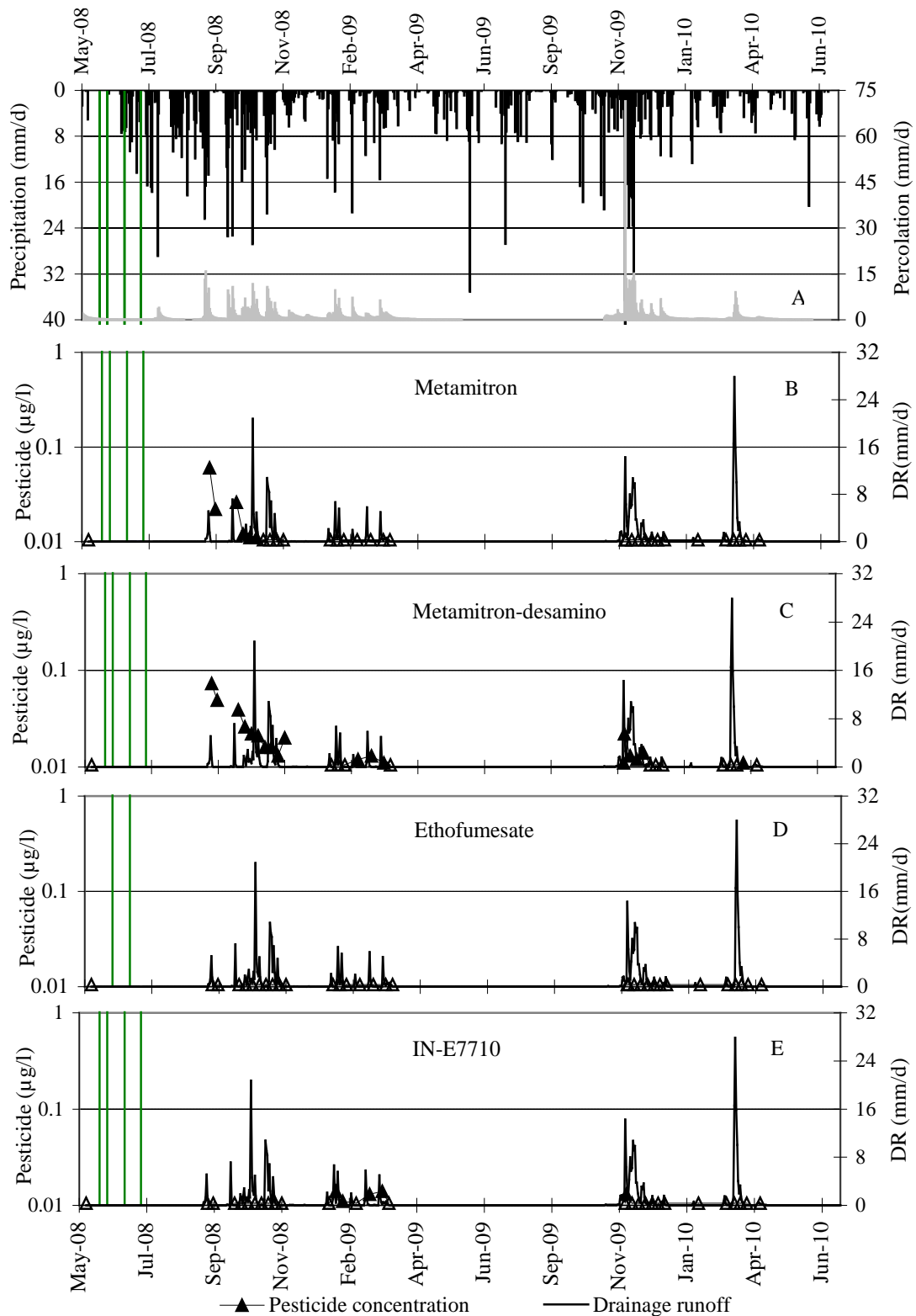
**Table 9 continued.** Pesticides analysed at **Silstrup** with the product used shown in parentheses. Degradation products are in italics. Precipitation (prec.) and percolation (perc.) are accumulated from date of first application until end of monitoring. 1<sup>st</sup> month perc. refers to accumulated percolation within the first month after application. C<sub>mean</sub> refers to average leachate concentration in the drainage water within the first drainage season after application (See Appendix 2 for calculation methods).

Crop and analysed pesticides	Application date	End of monitoring	Prec. (mm)	Perc. (mm)	1 <sup>st</sup> month Perc. (mm)	C <sub>mean</sub> (µg/l)
<b>Spring barley 2005</b>						
Fluroxypyr (Starane 180 S)	May 05	Jul 07	2012	830	11	<0.02
Azoxystrobin (Amistar)	Jun 05	Jul 06	862	332	10	0.01
- <i>CyPM</i>	Jun 05	Jul 07	2012	828	10	0.02
Pirimicarb (Pirimor G)	Jul 05	Jul 07	1933	818	0	<0.01
- <i>Pirimicarb-desmethyl</i>						<0.01
- <i>Pirimicarb-desmethyl-formamido</i>						<0.01
<b>Winter rape 2006</b>						
Propyzamide (Kerb 500 SC)	Nov 05	Apr 08	2345	1115	75	0.22 <sup>1)</sup>
- <i>RH-24644</i>						0.01 <sup>1)</sup>
- <i>RH-24580</i>						<0.01 <sup>1)</sup>
- <i>RH-24655</i>						<0.01 <sup>1)</sup>
Clopyralid (Matrignon)	Apr 06	Apr 08	2009	859	8	<0.01
<b>Winter wheat 2007</b>						
Pendimethalin (Stomp Pentagon)	Sep 06	Apr 08	1686	865	0	<0.04
Iodosulfuron-methyl-sodium (Hussar OD)	Apr 07	Apr 09	1940	875	3	<0.01
- <i>Metsulfuron-methyl</i>						<0.01
- <i>Triazinamin</i>						<0.01
Chlormequat (Cycocel 750)	Apr 07	Jul 08	1099	392	3	<0.01
Epoxiconazole (Opus)	Jun 07	Apr 09	1867	873	0	<0.01
<b>Fodder beet 2008</b>						
Triflurosulfuron (Safari)	May 08	Jul 10	1894	895	4	<0.01
- <i>IN-D8526</i>						<0.01
- <i>IN-E7710</i>						<0.01
- <i>IN-M7222</i>						<0.01
Metamitron (Goliath)	May 08	Jul 10 <sup>†</sup>	1894	895	4	0.01
- <i>Metamitron-desamino</i>						0.01
Ethofumesate	May 08	Jul 10 <sup>†</sup>	1893	893	3	<0.01
- <i>Fluazifop-P<sup>2)</sup></i> (Fusilade Max)	Jul 08	Jul 10 <sup>†</sup>	1820	890	21	<0.01
- <i>TFMP<sup>2)</sup></i> (Fusilade Max)						0.22
<b>Spring barley 2009</b>						
Bentazone (Fighter 480)	May 09	Jul 10 <sup>†</sup>	929	397	1	<0.01
Azoxystrobin (Amistar)	Jun 09	Jul 10 <sup>†</sup>	835	396	0	0.01
- <i>CyPM</i>						0.06
Iodosulfuron (Hussar OD)	Aug 09	Jul 10 <sup>†</sup>	736	401	0	<0.01
- <i>Metsulfuron-methyl</i>						<0.01
- <i>Triazinamin</i>						<0.01
Bifenox (Fox 480 SC)	Sep 09	Jul 10 <sup>†</sup>	710	402	0	<0.01
- <i>Bifenox acid</i>						2.22
- <i>Nitrofen</i>						<0.01

<sup>1)</sup> 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.

<sup>2)</sup> Degradation product of fluazifop-P-butyl. The parent compound degrades too rapidly to be detected by monitoring.

<sup>†</sup> Monitoring will continue for an additional year. The values for prec. and perc. are accumulated up to July 2009.



**Figure 21.** Precipitation and simulated percolation 1 m b.g.s. (A) together with the concentration of metamitron (B), metamitron-desamino (C) Ethofumesate (D) and IN-E7710 (E) in the drainage runoff at **Silstrup**. The green vertical lines indicate the dates of applications. Open symbols indicate values below the detection limit of 0.01 µg/l. While ethofumesate and IN-E7710 were not detected in any samples from groundwater monitoring, metamitron and metamitron-desamino have been found occasionally (see text).



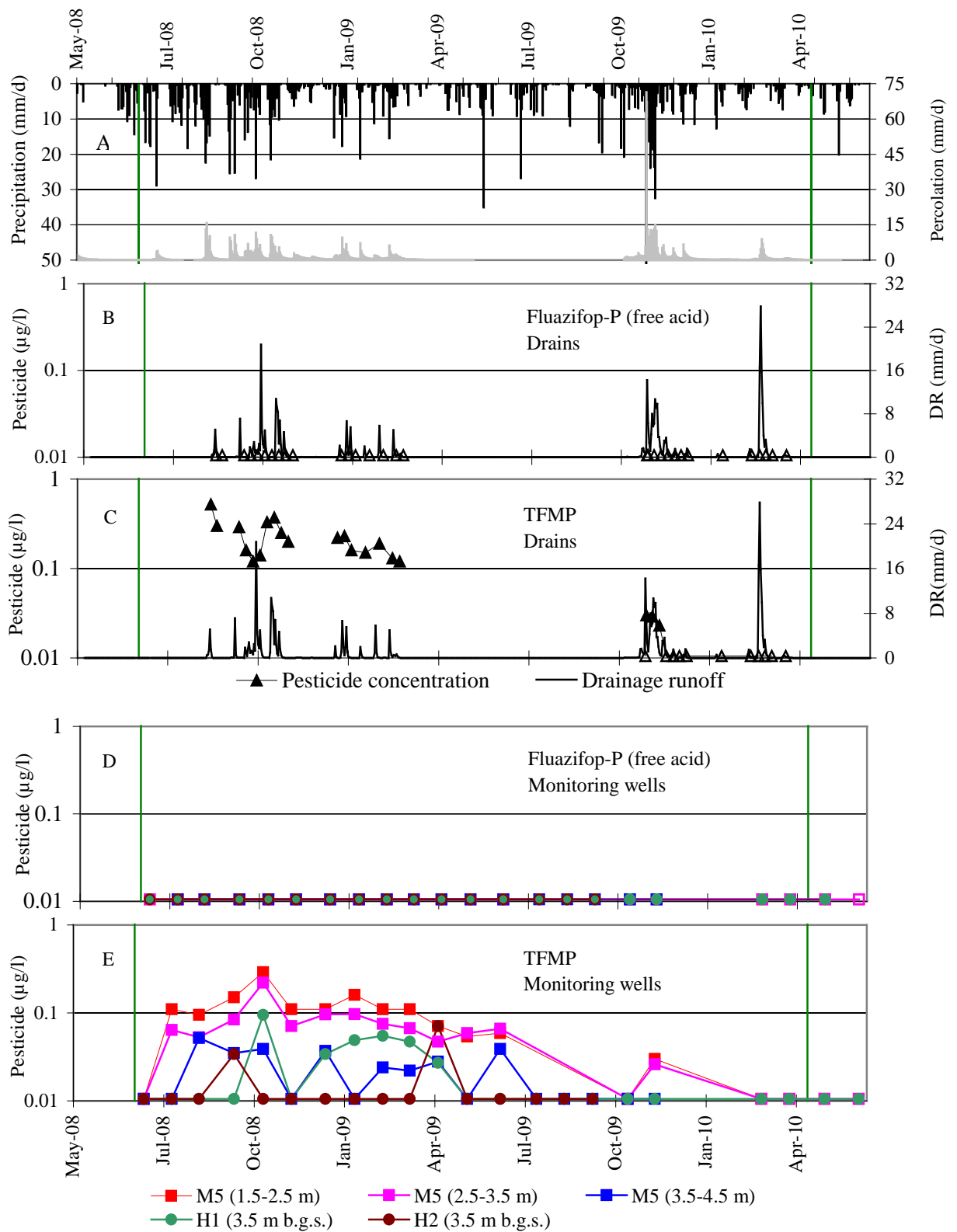
Hitherto, there has been no leaching of triflusaluron, whereas one of its degradation products IN-E7710 (Table 9 and Figure 21E) was found on four occasions in drainage water. The two other degradation products included in the monitoring programme (IN-D8526 and IN-M7222) could not be detected.

At Silstrup, the herbicides ethofumesate and metamiltron have now been applied both in 2000 and 2008 (Table 9). Whereas 345 g/ha of ethofumesate was applied in 2000, only 70 g/ha of ethofumesate was applied in 2008 (71 g/ha every 3<sup>rd</sup> year being the admissible dose). The reduced application may be part of the reason why there was only a single detection following the 2008 application, as compared to the 24 following the application in 2000, where the average yearly concentrations reduced from 0.03 to less than 0.01 µg/l over the eight-year period. An additional explanation for the reduced leaching could also be that percolation following application was much lower in 2008 than in 2000 (see Table 9).

The maximum allowed doses of metamiltron were not regulated between the 2000 and the 2008 application remaining at 2,100 g/ha of metamiltron. However, in the PLAP only 1,400 g/ha was applied in 2008. Although both metamiltron and its degradation product metamiltron-desamino were found in drainage (Table 9, Figure 21B and 21C) and groundwater samples (Table A5.3), the number of findings as well as the concentrations were lower than seen after the application in 2000, and the limit of 0.1 µg/l was in no case exceeded.

The herbicide triflusaluron was applied concomitantly with metamiltron, and the substance as well as three of its metabolites (IN-D8526, IN-M7222 and IN-E7710) was monitored. Triflusaluron and the metabolite IN-D8526 were not found at all, and IN-M7222 only once (Table A5.3). IN-E7710 was detected on four occasions (Figure 21E and Table 18).

Fluazifop-P-butyl, a herbicide used against monocotyledons, in this case couch grass (*Agropyrum repens*, L.), has been included in the PLAP several times over the past 10 years. As fluazifop-P-butyl rapidly degrades, focus has so far been on its degradation product fluazifop-P (free acid). Similar to the 2000/2001 growing season at Silstrup (Kjær *et al.*, 2003), this compound, was found in neither drainage water (Figure 22B) nor groundwater (Figure 22D). When applying fluazifop-P-butyl in July 2008 and including its degradation product TFMP in the monitoring programme, a different picture emerged (Figure 22C and Figure 22E). At the onset of the drainage flow on 11 September 2008, a concentration of 0.52 µg/l TFMP was found. Concentrations remained above 0.1 µg/l throughout the period of drainage runoff. Further, TFMP was found in the screens of the vertical monitoring wells M5.1 (1.5 to 2.5 m b.g.s) and M5.2 (2.5 to 3.5 m b.g.s.) more than one month prior to the detection in the drainage water, in concentrations of 0.11 and 0.064 µg/l, respectively (Figure 22C). With the groundwater table minimum 1.6 m b.g.s., the root zone being relatively dry, and with percolation 1 m b.g.s. in July-August 2008 (Figure 17 and Figure 22A), this indicates pronounced macropore transport bypassing the tile drainage system.



**Figure 22.** Precipitation and simulated percolation 1 m b.g.s. (A) together with the concentration of fluazifop-P (free acid) (B) and TFMP (C) in the drainage runoff, and the concentration of fluazifop-P (free acid) (D) and TFMP (E) in the groundwater monitoring screens at **Silstrup**. The green vertical lines indicate the dates of fluazifop-P-butyl applications. Values below the detection limit of 0.01 µg/l are shown as 0.01µg/l (all graphs) and further represented by open symbols in A, B and C.

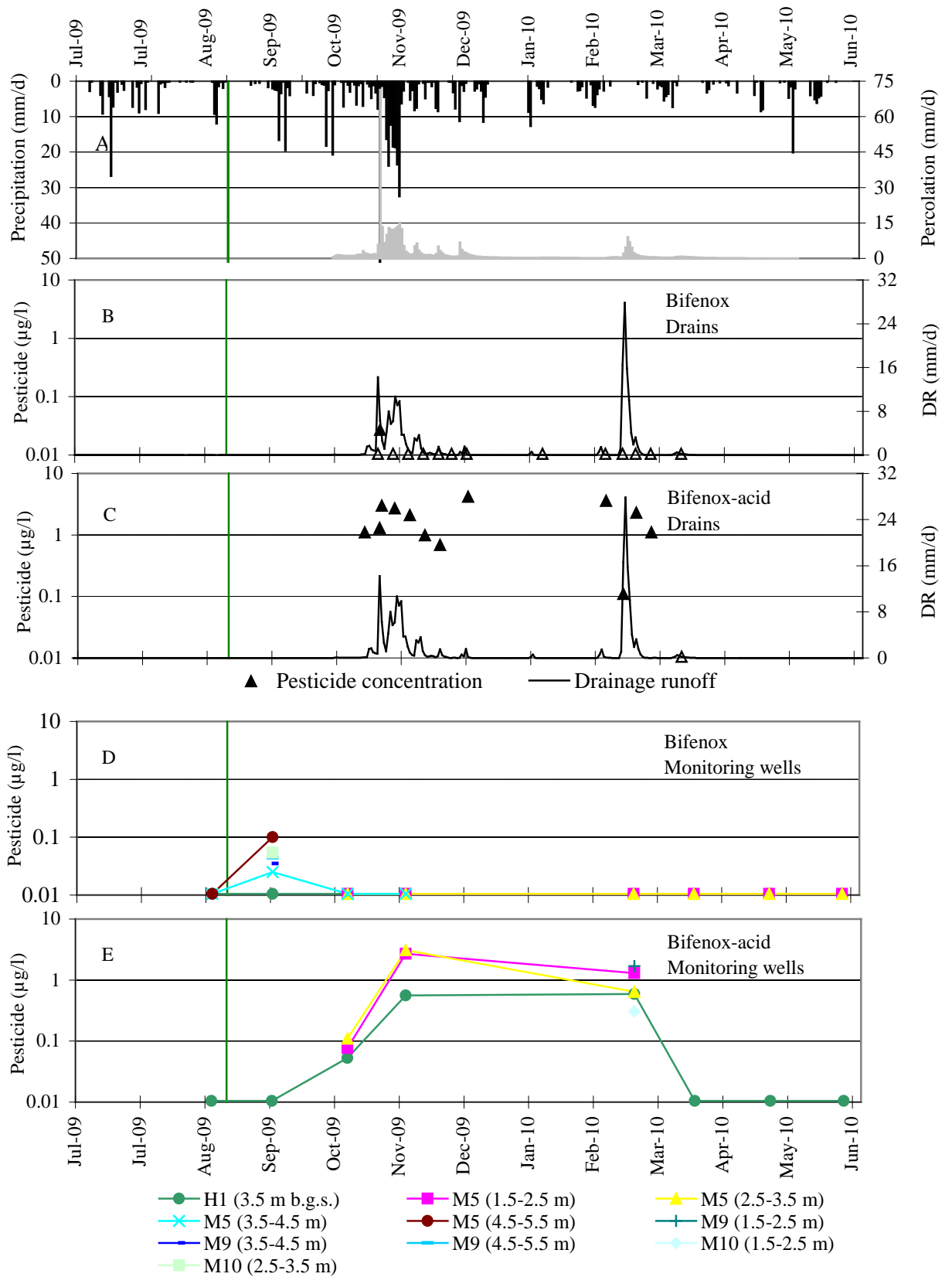
During the summer of 2009 there was no drainage flow. However, at the onset of flow in the autumn of 2009, TFMP was still present (Figure 22C), the last detection being 0.023 µg/l on 2 December 2009. Since 18 March 2009 there has been no exceedance of the 0.1 µg/l in the drainage water, and since 1 April 2009 in the groundwater. The most recent detection of TFMP was 0.03 µg/l on 1 December 2009. The average leaching concentration in drainage water within the first year of application of fluazifop-p-butyl, amounted to 0.22 µg/l of TFMP (Table 9). Maximum concentration of TFMP in the groundwater at Silstrup was 0.29 µg/l (Table 20).

Bifenox, applied in the spring barley on 9 September 2009, was found only in the sampling on 30 September in five screens of three different monitoring wells (Figure 23B); in all but one, the concentrations were less than 0.1 µg/l. In the groundwater, bifenox acid was found in screens from both horizontal and vertical wells (Figure 23E). Four of the five detections from the horizontal wells exceeded 0.1 µg/l, maximum, concentrations being 0.86 µg/l. Concentrations found in the vertical wells were even higher, amounting to 3.1 µg/l. The bifenox acid appeared in the groundwater before it was found in drainage water, in this case seven days earlier.

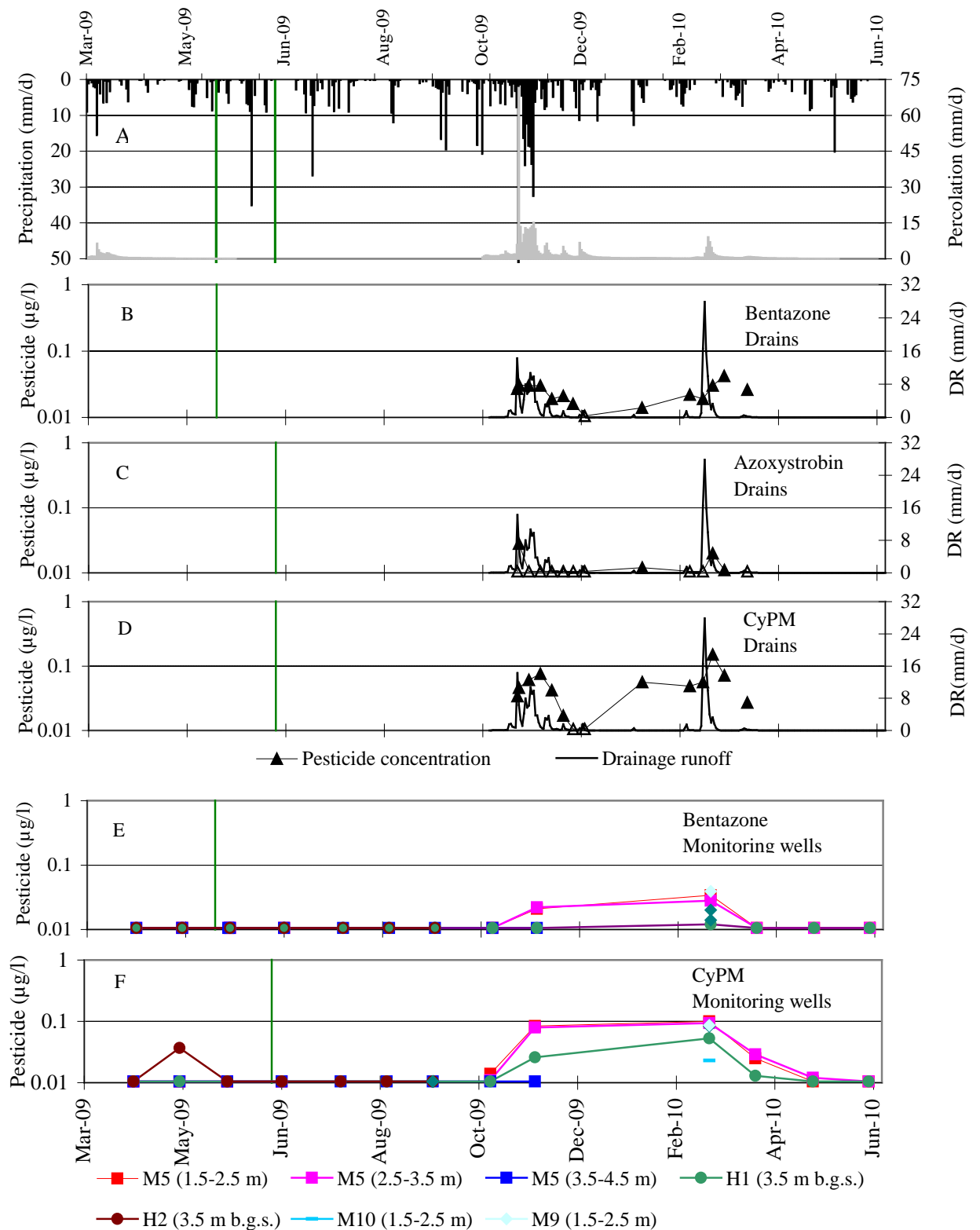
Bentazone applied on 19 May 2009 had also been applied in May 2003. Although the amount of active ingredient was the same in both years, the 2003 application was followed by concentrations that were above 0.1 µg/l in both drainage and groundwater (Kjær et al., 2005), as opposed to the 2009 application where 0.1 µg/l was never exceeded (Figure 24B, 24E and Table 9). These results may reflect the importance of different climatic conditions following a spraying.

Azoxystrobin, applied on 24 June 2009, as well as its metabolite CyPM were found in drainage water (Figure 24C and 24D). The concentrations of the metabolite were generally higher than those of the parent compound. All concentrations but one of CyPM were below 0.1 µg/l. Average yearly concentrations in drainage water amounted to 0.01 and 0.06 for azoxystrobin and CyPM, respectively (Table 9), which is about the same as for the two previous applications in 2004 and 2005 (Table 9). Whereas there were no detections of azoxystrobin in the groundwater, CyPM could be found in both horizontal and vertical wells, concentrations ranging between 0.013 and 0.086 µg/l and 0.011 and 0.1 µg/l, respectively.

When evaluating the leaching occurring during the 2009/2010 drainage season (Figure 21–24) it should be noted that the large drainage event that took place during the snowmelt on 12 March 2010 (28 mm/d) could not be sampled due to technical problems caused by the extreme intensity of the drainage runoff. Likewise the drainage runoff could not be measured, and the estimated value for this day is likely to be overestimated (see section 4.2.1 for details).



**Figure 23.** Precipitation and simulated percolation 1 m b.g.s. (A) together with the concentration of bifenoX (B) and bifenoX acid (C) in the drainage runoff, and the concentration of bifenoX (D) and bifenoX acid (E) in the groundwater monitoring screens at **Silstrup**. The green vertical line indicates the date of bifenoX application. Values below the detection limit of 0.01 µg/l are shown as 0.01 µg/l (all graphs) and further represented as open symbols in B and C.



**Figure 24.** Precipitation and simulated percolation 1 m b.g.s. (A) together with the concentration of bentazone (B), azoxystrobin (C) and CyPM (D) in the drainage runoff, and the concentration of bentazone (E) and CyPM (F) in the groundwater monitoring screens at **Silstrup**. The green vertical lines indicate the dates of bentazone and azoxystrobin applications. Values below the detection limit of 0.01 µg/l are shown as 0.01µg/l (all graphs) and further represented as open symbols in B, C and D.



## 5 Pesticide leaching at Estrup

### 5.1 Materials 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 till 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 Abrupt Argiudoll, Aqua Argiudoll and Fragiaquic Glossudalf (Soil Survey Staff, 1999). The topsoil is characterised 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 characterises the site. The saturated hydraulic conductivity in the C-horizon is  $10^{-8}$  m/s, which is about two orders of magnitude lower than at the other loamy sites (Table 1). The geological structure is complex comprising a clay till core with deposits of different age and composition (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.

#### 5.1.2 Agricultural management

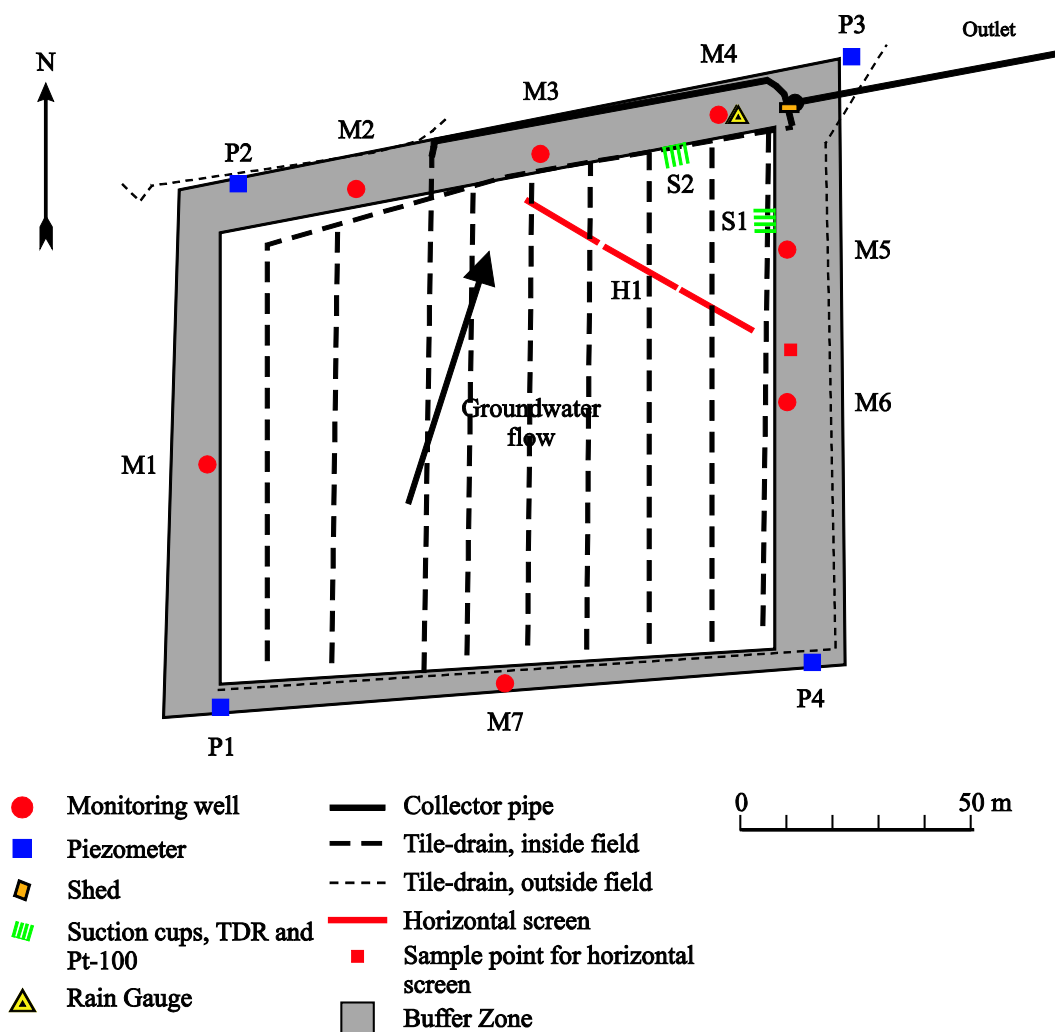
Management practice during the 2005-2009 growing seasons is briefly summarized below and detailed in Appendix 3 (Table A3.4). For information about management practice during the previous monitoring periods, see previous monitoring reports available on [http://pesticidvarsling.dk/publ\\_result/index.html](http://pesticidvarsling.dk/publ_result/index.html).

On 6 April 2009, 30 kg/ha of KBr was applied as a tracer. Two days later the field was sown with spring barley (cv. Keops), which emerged 10 days later. On 1 May, at the beginning of tillering, the herbicide bifenox was used. When on 14 May six tillers were detectable, bentazone, and MCPA were used against weeds. Only bentazone was included in the monitoring. On 4 June, when the first awns were visible, azoxystrobin was used against fungi. At harvest on 7 August, barley yielded 71.4 hkg/ha of grain (85% DM) and 39.9 hkg/ha of straw (100 DM), the latter being shredded at harvest and ploughed in on 24 August 2009. The yield of barley was about 25% above the average for the year and soil type (Plantedirektoratet, 2009).

On the 24 August 2009 the field was ploughed and rotor-harrowed and sown with winter rape (cv. Cabernet). The following day the herbicide clomazone was applied but not included in the monitoring. The herbicide bifenox was used on 30 September when four leaves had unfolded. Pesticide treatment was applied on 9 October using

cypermethrin, but the substance was not monitored. Due to poor overwintering of the winter rape, the field was partially resown on 20 April 2010 using the spring rape variety Pluto.

An area of 2.265 m<sup>2</sup> was resown after a rotor-harrowing, whereas an area of 2.412 m<sup>2</sup> was resown without soil cultivation – direct seeding. The resown area amounted to 37% of the total field area. Thiacloprid was used against pests on 10 May and included in the monitoring programme. Harvest of the rape was a two-step procedure. On 23 August the area grown with winter rape was harvested, yielding 38.3 hkg/ha (91% DM) and 41.8 hkg being shredded at harvest (100% DM). On 23 August the section of the field grown with spring rape was shredded, and the resulting biomass of 11.64 hkg/ha spread on the surface. The field was ploughed on 14 September 2010.



**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). Pesticide monitoring is conducted weekly from the drainage system (during period of continuous drainage runoff) and monthly and half-yearly from selected groundwater monitoring wells as described in Table A2.1 in Appendix 2.



### 5.1.3 Model setup 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 2010 and to establish an annual water balance.

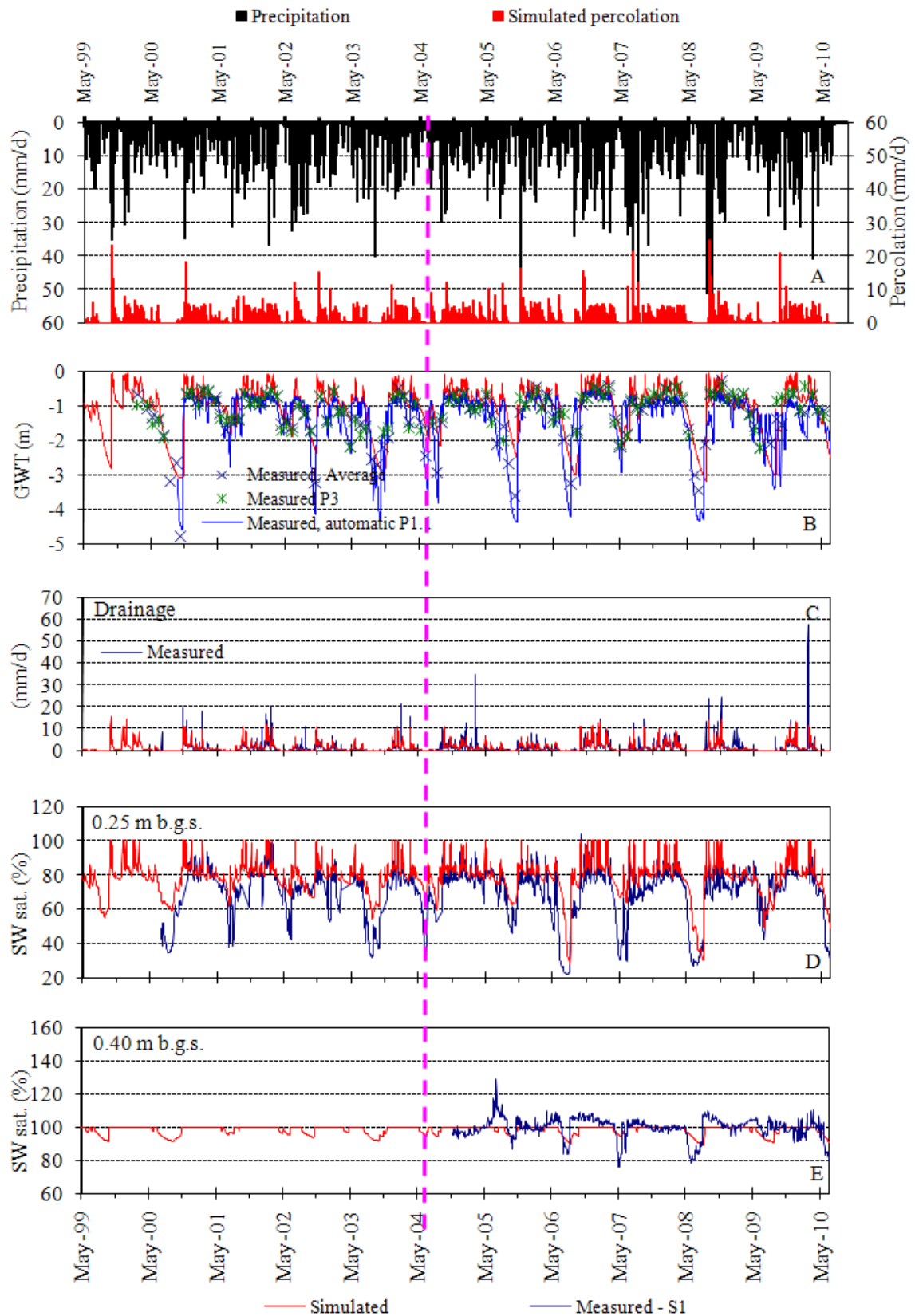
Compared to the setup in Rosenbom *et al.* (2010b), a year of validation was added to the MACRO setup for the Estrup site. The setup was subsequently calibrated for the monitoring period May 1999 June 2004 and validated for the monitoring period July 2004 June 2010. For this purpose, the following time 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 unreliable soil water 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 with water ponding above the TDR probes installed at S2, as mentioned in Kjær *et al.* (2003). Finally, TDR-measurements at 25 cm b.g.s. in February 2010 were discarded given freezing soils (soil temperatures at or below zero degrees Celsius). The soil water content is measured with TDR based on Topp calibration (Topp *et al.*, 1980), which will underestimate the total soil water content at the soil water freezing point as the permittivity of frozen water is much less than that of liquid water (Flerchinger *et al.*, 2006).

Because of the erratic TDR data, calibration data are limited at this site. Data acquisition, model setup as well as results related to simulated bromide transport are described in Barlebo *et al.* (2007).

## 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. As in the previous hydrological year, a drop in the measured groundwater table was seen after short periods of low precipitation (Figure 26B). Also here the simulated groundwater table 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 subsoil TDR data are limited, a more detailed study of soil water dynamics in these layers is difficult. However, the overall soil water saturation at 25 and 40 cm b.g.s. was captured (Figure 26D and 26E). Nothing special is noted for the groundwater table in the latest monitoring period (July 2009-June 2010). As in previous years (Rosenbom *et al.*, 2010b), 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 (Figure 23). The broken vertical line indicates the beginning of the validation period (July 2004-June 2010).

**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 <sup>2)</sup>	Precipitation	Actual evapotranspiration	Measured drainage	Simulated drainage	Groundwater recharge <sup>3)</sup>
1.7.99–30.6.00 <sup>1)</sup>	968	1173	466	–	553	154 <sup>4)</sup>
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
1.7.07–30.6.08	968	1045	478	521	556	46
1.7.08–30.6.09	968	1065	480	523	362	62
1.7.09–30.6.10	968	1190	531	499	522	160

<sup>1)</sup> Monitoring started in April 2000.

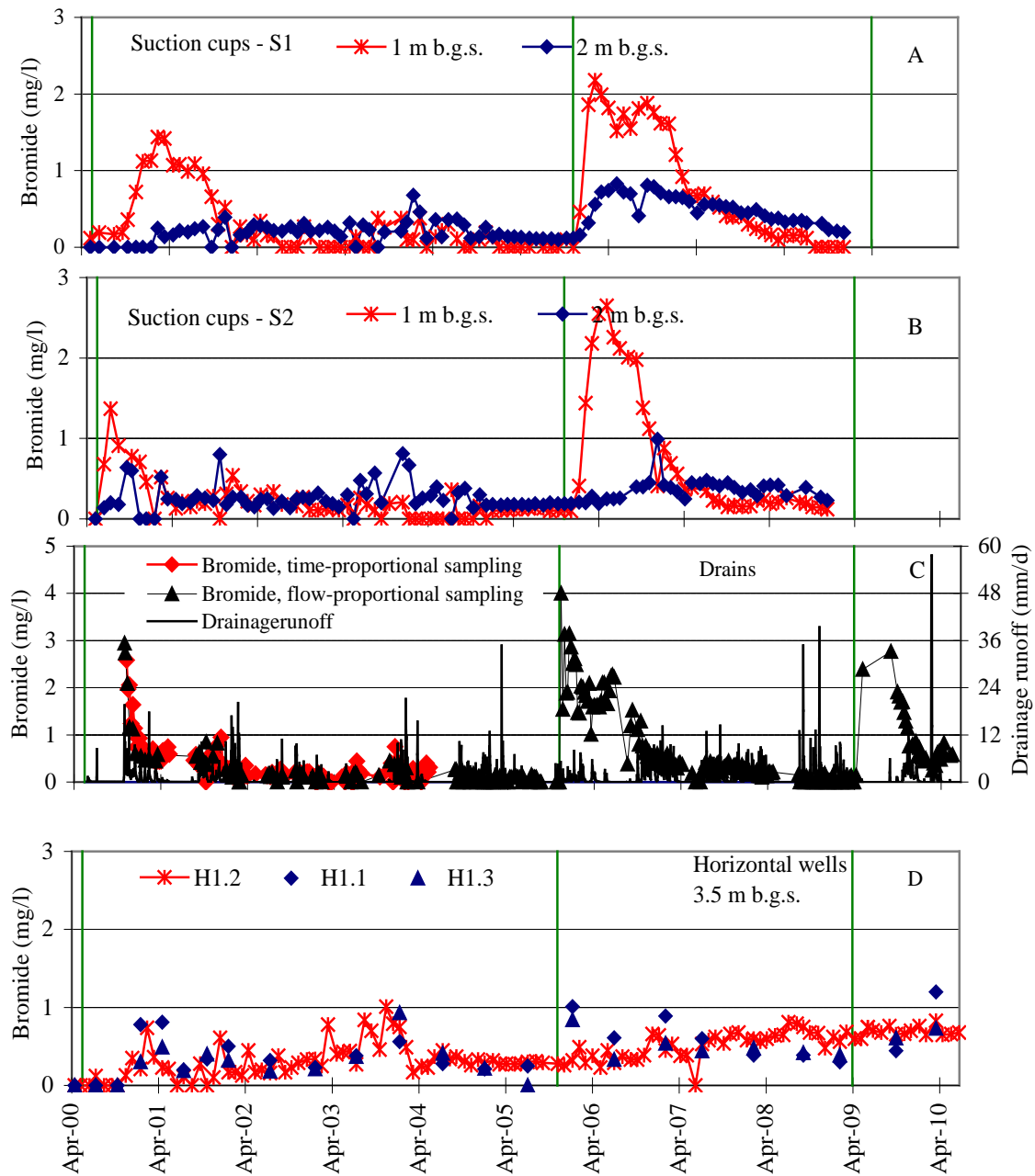
<sup>2)</sup> Normal values based on time series for 1961–1990 corrected to the soil surface.

<sup>3)</sup> Groundwater recharge is calculated as precipitation minus actual evapotranspiration minus measured drainage.

<sup>4)</sup> 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. The initiation and magnitude of the spring 2010 drainage period was, however, not well captured. The period preceding this drainage period can be characterised by frozen soil and precipitation in the form of snow – a situation which MACRO has difficulties in describing. Drainage runoff over the whole monitoring period was high compared to that of the other two till sites investigated in the PLAP. This was due to a significantly lower permeability of the C-horizon than of the overlying A and B horizons (see Kjær *et al.* (2005c) for details). Due to the extreme water flow generated during the snowmelt on 28 February 2010, adequate measurement of the drainage flow as well as water sampling was not possible at the Estrup site. A similar situation occurred at the Silstrup site and further information about the technical problems is given in section 4.2.1.

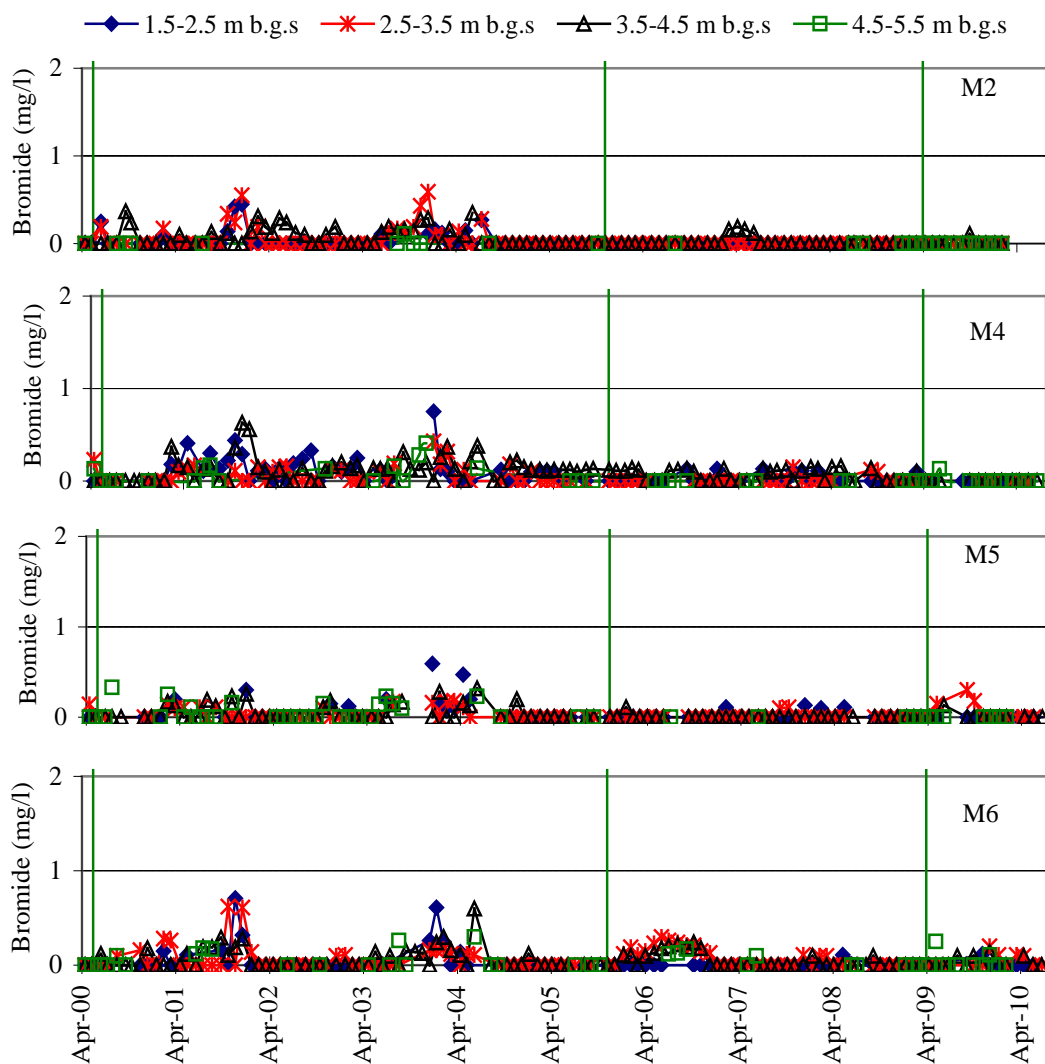
The resulting water balance for Estrup for the entire monitoring period is shown in Table 10. Compared with the previous ten years, the latest hydraulic year July 2009–June 2010 was characterised by having the third-highest precipitation, the highest simulated actual evapotranspiration and medium measured drainage. Even though the model did not capture the snowmelt, there were no large differences between the measured and simulated drainage. Precipitation in this year was characterised by November–December being very wet and January–February and May–June being very dry (Appendix 4). Due to this precipitation pattern, the simulated percolation pattern of the year July 2009–June 2010 left the summer without percolation, the autumn with high percolation, and the winter with a decreasing percolation with scattered periods of both percolation and drainage runoff (Figure 26A, 26B, and 26C).



**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). In September 2008, bromide measurements in the suction cups were suspended (Appendix 2). The green vertical lines indicate the dates of bromide applications.

### 5.2.2 Bromide leaching

Bromide has now been applied three times 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) and Barlebo *et al.* (2007). In March 2009, bromide measurements in the suction cups and monitoring wells M3 and M7 were suspended.



**Figure 28.** Bromide concentration at **Estrup**. The data derive from the vertical monitoring wells (M2–M6). Screen depth is indicated in m b.g.s. In September 2008, monitoring wells M3 and M7 were suspended (Appendix 2). The green vertical lines indicate the dates of bromide applications.

### 5.2.3 Pesticide leaching

Monitoring at Estrup began in May 2000. Pesticides and degradation products monitored so far can be seen from Table 11. Pesticide application during the two most recent growing seasons (2008/2009 and 2009/2010) 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 than April 2010 are not evaluated in this report and hence not included in Table 11.

**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.  $C_{\text{mean}}$  refers to average leachate concentration in the drainage water within the first drainage season after application (See Appendix 2 for calculation methods).

Crop and analysed pesticides	Application Date	End of monitoring	Prec. (mm)	Perc. (mm)	1 <sup>st</sup> month Perc. (mm)	$C_{\text{mean}}$ ( $\mu\text{g/l}$ )
<b>Spring barley 2000</b>						
Metsulfuron-methyl (Ally)	May 00	Apr 03	2990	1456	29	<0.01
- <i>triazinamin</i>						<0.02
Flamprop-M-isopropyl (Barnon Plus 3)	May 00	Apr 03	2914	1434	2	0.02
- <i>flamprop (free acid)</i>						0.01
Propiconazole (Tilt Top)	Jun 00	Apr 05	4938	2294	0	0.01
Fenpropimorph (Tilt Top)	Jun 00	Jul 02	2211	1048	0	<0.01
- <i>fenpropimorphic acid</i>						<0.02
Dimethoate (Perfekthion 500 S)	Jun 00	Jul 02	2211	1048	0	<0.01
<b>Pea 2001</b>						
Glyphosate (Roundup Bio)	Oct 00	Jul 10 <sup>†</sup>	10484	4977	123	0.54
- <i>AMPA</i>						0.17
Bentazone (Basagran 480)	May 01	Jul 08	7629	3621	9	0.03
- <i>AIBA</i>						<0.01
Pendimethalin (Stomp SC)	May 01	Jul 03	2208	1096	9	<0.01
Pirimicarb (Pirimor G)	Jun 01	Jul 05	4251	1995	10	0.01
- <i>pirimicarb-desmethyl</i>						<0.02
- <i>pirimicarb-desmethyl-formamido</i>						<0.02
<b>Winter wheat 2002</b>						
Ioxynil (Oxitril CM)	Nov 01	Jul 03	1580	860	52	0.04 <sup>1)</sup>
Bromoxynil (Oxitril CM)	Nov 01	Jul 03	1580	860	52	0.01 <sup>1)</sup>
Amidosulfuron (Gratil 75 WG)	Apr 02	Jul 04	2148	928	8	<0.01
MCPA (Metaxon)	May 02	Jul 04	2091	928	0	<0.01
- <i>4-chlor,2-methylphenol</i>						<0.01
Propiconazole (Tilt 250 EC)	May 02	Apr 05	2920	1336	39	0.02
Pirimicarb (Pirimor G)	Jun 02	Jul 05	2982	1403	58	0.01
- <i>pirimicarb-desmethyl</i>						<0.02
- <i>pirimicarb-desmethyl-formamido</i>		Apr 06				<0.02

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

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

<sup>1)</sup> 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 current report focuses on pesticides applied from 2008 and onwards, while leaching risk of pesticides applied before 2008 has been evaluated in previous monitoring reports (see [http://pesticidvarsling.dk/publ\\_result/index.html](http://pesticidvarsling.dk/publ_result/index.html)).

Azoxystrobin has now been applied three times at Estrup: 22 June 2004, 29 June 2006, and 13 June 2008 (Figure 30). The last application before then was in June 1998 (Lindhardt *et al.*, 2001). Following all three applications azoxystrobin and the metabolite CyPM leached to the depth of the drainage system at the onset of drainage due to infiltration of excess rain. Concentrations in drainage water of both parent and metabolite are shown in Figure 30. At all three applications, the surface had desiccation cracks. The maximum measured concentration of azoxystrobin was 1.4  $\mu\text{g/l}$  on 24 August 2006 and 2.1  $\mu\text{g/l}$  of CyPM on 11 September 2008. The picture emerging from Figure 30 is that the leaching of the parent compound to drainage water was always highest within the year of spraying (Figure 30B). The following year concentrations would always be lower, but tended to increase with each new application. Regarding the metabolite CyPM (Figure 30C), concentrations within the year of application were, on average, higher than those of the parent compound.

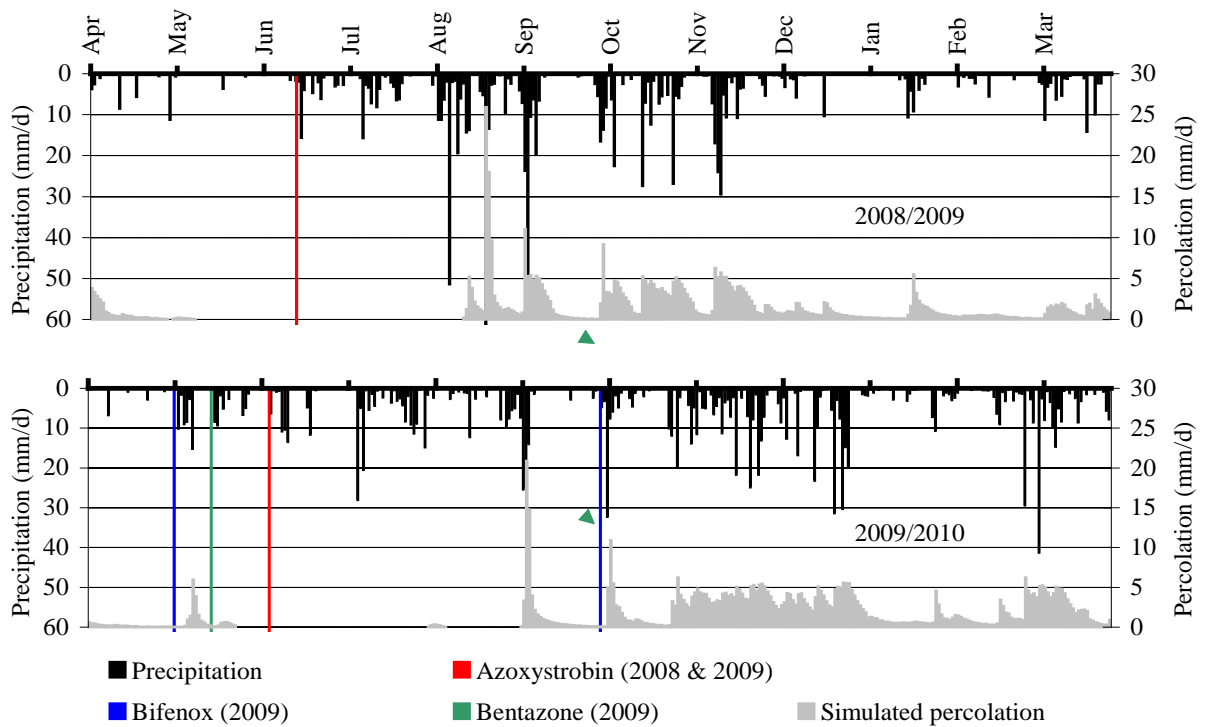
**Table 11 continued.** Pesticides analysed at **Estrup** with the product used shown in parentheses. Degradation products are in italics. Precipitation (prec.) and percolation (perc.) are accumulated from the date of first application until the end of monitoring. 1st month perc. refers to accumulated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

Crop and analysed pesticides	Application Date	End of monitoring	Prec. (mm)	Perc. (mm)	1 <sup>st</sup> month perc. (mm)	$C_{\text{mean}}$ ( $\mu\text{g/l}$ )
<b>Fodder beet 2003</b>						
Glyphosate (Roundup Bio)	Sep 02	Jul 10 <sup>†</sup>	8289	3900	0	0.43
- <i>AMPA</i>						0.19
Ethofumesate (Betanal Optima)	May 03	Apr 06	2901	1371	50	0.11
Metamitron (Goltix WG)	May 03	Apr 06	2901	1371	50	1.1
- <i>metamitron-desamino</i>						0.21
Pirimicarb (Pirimor G)	Jul 03	Jul 05	2071	939	0	<0.01
- <i>pirimicarb-desmethyl</i>		Jul 05				<0.01
- <i>pirimicarb-desmethyl-formamido</i>		Apr 06				0.12
<b>Spring barley 2004</b>						
Fluroxypyr (Starane 180)	May 04	Jul 06	2073	1030	0	<0.02
Azoxystrobin (Amistar)	Jun 04	Jul 08	4452	2209	38	0.12
- <i>CyPM</i>						0.23
<b>Maize 2005</b>						
Terbuthylazine (Inter-Terbuthylazin)	May 05	Apr 09	4247	2042	32	0.48
- <i>desethyl-terbuthylazine</i>		Jul 09	4406	2051	32	0.31
- <i>2-hydroxy-terbuthylazine</i>		Jul 08	3338	1628	32	0.11
- <i>desisopropyl-atrazine</i>		Apr 09	4247	2042	32	0.02
- <i>2-hydroxy-desethyl-terbuthylazine</i>		Jul 08	3338	1628	32	0.24
Bentazone (Laddok TE)	Jun 05	Jul 08	3338	1628	10	0.18
- <i>ALBA</i>						<0.01
Glyphosate (Roundup Bio)	Nov 05	Jul 10 <sup>†</sup>	5191	2460	68	4.04 <sup>1)</sup>
- <i>AMPA</i>						0.42 <sup>1)</sup>
<b>Spring barley 2006</b>						
Florasulam (Primus)	Jun 06	Jul 08	2442	1163	0	<0.01
- <i>florasulam-desmethyl</i>						<0.03
Azoxystrobin (Amistar)	Jun 06	Jul 08	2414	1170	0	0.03
- <i>CyPM</i>						0.13
<b>Winter wheat 2007</b>						
Mesosulfuron-methyl (Atlantis WG)	Oct 06	Jul 08	2059	1095	63	<0.01 <sup>1)</sup>
- <i>mesosulfuron</i>						<0.02
Chlormequat (Cycocel 750)	Apr 07	Jul 08	1337	603	0	<0.01
Epoxiconazole (Opus)	May 07	Jul 08	1199	600	45	0.01
Glyphosate (Roundup Bio)	Sep 07	Jul 10 <sup>†</sup>	3006	1393	64	0.14 <sup>1)</sup>
- <i>AMPA</i>						0.10 <sup>1)</sup>
<b>Winter wheat 2008</b>						
Picolinafen (Pico 750 WG)	Oct 07	Mar 10	2706	1301	52	0.03 <sup>1)</sup>
- <i>CLI53815</i>						0.24 <sup>1)</sup>
Tebuconazole (Folicur EC 250)	Nov 07	Mar 10	2658	1265	77	0.43 <sup>1)</sup>
<b>Spring barley 2009</b>						
Bifenox (Fox 480 SC)	May 09	Jul 10 <sup>†</sup>	1337	520	17	0.002
- <i>bifenox acid</i>						0.153
- <i>nitrofen</i>						<0.01
Bentazone (Basagran M75)	May 09	Jul 10 <sup>†</sup>	1290	504	0	0.05
Azoxystrobin (Amistar)	Jun 09	Jul 10 <sup>†</sup>	1250	505	0	0.04
- <i>CyPM</i>						0.38

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

<sup>†</sup> Monitoring will continue during the following year. The values for prec. and perc. are accumulated up to July 2009.

<sup>1)</sup> Drainage runoff commenced prior to the application of pesticide and the weighted concentrations refer to the period from the date of application until 1 July the following year.

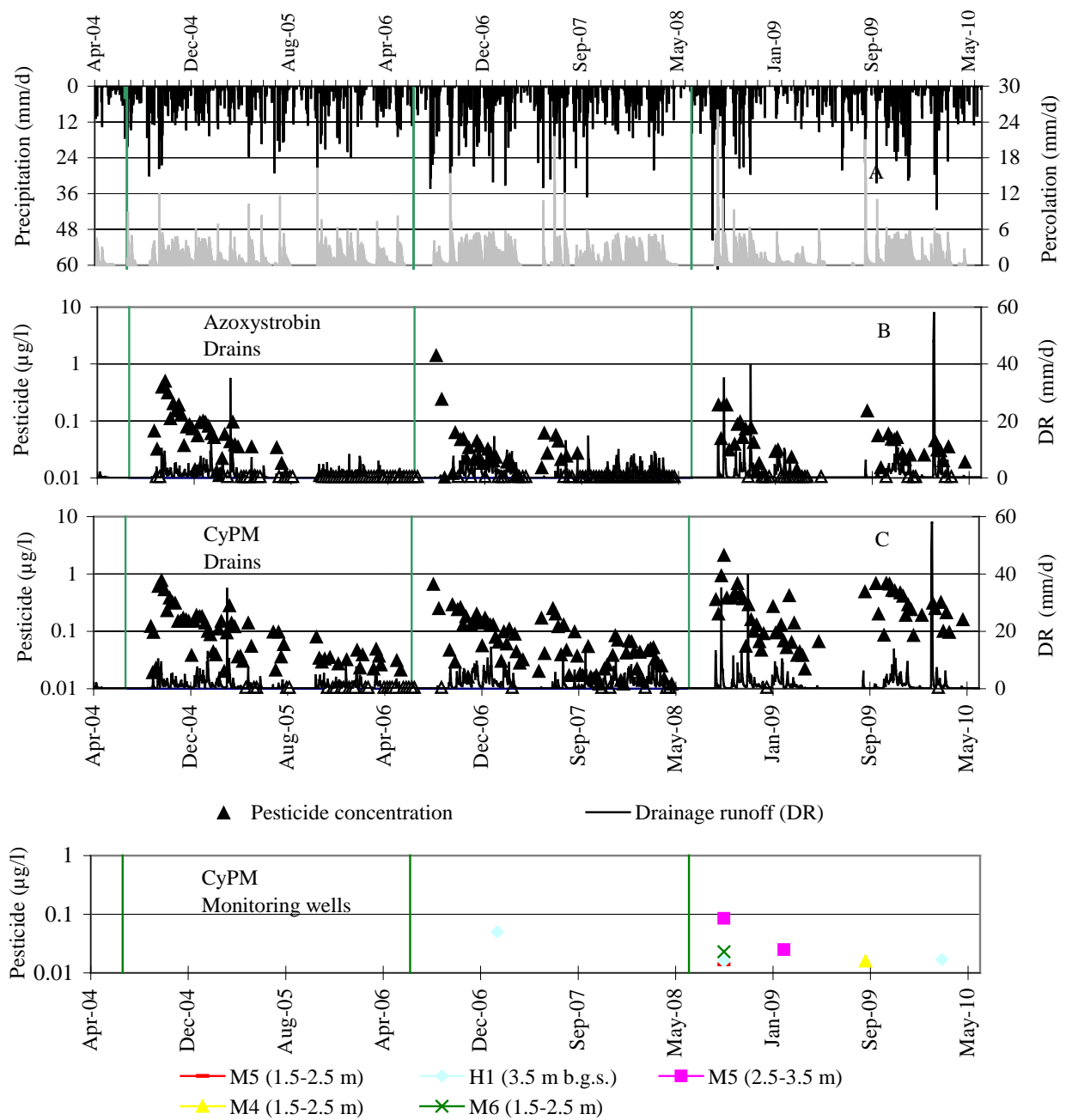


**Figure 29.** Application of pesticides included in the monitoring programme and precipitation (primary axis) together with simulated percolation 0.6 m b.g.s. (secondary axis) at **Estrup** in 2008/2009 (upper) and 2009/2010 (lower).

It is notable that concentrations of CyPM in the second year after spraying tended to increase even more with each new application of azoxystrobin. When looking at the groundwater there has so far been just one detection of azoxystrobin (0.011  $\mu\text{g/l}$  on 24 March 2010) in a horizontal well (data not shown). CyPM was found in the groundwater, in particular during the two last years of monitoring. There have been five detections from vertical wells, ranging between 0.014 and 0.085  $\mu\text{g/l}$  (Figure 30D and Table A5.4).

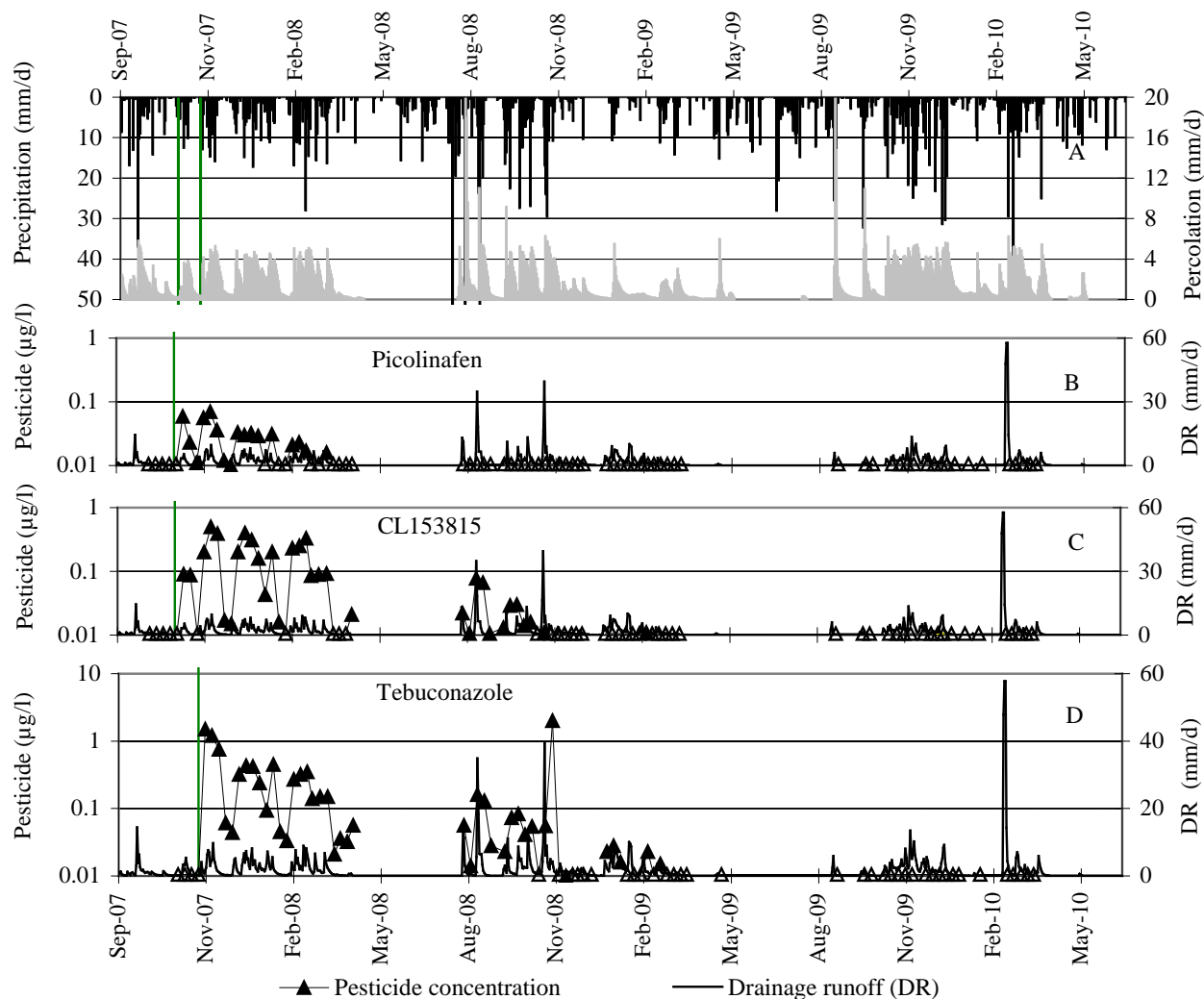
Picolinafen was applied on 30 October 2007. Concentrations of picolinafen never exceeded 0.1  $\mu\text{g/l}$  in drainage water (Figure 31B). However, its degradation product CL153815 did so in several instances (Figure 31C), reaching a maximum of 0.5  $\mu\text{g/l}$  on 6 December 2007, and was 0.016  $\mu\text{g/l}$  at its last detection on 3 April 2008. By comparing Figure 31B and Figure 31C, CL153815 can clearly be seen to be more persistent than picolinafen. Nearly a year after application of picolinafen (26 February 2009), CL153815 could be found in the drainage water at a concentration of 0.078  $\mu\text{g/l}$ .





**Figure 30.** Precipitation and simulated percolation 0.6 m b.g.s. (A) together with concentration of azoxystrobin (B) and CyPM (C) in the drainage runoff (DR on the secondary axis) at **Estrup**. Detections of CyPM in groundwater monitoring screen are indicated in D. Azoxystrobin was only detected once in groundwater monitoring screens (see text). The green vertical lines indicate the dates of applications. Open symbols in B and C indicate values below the detection limit of 0.01 µg/l.

It was last detected on 26 February 2009 at 0.011 µg/l. Neither picolinafen nor CL153815 were detected in groundwater (Table 5.4 in Appendix 5).



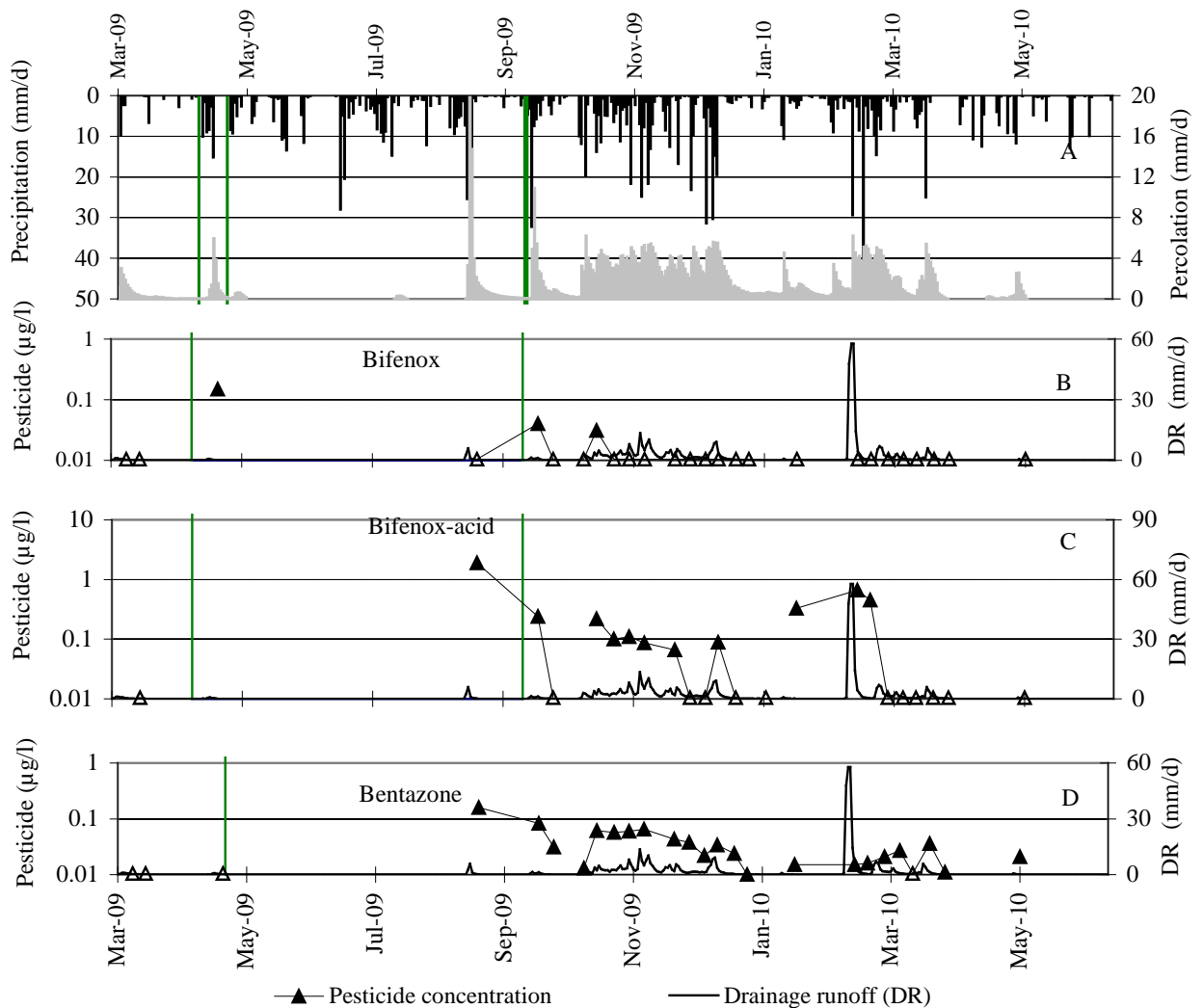
**Figure 31.** Precipitation and simulated percolation (A) together with concentration of picolinafen (B), CL153815 (C), and tebuconazole (E) in the drainage runoff (DR on the secondary axis) at **Estrup** in 2007/2010. The green vertical lines indicate the dates of applications. Open symbols indicate values below the detection limit of 0.01 µg/l. While picolinafen and CL153815 were not detected in any samples from groundwater monitoring, tebuconazole was detected in five samples (see text).

Tebuconazole, applied on 22 October 2007, was seen in drainage water on several occasions and reached a maximum concentration of 2.0 µg/l on 20 November 2008, over a year after application. Out of 80 drainage water samples analysed, 17 contained concentrations of tebuconazole above 0.1 µg/l (Figure 31D). Tebuconazole was detected in five groundwater samples taken more than two years after the application. Maximum concentrations found were 0.11 and 0.12 µg/l in samples taken from two different screens of a monitoring well on 24 March 2011 (Table A5.4 in Appendix 5).

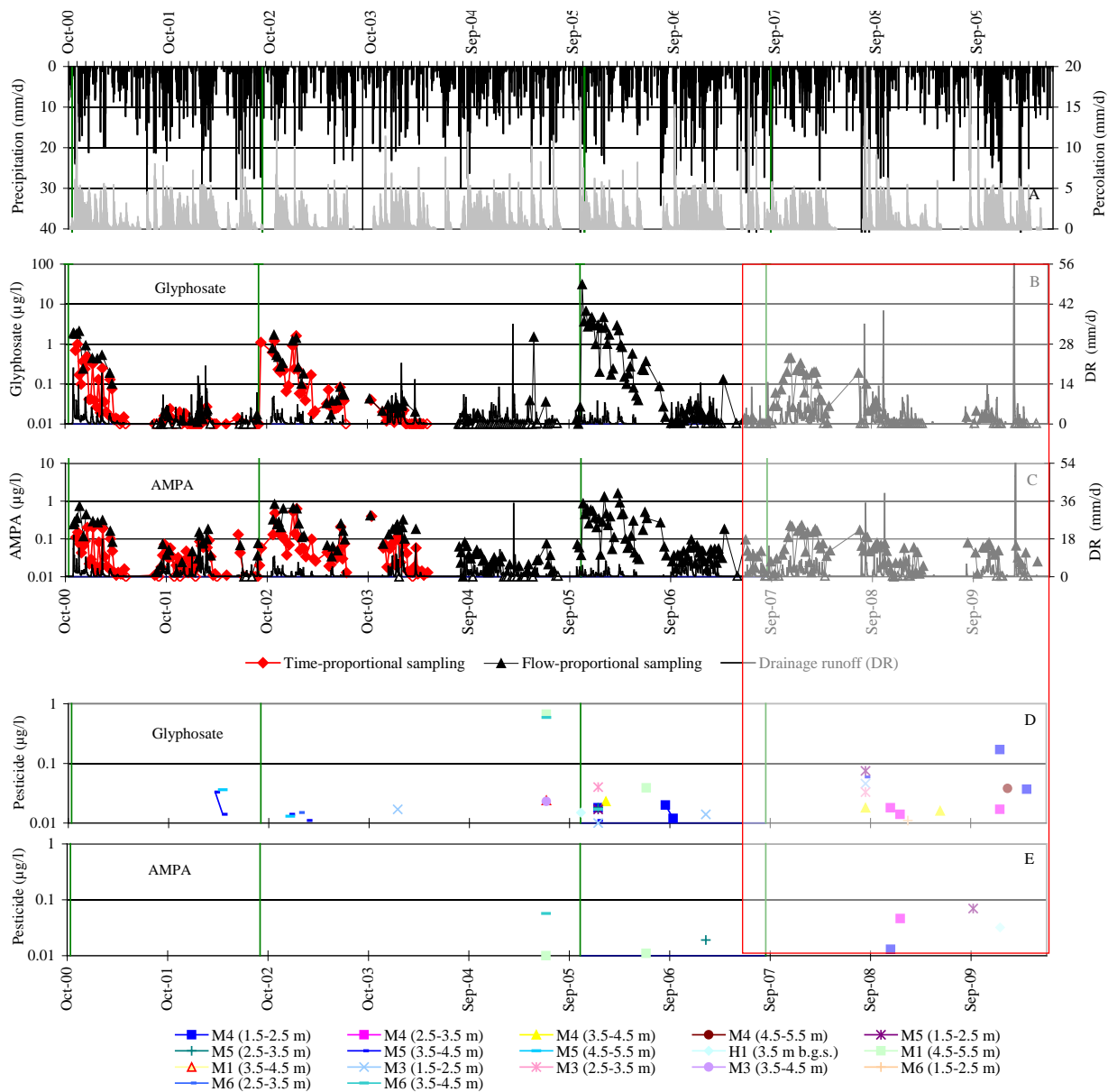
The herbicide bifenox was used on 1 May and on 30 September 2009. Less than two weeks later 0.15 µg/l of bifenox was detected in the drainage water (Figure 32B). Following the second application, bifenox was found twice, this time in concentrations less than 0.1 µg/l. The metabolite bifenox acid was found in connection with a small drain flow event on 9 September 2009 at a concentration of 1.9 µg/l (Figure 32C), whereas bifenox was below the detection limit of 0.01 µg/l. Following the application in September there were only two detections of bifenox, both less than 0.1 µg/l (Figure

32B), whereas eight out of ten bifenox acid detections were above 0.1 µg/l (Figure 32C). Bifenox acid leached from the root zone to the drainage system in an average concentration of 0.153 µg/l in the drainage water, whereas the figure for bifenox was 0.002 µg/l (Table 11). Neither bifenox nor bifenox acid was found in the groundwater monitoring screens.

The highest concentration in drainage water of bentazone following the 14 May 2009 application was 0.16 µg/l in connection with a small drain flow event in September 2009 (Figure 32D). None of the subsequent concentrations were above 0.1 µg/l and the average yearly concentrations amounted to 0.05 µg/l (Table 11). Bentazone was found four times in groundwater monitoring screens; concentrations did, however, not exceed 0.1 µg/l (Table A5.4, Appendix 5).



**Figure 32.** Precipitation and simulated percolation (A) together with concentration of bifenox (B), bifenox acid (C), and bentazone (E) in the drainage runoff (DR on the secondary axis) at Estrup in 2004/2010. The green vertical lines indicates the dates of applications. Open symbols indicate values below the detection limit of 0.01 µg/l. While bifenox and bifenox acid were not detected in any samples from groundwater monitoring, bentazone was detected in four samples (see text).



**Figure 33.** Precipitation and simulated percolation 0.6 m b.g.s. (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 nine-year period including four applications of glyphosate as indicated by the green vertical lines. Open symbols indicate values below the detection limit of 0.01 µg/l. Detection of glyphosate and AMPA in groundwater monitoring wells is shown in D and E. In the period June 2007 until July 2010, marked with the red outlined box, analytical problems caused the concentration of glyphosate to be underestimated (see text for details).

The herbicide glyphosate has now been applied at Estrup in 2000, 2002, 2005, and 2007 (Figure 33). Following all applications, both glyphosate and AMPA could be found in the drainage water. Out of 400 drainage water samples analysed for glyphosate and AMPA in the period 31 October 2000-19 May 2010, the concentrations of glyphosate and AMPA exceeded 0.1 µg/l in 89 and 98 samples, respectively (Figure 33B and 33C). In the same period, 708 groundwater samples were analysed for glyphosate and 712 for AMPA. During that period AMPA never exceeded 0.1 µg/l (Figure 33E and Table A5.4 in Appendix 5), whereas glyphosate did so in three samples, of which two were taken on 7 July 2005 from two different wells, concentrations being 0.67 and 0.59 µg/l, and

one on 13 January 2010 from a third well with a concentration of 0.17 µg/l (Figure 33D and Table A5.4 in Appendix 5). In Figure 33, the period June 2007 to July 2010 has been put inside a red box to indicate that within this period, analytical problems caused glyphosate to be underestimated. Results from the external quality assurance reveal that in the period June 2007 to July 2010 the concentration of glyphosate may have been underestimated by a factor of up to ~2 as compared to previous periods (See section 7.2.2.).

When comparing the three-year periods following the application of glyphosate in September 2002 and September 2007, a pattern of longevity/persistence seems to emerge, in particular for the metabolite AMPA. Three years following spraying with glyphosate there will still be a leaching of AMPA, whereas that of glyphosate is much less (Figure 33B and Figure 33C). This long-term leaching of AMPA may indicate that AMPA is retained within the soil and gradually released over a very long time, as described in Kjær *et al.* (2005a), or that glyphosate is retained within the soil and then gradually degraded into AMPA. With an increased detection of glyphosate in the groundwater samples at Estrup following high precipitation events in September 2005 (nearly three years after latest application), September 2008 and January 2010 (one and two and a half years after the latest application, respectively), evidence of the latter pattern seems also to be recognizable.

It is remarkable that detections of particularly glyphosate in groundwater monitoring wells seem to increase over the years (Figure 33D). Within the first four years, detections of glyphosate were scarce, and AMPA is not found at all (Figure 33E). Following these four years there is a gradual increase, particularly in detections and concentrations of glyphosate. A similar tendency was observed for AMPA, although detections are less frequent and the concentrations comparatively lower. In this respect it should be noted that there had been no application of glyphosate for at least seven years prior to the 2000 application (Lindhardt *et al.*, 2001).

Pesticide leaching at Estrup is mostly confined to the depth of the drainage system. Apart from AMPA, CyPM, bentazone, desethyl-terbuthylazine, deisopropylatrazine, and glyphosate having been detected in 8, 9, 16, 7, 27, and 39 groundwater samples, respectively, 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 is 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). An indication thereof are the long periods with groundwater table beyond drainage depth in which an increasing lateral transport to the drainage system and decreased leaching to the deeper groundwater will occur.



## 6 Pesticide leaching at Faardrup

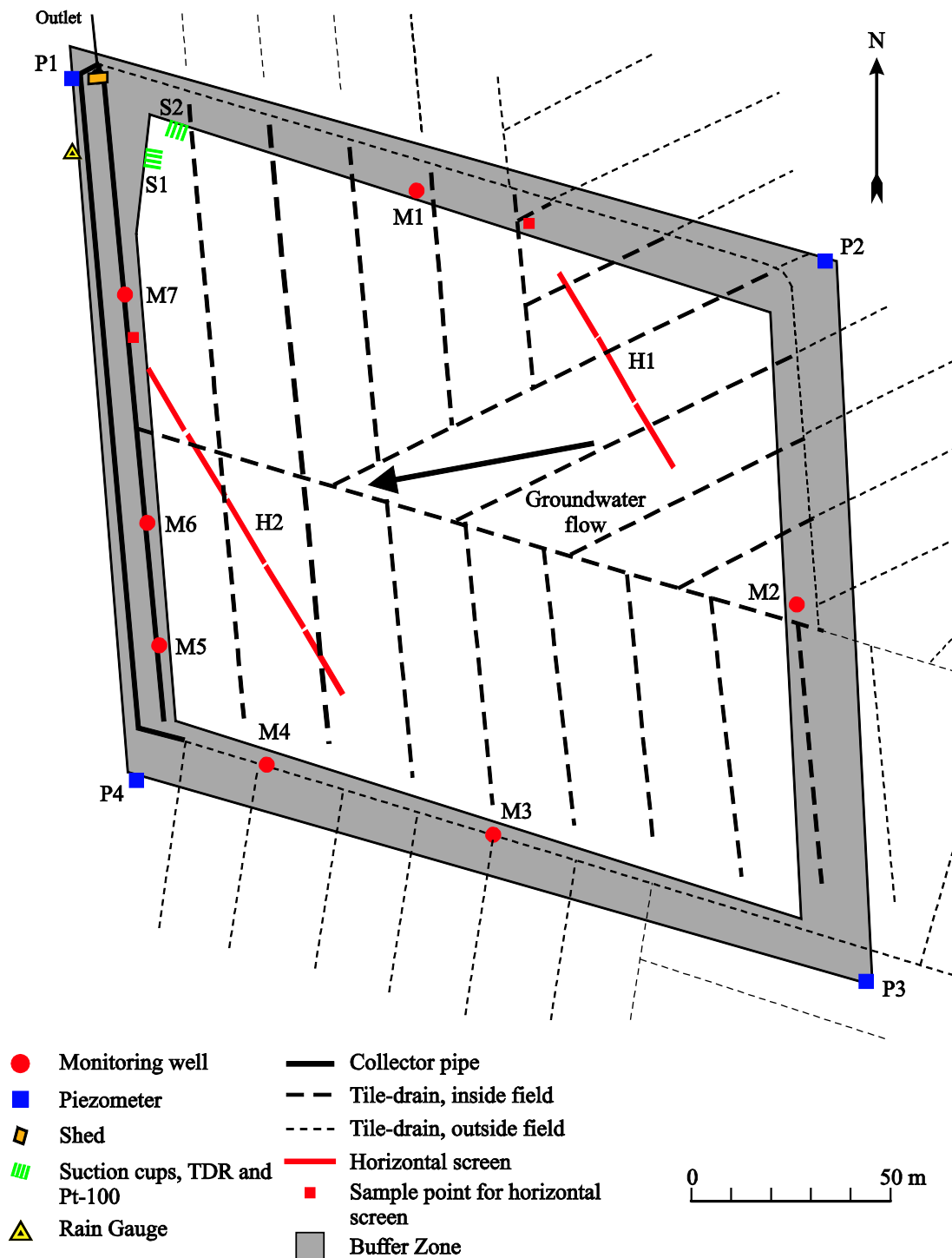
### 6.1 Materials and methods

#### 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 34). 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 characterised 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 34). 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 facilitate parts 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 35 and Figure 38), 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 34.** 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). Pesticide monitoring is conducted weekly from the drainage system (during period of continuous drainage runoff) and monthly and half-yearly from selected groundwater monitoring wells as described in Table A2.1 in Appendix 2.



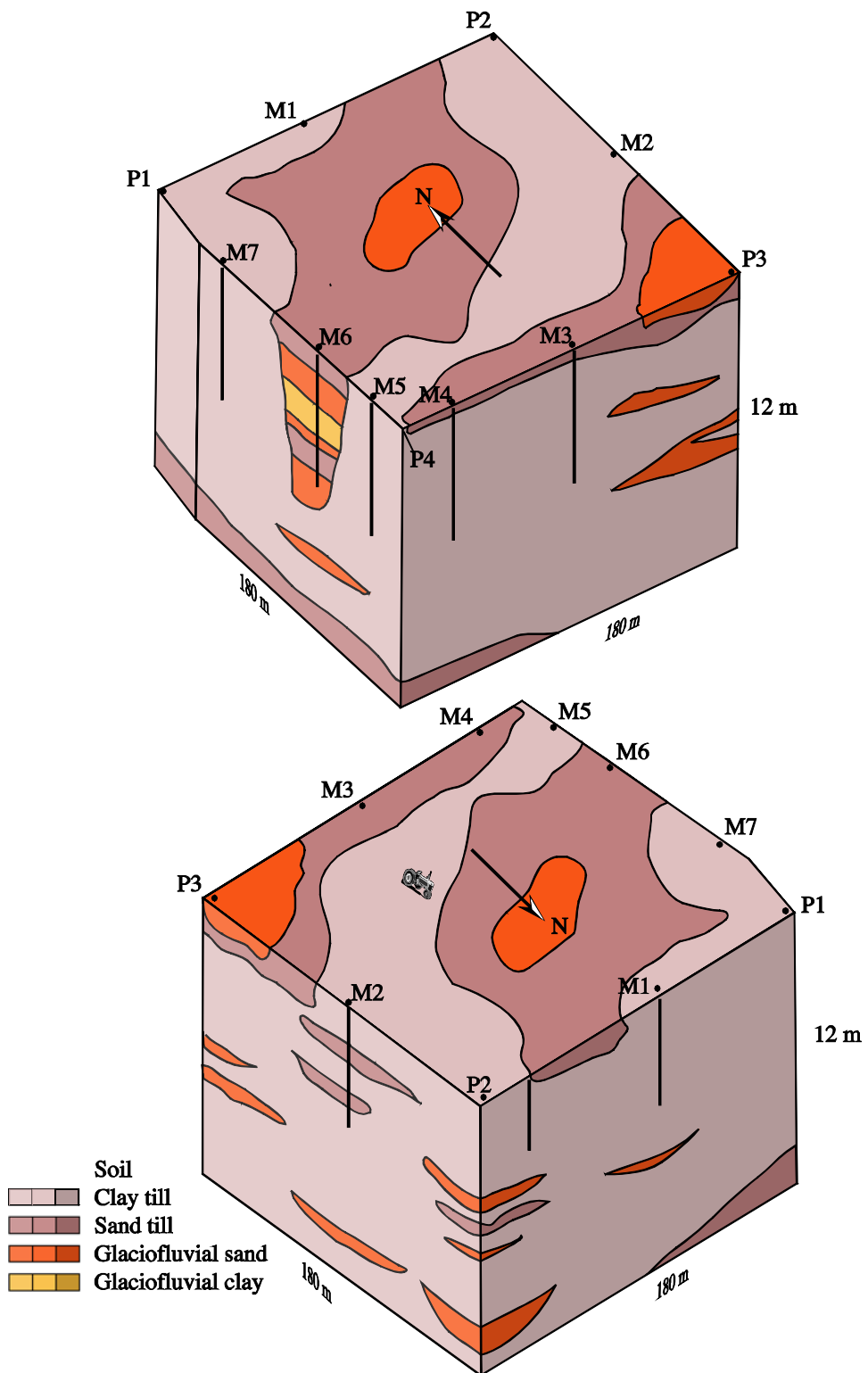


Figure 35. Geological description of Faardrup (Lindhardt *et al.*, 2001).

### 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 previous monitoring reports available on [http://pesticidvarsling.dk/publ\\_result/index.html](http://pesticidvarsling.dk/publ_result/index.html).

On 26 August 2008, 30 kg/ha of KBr was applied as a tracer. Ploughing of the field took place 1 December 2008. On 5 April 2009 a crop of sugar beets (cv. Palace) was sown, emerging on 16 April. The first weed spraying was done on 24 April, when the first leaf was visible (pinhead-size) and the cotyledons horizontally unfurled, using phenmedipham and met amitron. On 30 April, when the first pair of beet leaves were visible, but not yet unfurled (pea-size), weeds were sprayed with triflusaluron, met amitron, ethofumesate and phenmedipham. The latter was not included in the monitoring, however. On 11 May, where the plants had four leaves unfurled, weeds were again sprayed with triflusaluron, met amitron, ethofumesate and phenmedipham, and again the latter was not included in the monitoring. Due to problems with couch grass (*Agropyrum repens*, L.), cycloxydim was used twice: on 14 May where five leaves had unfurled, and on 17 June when the beets covered from 10-40% of the area. Cycloxydim was not included in the monitoring programme. The sugar beets were harvested on 6 October, yielding 348.23 hkg/ha of beets and 189.3 hkg/ha of top (fresh weight). The top was ploughed in on 1 November 2009.

On 22 April 2010 the field was sown with a mixture of spring barley varieties. The barley was undersown with red fescue (cv. Maximum). When four to six tillers were detectable on the barley it was sprayed with the herbicide bentazone. The fungicide azoxystrobin was applied on 2 July, but not included in the monitoring. The barley was harvested on 21 August yielding 58.5 hkg/ha of grain (85% DM) and approximately 27 hkg/ha of straw (100% DM).

### 6.1.3 Model setup 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 2010 and to establish an annual water balance.

Compared to the setup in Rosenbom *et al.* (2010b), a year of validation was added to the MACRO setup for the Faardrup site. The setup was accordingly calibrated for the monitoring period May 1999-June 2004 and validated for the monitoring period July 2004-June 2010. 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 34) and measured drainage flow. Data acquisition and model setup are described in Barlebo *et al.* (2007).

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

	Normal precipitation <sup>1)</sup>	Precipitation <sup>2)</sup>	Actual evapotranspiration	Measured drainage	Simulated drainage	Groundwater recharge <sup>3)</sup>
1.7.99–30.6.00	626	715	572	192	152	-50
1.7.00–30.6.01	626	639	383	50	35	206
1.7.01–30.6.02	626	810	514	197	201	99
1.7.02–30.6.03	626	636	480	49	72	107
1.7.03–30.6.04	626	685	505	36	19	144
1.7.04–30.6.05	626	671	469	131	55	72
1.7.05–30.6.06	626	557	372	28	16	158
1.7.06–30.6.07	626	796	518	202	212	77
1.7.07–30.6.08	626	645	522	111	65	12
1.7.08–30.6.09	626	713	463	46	21	204
1.7.09–30.6.10	626	624	445	54	48	125

<sup>1)</sup> Normal values based on time series for 1961–1990.

<sup>2)</sup> 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).

<sup>3)</sup> Groundwater recharge is calculated as precipitation minus actual evapotranspiration minus measured drainage.

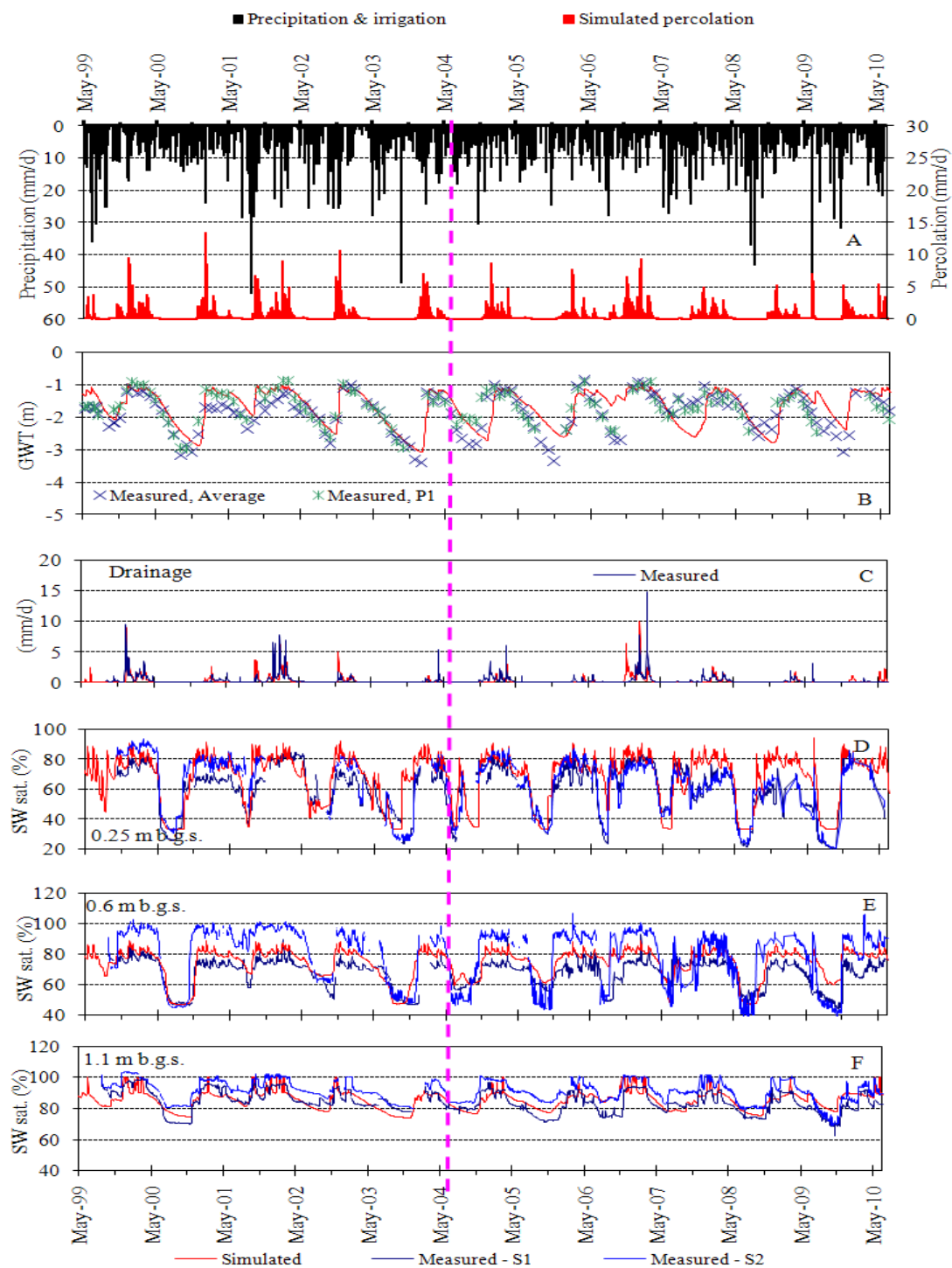
Due to electronic problems, precipitation measured at Flakkebjerg located 3 km east of Faarstrup was used for the monitoring periods: July 1999-June 2002, July 2003-June 2004, January and February of both 2005 and 2006, and July 2006-June 2007. Precipitation measured locally at Faarstrup was used for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

## 6.2 Results and discussion

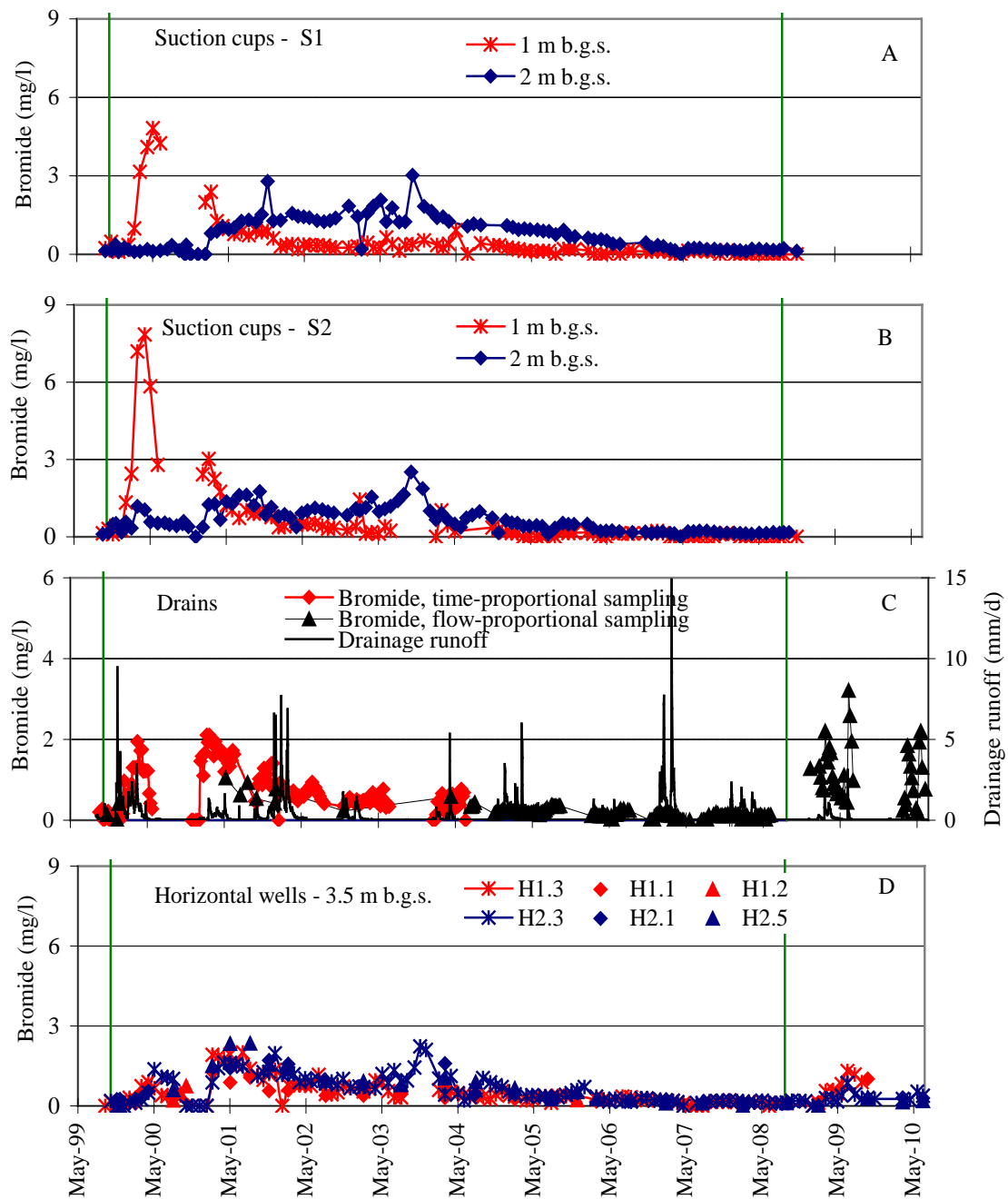
### 6.2.1 Soil water dynamics and water balances

The level and dynamics of the soil water saturation in all three horizons in the hydraulic year July 2009-June 2010 were generally well described by the model (Figure 36D, 36E, and 36F). However, for the summer period 2010 the model underestimated the drop in the measured groundwater table (Figure 36B).

The resulting water balance for Faarstrup for the 11 monitoring periods is shown in Table 12. Compared with the previous ten years, the latest hydraulic year July 2009-June 2010 was characterised by having the second-lowest precipitation, the third-lowest simulated actual evapotranspiration, and the sixth-lowest measured and fifth-lowest simulated drainage. Precipitation in this year was characterised by August, January, and February being very dry and November and May being very wet (Appendix 4). Due to this precipitation pattern, the duration of the simulated percolation period of the year July 2009-June 2010 was represented by continuous percolation throughout the period November - June (Figure 36A). Compared to the other years, the climate this year gave rise to a short period, where the groundwater table was a bit higher than the drainage level, causing a low short-term contribution to the drains (Figure 36B and 36C).



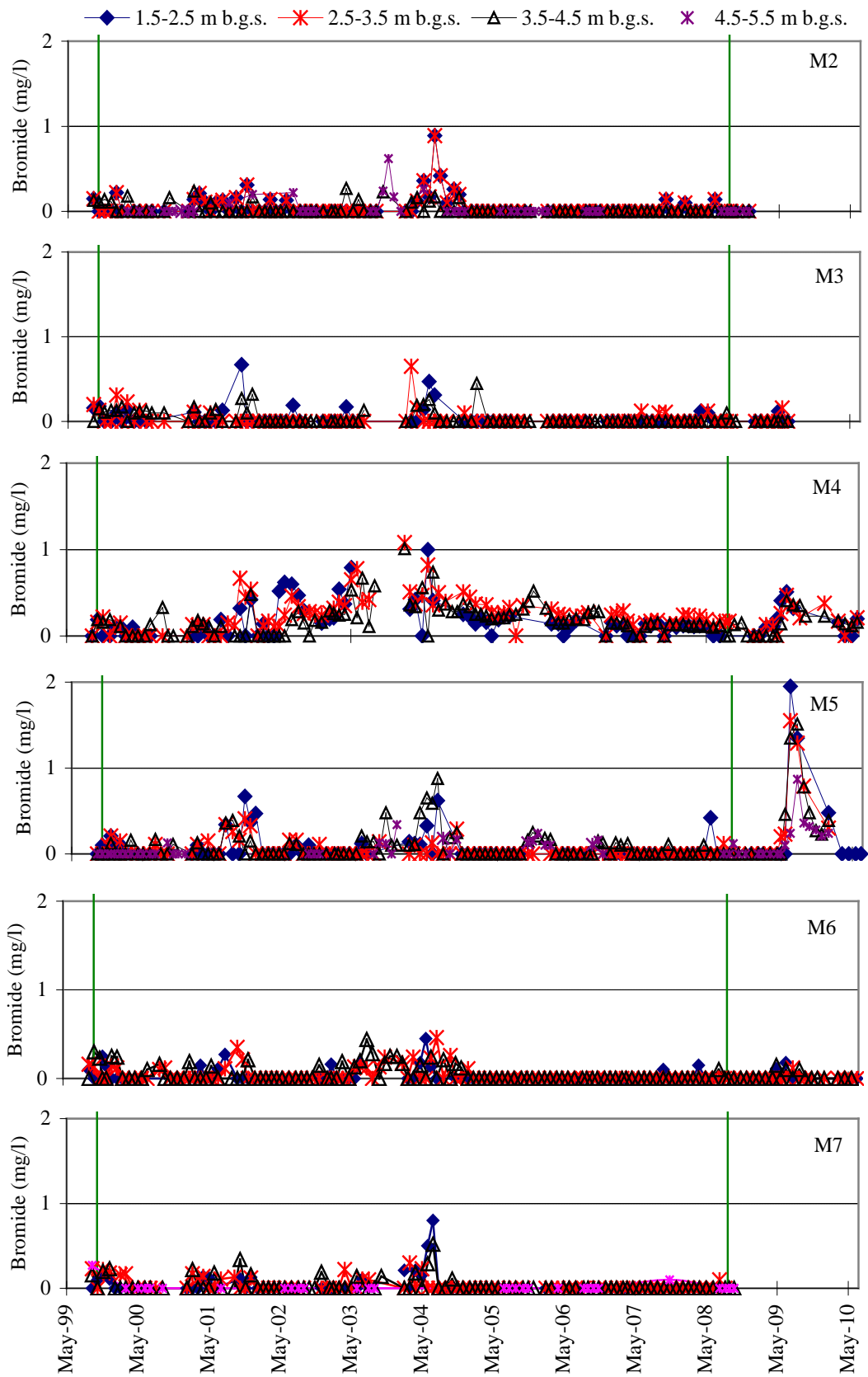
**Figure 36.** Soil water dynamics at **Faardrup**: Measured precipitation and simulated percolation 1 m b.g.s. (A), simulated and measured groundwater level GWT (B), simulated and measured drainage flow (C) and simulated and measured soil water saturation (SW sat.) at three different soil depths (D, 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 32). The broken vertical line indicates the beginning of the validation period (July 2004-June 2010).



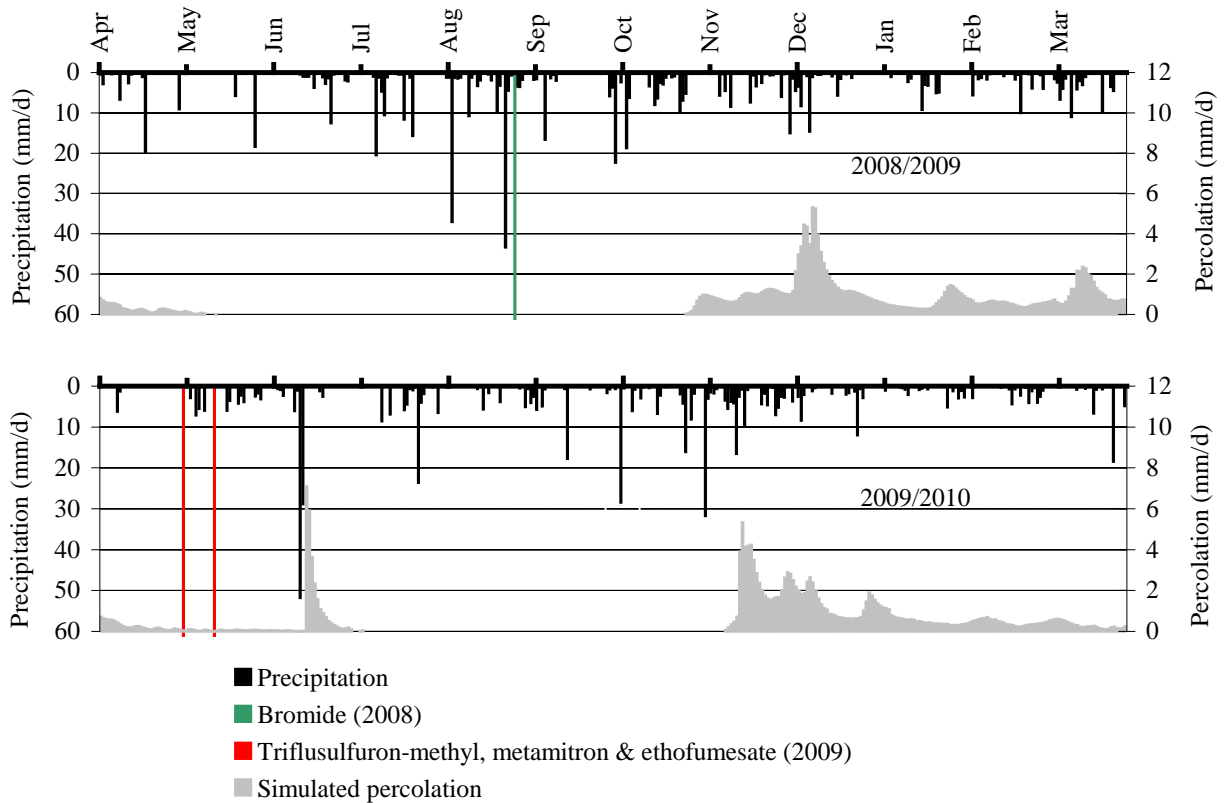
**Figure 37.** Bromide concentrations at **Faardrup**. A and B refer to suction cups located at S1 and S2. The bromide concentration is also shown for drainage runoff (C) and the horizontal monitoring wells (D). In September 2008, bromide measurements in the suction cups were suspended. The green vertical lines indicate the dates of bromide applications.

### 6.2.2 Bromide leaching

The bromide concentration shown in Figure 37 and Figure 38 relates primarily to the bromide applied in May 2000, as described further in Kjær *et al.* (2003), and further evaluated in Barlebo *et al.* (2007). In August 2008, 30 kg/ha potassium bromide was applied for the second time. In September 2008, bromide measurements in the suction cups and monitoring wells M2 and M7 were suspended. A drastic increase in bromide concentration in M4 and M5 was detected in May-June 2009 (Figure 38).



**Figure 38.** Bromide concentrations at **Faardrup**. The data derive from the vertical monitoring wells (M2–M7). Screen depth is indicated in m b.g.s. In September 2008, monitoring wells M2 and M7 were suspended (Appendix 2). The green vertical line indicates the dates of bromide applications.



**Figure 39.** Application of pesticides included in the monitoring programme and precipitation (primary axis) together with simulated percolation (secondary axis) at **Faardrup** in 2008/09 (upper) 2009/2010 (lower).

### 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. The application time of the pesticides included in the monitoring during the two most recent growing seasons is shown together with precipitation and simulated precipitation in Figure 39. 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 e.g. tribenuronmethyl (applied 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 compounds that is monitored in the PLAP (Table 13).

**Table 13.** Pesticides analysed at **Faardrup** with the product used shown in parentheses. Degradation products are in italics. Precipitation (prec.) and percolation (perc.) are accumulated from the date of first application (app. date) until the end of monitoring. 1<sup>st</sup> month perc. refers to accumulated percolation within the first month after application. C<sub>mean</sub> refers to average leachate concentration in the drainage water the first drainage season after application (See Appendix 2 for calculation methods).

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

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

<sup>1)</sup> Degradation product of tribenuron-methyl. The parent compound degrades too rapidly to be detected by monitoring.

The current report focuses on the pesticides applied from 2008 and onwards, while the leaching risk of pesticides applied before 2008 has been evaluated in previous monitoring reports (see [http://pesticidvarsling.dk/publ\\_result/index.html](http://pesticidvarsling.dk/publ_result/index.html)).



**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. 1<sup>st</sup> month perc. refers to accumulated percolation within the first month after application. C<sub>mean</sub> 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)	1 <sup>st</sup> month perc. (mm)	C <sub>mean</sub> (µg/l)
<b>Winter rape 2003</b>						
Clomazone (Command CS) - <i>FMC65317 (propanamide-clomazon)</i>	Aug 02	Apr 05	1761	509	4	<0.02 <0.02
<b>Winter wheat 2004</b>						
Prosulfocarb (Boxer EC)	Oct 03	Apr 06	1542	454	0	<0.01
MCPA (Metaxon) - <i>4-chlor,2-methylphenol</i>	Jun 04	Jul 06	1307	331	0	<0.01 <0.01
Azoxystrobin (Amistar) - <i>CyPM</i>	Jun 04	Jul 07	2098	636	0	<0.01 <0.01
<b>Maize 2005</b>						
Terbutylazine (Inter-Terbutylazin) - <i>desethyl-terbutylazine</i>	May 05	Jul 08	2078	666	4	0.67 0.59
- <i>2-hydroxy-terbutylazine</i>	May 05	Jul 08	2078	666		0.04
- <i>desisopropyl-atrazine</i>	May 05	Jul 08	2078	666		0.03
- <i>2-hydroxy-desethyl-terbutylazine</i>	May 05	Jul 07	1428	465	4	0.07
Bentazone (Laddok TE) - <i>AIBA</i>	May 05	Jul 07	1408	464	6	2.82 <0.01
<b>Spring barley 2006</b>						
Fluroxypyr (Starane 180 S)	May 06	Jul 08	1496	524	17	<0.02
Epoxiconazole (Opus)	Jun 06	Jul 08	1441	507	3	<0.01
<b>Winter Rape 2007</b>						
Thiamethoxam (Cruiser RAPS) - <i>CGA 322704</i>	Aug 06	Jul 08	1304	505	27	<0.01 <0.02
Propyzamide (Kerb 500 SC) - <i>RH-24644</i> - <i>RH-24580</i> - <i>RH-24655</i>	Feb 07	Apr 09	1476	375	46	0.138 <sup>1)</sup> <0.01 <sup>1)</sup> <0.01 <sup>1)</sup> <0.01 <sup>1)</sup>
<b>Winter wheat 2008</b>						
Pendimethalin (Stomp)	Oct 07	Dec 09	1462	451	24	<0.01
Tebuconazole (Folicur EC 250)	Nov 07	Dec 09	1405	413	56	<0.01
<b>Sugar beet 2009</b>						
Triflurosulfuron (Safari) - <i>IN-D8526</i> - <i>IN-E7710</i> - <i>IN-M7222</i>	Apr 09	Jul 10 <sup>†</sup>	769	210	2	<0.01 <0.01 <0.01 <0.01
Ethofumesate (Ethosan)	Apr 09	Jul 10 <sup>†</sup>	769	210	2	<0.01
Metamitron (Goliath) - Metamitron-desamino	Apr 09	Jul 10 <sup>†</sup>	769	210	2	<0.01 <0.01

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

<sup>†</sup> Monitoring will continue during the following year. The values for prec. and perc. are accumulated up to July 2009.

<sup>1)</sup> 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.

Tebuconazole and pendimethalin were applied in 2007 and these pesticides have until now been detected in five and two samples (data not shown, see Rosenbom *et al.*, 2010b), respectively. Measured concentrations, however, never exceeded 0.1 µg/l. Triasulfuron-methyl was applied in April 2009, but neither the parent compound nor its degradations products have so far been detected.

Metamitron, ethofumesate and triflurosulfuron were applied April 2009 (Figure 39) and so far neither of the pesticides nor their metabolites have been detected in water samples from Faardrup.



## 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 *externally 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 2009 to June 2010 are presented below, while those for the preceding monitoring periods are given in previous monitoring reports (available on [http://pesticidvarsling.dk/publ\\_result/index.html](http://pesticidvarsling.dk/publ_result/index.html)).

### 7.1 Materials and methods

All 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 0.03–0.13 µg/l. Using these data it was possible to calculate and separate the analytical standard deviation into within-day ( $S_w$ ), between-day ( $S_b$ ) and total standard deviation ( $S_t$ ). Total standard deviation was calculated using the following formula (Wilson 1970, Danish EPA 1997):

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

#### 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. The standard solutions were prepared two days before a sampling day and stored in darkness and cold until use. For the preparation of stock solutions 150 µl (low level) or 350 µl (high level) of the pesticide mixture was pipetted into a preparation glass containing 10 ml of ultrapure water. The glass was closed and shaken thoroughly

and shipped to the staff collecting the samples. The staff finished the preparation of control samples in the field by quantitatively transferring the standard solution to a 3.0 l measuring flask. The standard solution was diluted and adjusted to the mark with groundwater from a groundwater well. In the present report period the final concentrations correspond to 50 and 117 µg/l in the final solution for low and high spike levels, respectively. After a thorough mixing, the control sample was transferred to a sample bottle and transported to the laboratories together with the regular samples. As water sample supply was occasionally limiting at Faardrup, all volumes were reduced by a factor of three for this location, keeping the concentrations in the final control samples identical to the other locations.

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 sample were labelled with coded reference numbers, so that the laboratory was 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	Ampoule Concentration (mg/l)	Ampoule	High-level control (µg/l)	Low-level control (µg/l)
AMPA	1.000	2	0.117	0.050
CyPM	1.000	1	0.117	0.050
Bentazone	1.000	1	0.117	0.050
Bifenox (free acid)	1.000	1	0.117	0.050
CL153815	1.000	1	0.117	0.050
Epoxiconazole	1.000	1	0.117	0.050
Ethofumesate	1.000	1	0.117	0.050
Glyphosate	1.000	2	0.117	0.050
IN70941 (PPU)	1.000	1	0.117	0.050
IN-M7222	1.000	1	0.117	0.050
Metsulfuron-methyl	1.000	1	0.117	0.050
Metamirton	1.000	1	0.117	0.050
Pendimethalin	1.000	1	0.117	0.050
Tebuconazole	1.000	1	0.117	0.050
TFMP	1.000	1	0.117	0.050

## 7.2 Results and discussion

### 7.2.1 Internal QA

Ideally, the analytical procedure provides precise and accurate results. However, in the real world results from analysis 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 these 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 PPU, desethyl-terbuthylazine and desisopropyl-atrazine. When all compounds are considered, a particularly high  $S_b/S_w$  ratio is apparent for desethyl-terbuthylazine and triazinamine. Such relatively high ratios can be caused by very low within-day standard deviations, i.e. within each laboratory day, the variation on the analysis is small compared to the other compounds, whereas the variation between days is comparable to the other compounds analysed. This is the case for desethyl-terbuthylazine. Thus, low values of  $S_w$  rather than critical values of  $S_b$  caused the high ratios, as reflected by a reasonably low  $S_t$ . In contrast, for the compound triazinamine and others it is apparent that it is the between-day ( $S_b$ ) contribution that is causing a high  $S_b/S_w$  ratio. As reflected by the data in Table 15, the three compounds with the highest observed between-day contribution were triazinamine, bifenox acid and picolinafen.

The total standard deviations ( $S_t$ ) of the various analyses of pesticides and degradation products lie within the range 0.005-0.652  $\mu\text{g/l}$ , the highest value being observed for triazinamin (max  $S_t$  for compounds other than triazinamine was 0.044  $\mu\text{g/l}$ ). In general, the data suggest that the analytical procedure used for the quantification of triazinamine may benefit from a critical review. Excluding the triazinamine data, the overall mean  $S_t$  was 0.014  $\mu\text{g/l}$ .

**Table 15.** Internal QA of pesticide analyses carried out in the period 1.7.2008-30.6.2009. 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. For test the P value  $\alpha=0.05$  was used.

Compound	Normal distribution $\alpha=0.05$	Significant Sb Between day contribution ANOVA $\alpha=0.05$	Sw ( $\mu\text{g/l}$ )	Sb ( $\mu\text{g/l}$ )	St ( $\mu\text{g/l}$ )	Ratio Sb/Sw	N	Conc. ( $\mu\text{g/l}$ )
AMPA*			0.016	0.006	0.017	0.38	27	0.03
Azoxystrobin	yes	yes	0.002	0.006	0.006	2.93	48	0.05
Bentazone		yes	0.001	0.005	0.005	5.83	48	0.05
Bifenox		yes	0.007	0.010	0.012	1.43	34	0.05
Bifenox acid*		yes	0.017	0.041	0.044	2.33	30	0.10
CL153815*		yes	0.012	0.029	0.031	2.37	26	0.13
Desethyl-terbuthylazine*		yes	0.001	0.017	0.017	17.28	3	0.05
Epoxiconazole	yes	yes	0.003	0.007	0.008	2.47	7	0.05
Glyphosate			0.010	0.005	0.011	0.56	27	0.03
IN70941*	yes	yes	0.003	0.014	0.014	4.88	24	0.05
IN70942*		yes	0.001	0.008	0.008	6.78	24	0.05
Iodosulfuron-methyl	yes		0.005	0.000	0.005	0.10	5	0.05
Mesosulfuron*	yes	yes	0.003	0.008	0.008	2.49	5	0.10
Mesosulfuron-methyl	yes	yes	0.008	0.014	0.017	1.70	6	0.05
Metribuzin-diketo*	yes	yes	0.002	0.006	0.006	3.54	12	0.05
Metsulfuron-methyl*			0.016	0.012	0.020	0.72	5	0.05
Nitrofen*	yes	yes	0.002	0.010	0.010	4.39	34	0.05
Pendimethalin			0.009	0.006	0.011	0.61	14	0.05
Picolinafen		yes	0.016	0.029	0.033	1.76	26	0.11
Tebuconazole		yes	0.003	0.008	0.008	3.00	38	0.05
Triazinamin*		yes	0.051	0.650	0.652	12.73	15	0.11

\*Degradation product.

## 7.2.2 External QA

As part of the quality control a set of blanks are analysed to evaluate the possibility of false positive findings in the programme. From these results it can be concluded that contamination of samples during collection, storage and analysis is not likely to occur. In a total of 26 blank samples consisting of HPLC water a trace of glyphosate ( $< 0.02 \mu\text{g/l}$  well below the residue limit of  $0.1 \mu\text{g/l}$  and close to the detection limit) was found in a single sample. Samples found to contain pesticides or their degradation product are thus regarded as true positive findings.

Table 16 provides an overview of the recovery of all externally spiked samples. As the results for each field site in Table 16 are based on only a few observations for each concentration level (high/low), the data should not be interpreted too rigorously.

**Table 16.** Externally spiked samples. Average recovery (%) of the nominal concentration at low/high concentration level indicated for each site.  $n_{low}$  and  $n_{high}$  refer to the total number of samples being spiked at low and high concentrations, respectively. Bold font is used for recoveries outside the range 70% to 120%.

	Tylstrup		Jyndevad		Silstrup		Estrup		Faardrup		Average	$n_{low}/n_{high}$
	Low	High	Low	High	Low	High	Low	High	Low	High		
AMPA*							<b>62</b>	86			74	3/3
Bentazone	102	102	100	102			110	102	<b>126</b>	111	105	10/10
Bifenox acid*				<b>68</b>				<b>60</b>			64	[0/5]
CL153815*			72	70			78	75			75	3/3
CyPM*	87	90					<b>67</b>	<b>64</b>			78	6/6
Epoxiconazole			<b>174</b>	<b>153</b>							<b>164</b>	1/1
Ethofumesate					99	99			104	102	101	5/6
Glyphosate							<b>58</b>	<b>54</b>			<b>57</b>	3/3
IN70941(PPU)*	<b>34</b>	<b>26</b>	<b>61</b>	<b>41</b>							<b>42</b>	4/6
IN-M7222*					<b>130</b>	<b>122</b>			116	108	120	5/6
Metamitron					74	74			87	79	78	5/6
Metsulfuron-methyl*					<b>67</b>	<b>68</b>					<b>68</b>	3/3
Pendimethalin	84	82							100	102	92	2/2
Tebuconazole	113	111	<b>135</b>	<b>123</b>			104	102	118	119	115	7/7
TFMP*					<b>157</b>	<b>133</b>					<b>146</b>	3/3

\*Degradation produkt.

Whereas the recovery of the most spiked compounds in the samples is generally good (i.e. in the range 70% to 120%), the broad range of average recoveries indicates that for some compounds there may be reason for concern. In the current reporting period one exception has been made concerning spiking, as traces of Bifenox acid, CyPM and bentazone were found in the groundwater used for spiking at Silstrup, and data from this site have been omitted due to this bias. The somewhat low levels of recovery found for bifenox acid at Jyndevad and Estrup indicate that the QA needs to be reevaluated for this compound when more results are available (at present the QA is based on five samples). Also, the detection limit for Bifenox acid at 0.05 makes the QA spiking less informative at this level compared to the other compounds in the programme that have detection limits around 0.01 and 0.02. Considering the low recovery of glyphosate, identified in previous reports, analytical procedures have now been optimised and implemented in the programme with effect from 1 July 2010 and will thus be reflected in the next reporting period. However, it is anticipated that the QA data in the reports to follow will verify the improved methodologies for this compound. In the programme a shift from GC/MS to LC/MS analytical procedure was made in June 2007. The low recoveries relate to the analytical LC/MS procedure used in the programme during the period June 2007 to July 2010. During this period the concentration of glyphosate may have been underestimated. Due to the analytical cause of the problem, it is not possible to give an exact value for such a possible underestimation. However, a preliminary estimate has been made using all the QA data available for glyphosate and AMPA, i.e. all spiked QA samples analysed for these two compounds in the period October 2007 to June 2010. For glyphosate the mean recovery was 86% ( $n=73$ , std dev 24%) compared to 40% ( $n=18$ , std dev 16%) using LC/MS. For AMPA the GC/MS recoveries were 76% ( $n=31$ , std dev 24%) compared to 68% ( $n=16$ , std dev 15%) using LC/MS. A simple t-test indicates that there is a difference in the recoveries for glyphosate ( $P < 0.001$ ), whereas no significant difference was found for the AMPA recovery. A rough estimate based on the mean recovery obtained using the two glyphosate methods would indicate that analytical results reported in the period June 2007 to July 2010 may have underestimated the concentration of glyphosate by a factor of ~2 as compared to previous result based on a GC/MS analysis.

All the compounds included in the spiking procedure (Table 14) were detected in the laboratory. Additionally, a number of compounds were measured at the threshold of detection of the analytical procedure (i.e. close to 0.01 µg/l). The occurrence of a limited number of false positives is expected when analysing environmental matrices, and these findings do not cause a general concern in relation to the reliability of the analytical procedures used in the programme. Also, there were 12 reportings with a mean content of 0.05 µg/l for the compound PPU-desamino (IN70942), which was not included in the spiking ampoule. The compound PPU –desamino (IN70942) is a degradation product of PPU (IN70941), which was included in the spiking, and the presence of a degradation product indicates that the estimated leaching of PPU (IN70941) may be underestimated as described in Rosenbom *et al.* (2009). The same aspect relates to 11 reportings of metamitron-desamino, a degradation product of metamitron that was included in the spike solution. Thus, these compounds may be formed from compounds present in the spiking solution, In general, since the levels were low and in the range of the detection limit and well below the residue limit, these findings do not cause concern for the overall quality of the programme.

During the 2009/2010 monitoring period a total of five pesticides and nine degradation products were detected in samples from the experimental fields, and the external and internal QA data relating to these particular pesticides/degradation products are of special interest. These data (when available) are therefore illustrated in Appendix 6.

### **7.3 Summary and concluding remarks**

The QA system showed that:

- The internal QA indicates that the reproducibility of the pesticide analyses was good with total standard deviation (St) in the range 0.005-0.044 µg/l, except for triazinamin with a large St of 0.652 caused in particular by Sb.
- As demonstrated by the external QA, recovery was generally good in externally spiked samples. Low recovery of glyphosate was, however, observed in all samples, but a revision of the analytical procedure being implemented in parallel with the current reporting period is anticipated to solve these issues in the PLAP-programme.
- Contamination of samples during collection, storage and analysis is not likely to occur. In a single sample out of a total of 26 blank samples a trace of glyphosate was reported. No other pesticides or pesticide degradation products were detected.



## 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 available on [http://pesticidvarsling.dk/publ\\_result/index.html](http://pesticidvarsling.dk/publ_result/index.html)). Pesticide detections in samples from the drainage systems, suction cups and monitoring wells are detailed in Appendix 5. The monitoring data in 1 m b.g.s. (collected in drains and suction cups) reveal that the applied pesticides exhibit three different leaching patterns – no leaching, slight leaching and pronounced leaching (Table 17). Pronounced leaching in 1 m b.g.s. is defined as root zone leaching (1 m b.g.s.) exceeding an average concentration of 0.1 µg/l within the first season after application. On sandy and loamy soils, leaching is determined as the weighted average concentration in soil water and drainage water, respectively (Appendix 2). The monitoring data from the groundwater monitoring screens is divided into three categories: no detection of the pesticide (or its degradation products), detections of the pesticide (or its degradation products) not exceeding 0.1 µg/l, and detections of the pesticide (or its degradation products) exceeding 0.1 µg/l (Table 19). 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 and 19. Fourteen of the applied pesticides (or their degradation products) exhibited pronounced root zone leaching and 12 of these were also detected in the groundwater monitoring screens in concentrations exceeding 0.1 µg/l.

- Azoxystrobin, and in particular its degradation product CyPM, leached from the root zone (1 m b.g.s.) 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 Estrup (Table 17 and 18). At both sites, leaching of azoxystrobin and CyPM has hitherto mostly been confined to the depth of the drainage system, and they have rarely been detected in monitoring screens situated below drainage depth (Tables 19 and 20). However, detection of CyPM in groundwater monitoring wells has gradually increased over time with highest numbers of detection found after the latest applications (2009 at Silstrup, Figure 24 and 2008 at Estrup, Figure 30). Apart from one sample, however, concentrations detected were all below 0.1 µg/l. At the loamy Faardrup site azoxystrobin and CyPM were detected in only four samples from the drainage water, and in no samples from the sandy Jyndevad site (Appendix 5).


**Table 17.** Root zone leaching (1 m b.g.s.) 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, I, and GR indicate the type of pesticide: herbicide, fungicide, insecticide and growth retardant, respectively. Pesticides applied in spring 2010 are not included in the table.


	Tylstrup (Sandy soil)	Jydevad (Sandy soil)	Silstrup (Loamy soil)	Estrup (Loamy soil)	Faarstrup (Loamy soil)
Azoxystrobin (F)					
Bentazone (H)					
Bifenox (H)		*	*	*	
Ethofumesate (H)					
Fluazifop-P-butyl (H)	2)	2)	*		2)
Glyphosate (H)				*	
Metamitron (H)					
Metribuzin (H)	*	1)			
Picolinafen (H)					
Pirimicarb (I)					
Propyzamide (H)					
Rimsulfuron (H)					
Terbutylazine (H)					
Tebuconazole (F)					
Amidosulfuron (H)		2)		2)	
Bromoxynil (H)					
Clomazone (H)					
Dimethoate (I)					
Epoxiconazole (F)					
Flamprop-M-isopropyl (H)					
Fluroxypyr (H)					
Ioxynil (H)					
Mancozeb(F)					
MCPA (H)					
Mesosulfuron-methyl (H)					
Pendimethalin (H)					
Phenmedipham (H)					
Propiconazole (F)					
Prosulfocarb (H)					
Pyridate (H)					
Triflurosulfuron (H)					*
Chlormequat (GR)					
Clopyralid (H)					
Desmedipham (H)					
Fenpropimorph (F)					
Florasulam (H)					
Iodosulfuron-methyl-sodium (H)					
Linuron (H)					
Metsulfuron-methyl (H)					
Thiamethoxam (I)					
Tribenuron-methyl (H)					
Triasulfuron (H)					


\* Potential leaching period extends beyond the current monitoring period.

1) Derived from application before May 1999 (see Kjær *et al.*, 2002).

2) Degradation products are not monitored (see text).

 Pesticide (or its degradation products) leached 1 m b.g.s. in average concentrations exceeding 0.1 µg/l within the first season after application.

 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 within the first season after application.

 Pesticide either not detected or only detected in very few samples in concentrations below 0.1 µg/l.

**Table 18.** Number of samples from **1 m b.g.s.** in which the various pesticides and their degradation products were detected at each site with the maximum concentration ( $\mu\text{g/l}$ ) in parentheses. 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  $\mu\text{g/l}$ . Degradation products are indicated in italics. Pesticides applied in spring 2010 are not included.

	Tylstrup	Jyndeavad	Silstrup	Estrup	Faardrup
Azoxystrobin	0	0	10(0.034)	100(1.4)	0
- <i>CyPM</i>	0	0	64(0.34)	184(2.1)	4(0.059)
Bentazone	1(0.012)	39(1.6)	45(6.4)	145(20)	18(43)
- <i>AIBA</i>	0	2(0.034)	0	1(0.06)	1(0.057)
Bifenox		2(0.036)	1(0.027)	3(0.15)	
- <i>Bifenox acid</i>		1(0.1)	13(4.2)	11(1.9)	
- <i>Nitrofen</i>		0	1(0.023)		
Ethofumesate			15(0.227)	35(3.362)	13(12)
- <i>fluazifop-P<sup>2)</sup></i>	0	0	0	0	8(3.8)
- <i>TFMP<sup>2)</sup></i>			21(0.52)		
Glyphosate		0	67(4.7)	251(31)	4(0.093)
- <i>AMPA</i>		1(0.014)	122(0.35)	356(1.6)	10(0.11)
Metamitron			31(0.315)	42(26.369)	12(1.7)
- <i>metamitron-desamino</i>			46(0.399)	49(5.549)	16(2.5)
Metribuzin	2(0.024)	0			
- <i>metribuzin-desamino-diketo</i>	81(2.1)	0			
- <i>metribuzin-diketo</i>	242(0.69)	3(0.088)			
Picolinafen		1(0.015)		17(0.07)	
- <i>CL153815</i>		0		31(0.5)	
Pirimicarb	0	0	14(0.054)	39(0.077)	7(0.056)
- <i>pirimicarb-desmethyl</i>	0	1(0.011)	1(0.052)	0	6(0.053)
- <i>pirimicarb-desmethyl-</i>	0	0	0	26(0.379)	3(0.039)
Propyzamide	0		23(1.6)		4(0.51)
- <i>RH24580</i>	0		2(0.016)		0
- <i>RH24644</i>	0		15(0.051)		4(0.022)
- <i>RH24655</i>	0		0		1(0.017)
- <i>PPU<sup>3)</sup></i>	122(0.15)	154(0.29)			
- <i>PPU-desamino<sup>3)</sup></i>	35(0.042)	89(0.13)			
Terbuthylazine	0	0	60(1.55)	111(11)	41(10)
- <i>desethylterbuthylazine</i>	2(0.012)	18(0.056)	108(1.08)	145(8.2)	89(8.3)
- <i>desisopropyl-atrazine</i>	17(0.042)		43(0.041)*	71(0.44)	25(0.36)
- <i>2-hydroxy-desethyl-</i>	5(0.016)		28(0.11)*	86(6.3)	8(1)
- <i>2-hydroxy-terbuthylazin</i>	1(0.04)		26(0.039)*	87(0.99)	21(0.58)
Tebuconazole	0	0		41(2)	4(0.045)
Amidosulfuron		3(0.11)		0	
Bromoxynil	0	0		3(0.6)	0
Clomazone	0				1(0.28)
- <i>FMC65317(Propanamide-clomazone)</i>	0				0
Dimethoate	0	0	1(1.417)	0	0
Epoxiconazole	0	0	0	13(0.39)	0
ETU <sup>1)</sup>	7(0.038)				
Flamprop-M-isopropyl	0		12(0.109)	20(0.069)	1(0.037)
- <i>flamprop (free acid)</i>	0		7(0.096)	13(0.031)	1(0.089)
Fluroxypyr	0	0	0	3(0.025)	1(0.19)
Ioxynil	0	0		20(0.25)	1(0.011)
MCPA	0	0	0	11(3.894)	2(0.28)
- <i>4-chlor-2-methylphenol</i>		0	0	1(0.046)	1(0.24)
Mesosulfuron-methyl		0		13(0.059)	
Pendimethalin	0	0	14(0.064)		2(0.041)
Phenmedipham			0		0
- <i>MHPC</i>			0		2(0.19)
Propiconazole	0	0	6(0.033)	25(0.862)	0
Prosulfocarb			5(0.18)		0
Pyridate		0	0		
- <i>PHCP</i>			4(2.69)		
Triflusulfuron			0		0
- <i>IN-E7710</i>			5(0.014)		0

<sup>1)</sup>Degradation product of mancozeb.

<sup>2)</sup>Degradation product of fluazifop-P-butyl

<sup>3)</sup>Degradation product of rimsulfuron.

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

**Table 19.** Detections of pesticides and their degradation products in water samples from **the groundwater monitoring screens** at the five PLAP sites (see table 20 for details). An asterisk indicates pesticides that have been included in the monitoring programme for less than two years. The colours indicate the level of detection (see below) and the letters H, F, I, and GR indicate the type of pesticide: herbicide, fungicide, insecticide and growth retardant, respectively. Pesticides applied in spring 2010 are not included in the table.

	Tylstrup (Sandy soil)	Jyndevad (Sandy soil)	Silstrup (Loamy soil)	Estrup (Loamy soil)	Faarstrup (Loamy soil)
Azoxystrobin (F)					
Bentazone (H)					
Bifenox		*	*	*	
Ethofumesate (H)					
Fluazifop-P-butyl (H)	2)	2)			2)
Glyphosate (H)					
Metamitron (H)					
Metribuzin (H)		1)			
Picolinafen (H)					
Pirimicarb (I)					
Propyzamide (H)					
Rimsulfuron (H)					
Terbuthylazine (H)					
Tebuconazole (F)					
Amidosulfuron (H)		2)		2)	
Bromoxynil (H)					
Clomazone (H)					
Dimethoate (I)					
Epoxiconazole (F)					
Flamprop-M-isopropyl (H)					
Fluroxypyr (H)					
Ioxynil (H)					
Mancozeb (F)					
MCPA (H)					
Mesosulfuron-methyl (H)					
Pendimethalin (H)					
Phenmedipham (H)					
Propiconazole (F)					
Prosulfocarb (H)					
Pyridate (H)					
Triflurosulfuron (H)					*
Chlormequat (GR)					
Clopyralid (H)					
Desmedipham (H)					
Fenpropimorph (F)					
Florasulam (H)					
Iodosulfuron-methyl-sodium (H)					
Linuron (H)					
Metsulfuron-methyl (H)					
Thiamethoxam (I)					
Tribenuron-methyl (H)					
Triasulfuron (H)					

\* Potential leaching period extends beyond the current monitoring period.

1) Derived from application before May 1999 (see Kjær *et al.*, 2002).

2) Degradation products are not monitored (see text).

■ Pesticide (or its degradation products) detected in water samples from groundwater monitoring screens in concentrations exceeding 0.1 µg/l.

■ Pesticide (or its degradation products) detected in water samples from groundwater monitoring screens in concentrations not exceeding 0.1 µg/l.

■ Pesticide (or its degradation products) not detected in water samples from the groundwater monitoring screens.

**Table 20.** Number of samples from the **groundwater monitoring screens** in which the various pesticides and/or their degradation products were detected at each site with the maximum concentration ( $\mu\text{g/l}$ ) in parentheses (see Appendix 5 for further details). Degradation products are indicated in italics. Pesticides applied in spring 2010 are not included.

	Tylstrup	Jynde vad	Silstrup	Estrup	Faarstrup
Azoxystrobin	0	0	0	1(0.011)	0
- <i>CyPM</i>	0	0	28(0.1)	9(0.085)	0
Bentazone	0	0	29(0.44)	16(0.022)	11(0.6)
- <i>AIBA</i>	0	0	0	1(0.026)	0
Bifenox		2(0.05)	5(0.1)	0	
- <i>Bifenox acid</i>		0	13(3.1)	0	
- <i>nitrofen</i>		0	0	0	
Ethofumesate			5(0.038)	0	31(1.4)
- <i>fluazifop-P</i> <sup>2)</sup>	0	0	1(0.072)	0	6(0.17)
- <i>TFMP</i> <sup>2)</sup>			48(0.29)		
Glyphosate		0	4(0.031)	39(0.67)	3(0.017)
- <i>AMPA</i>		2(0.022)	15(0.08)	8(0.07)	2(0.029)
Metamitron			29(0.168)	0	24(0.63)
- <i>metamitron-desamino</i>			30(0.19)	0	48(1.3)
Metribuzin	1(0.014)	0			
- <i>metribuzin-desamino-diketo</i>	236(0.204)	20(1.831)			
- <i>metribuzin-diketo</i>	453(0.554)	26(1.372)			
Picolinafen		0		0	
- <i>CL153815</i>		0		0	
Pirimicarb	0	0	3(0.011)	1(0.015)	2(0.035)
- <i>pirimicarb-desmethyl</i>	0	0	0	0	3(0.042)
- <i>pirimicarb-desmethyl-</i>	0	0	0	0	2(0.076)
Propyzamide	0		9(0.14)		1(0.033)
- <i>RH24580</i>	0		0		0
- <i>RH24644</i>	0		2(0.032)		0
- <i>RH24655</i>	0		0		0
- <i>PPU</i> <sup>3)</sup>	2(0.045)	284(0.11)			
- <i>PPU-desammino</i> <sup>3)</sup>	0	71(0.028)			
Terbuthylazine	0	0	36(0.124)	1(0.022)	51(1.9)
- <i>desethyl-terbuthylazine</i>	0	24(0.023)	161(0.143)	7(0.053)	66(0.94)
- <i>desisopropyl-atrazine</i>	1(0.014)		4(0.047)*	27(0.034)	60(0.04)
- <i>2-hydroxy-desethyl-</i>	1(0.026)		1(0.016)*		7(0.092)
- <i>2-hydroxy-terbuthylazin</i>	0		0*		34(0.069)
Tebuconazole	1(0.011)	1(0.014)		5(0.12)	1(0.01)
Amidosulfuron		0		0	
Bromoxynil	0	0		0	0
Clomazone	0				0
- <i>FMC65317</i> ( <i>Propanamide-clomazone</i> )	0				0
Dimethoate	0	0	1(0.085)	0	0
- <i>ETU</i> <sup>1)</sup>	2(0.024)				
Epoxiconazole		1(0.011)			
Flamprop-M-isopropyl	0		1(0.024)	0	0
- <i>flamprop (free acid)</i>	0		0	0	0
Fluroxypyr	0	0	0	1(0.058)	1(0.072)
Ioxynil	0	0		0	1(0.01)
MCPA	0	0	0	1(0.019)	0
- <i>4-chlor-2-methylphenol</i>	0	0	0	0	0
Mesosulfuron-methyl		0		0	
Pendimethalin	0	0	0		0
Phenmedipham			0		2(0.025)
- <i>MHPC</i>			0		1(0.053)
Propiconazole	0	0	0	2(0.022)	1(0.035)
Prosulfocarb			1(0.027)		0
Pyridate		0	0		
- <i>PHCP</i>		0	14(0.309)		
Triflusulfuron			0		
- <i>IN-M7222</i>			1(0.052)		
Desmedipham			1(0.033)		0
Fenpropimorph	0	1(0.029)	0	0	1(0.015)
- <i>fenpropimorph-acid</i>	0	0	0	0	0
Metsulfuron-methyl				0	
- <i>triazinamin</i>				1(0.042)	

<sup>1)</sup>Degradation product of mancozeb. <sup>2)</sup>Degradation product of fluazifop-P-butyl.

<sup>3)</sup>Degradation product of rimsulfuron.

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

- Bentazone leached through the root zone (1 m b.g.s.) in average concentrations exceeding 0.1 µg/l in the drainage system at the loamy sites of Silstrup, Estrup, and Faardrup. Moreover, bentazone was frequently detected in the monitoring screens situated beneath the drainage system at Silstrup and Faardrup (Table 19 and 20). Apart from eight 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 was only detected once 1 m b.g.s. at Tylstrup. At Jyndevad 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. Although leached in high average concentrations (>0.1 µg/l) at four sites, bentazone was generally leached within a short period of time. Initial concentrations of bentazone were usually very high, but then decreased rapidly. In general, concentrations exceeding 0.1µg/l were only found within a period of one to four months following the application. The degradation product AIBA was detected twice in the vadose zone at Jyndevad, once in drainage water at Estrup and Faardrup (Table 18), and once in water from a horizontal well at Estrup (Table 20).
- Bifenox acid (degradation product of bifenox) leached through the root zone and entered the drainage water system in average concentrations exceeding 0.1 µg/l at the loamy sites of both Silstrup and Estrup. While leaching at Estrup seems to be confined to the depth of the drainage system, leaching to groundwater monitoring wells situated beneath the drainage system was observed at Silstrup, where concentrations exceeding 0.1 µg/l were observed up to six months after application.. Similar evidence of pronounced leaching was **not** observed on the coarse sandy soil as there was only a single detection of bifenox acid in soil water, whereas bifenox was detected very sporadically in soil and groundwater, concentrations always less than 0.1 µg/l.
- In the loamy soil of Estrup, ethofumesate, met amitron, and its degradation product met amitron-desamino leached through the root zone (1 m b.g.s.) into the drainage water in average concentrations exceeding 0.1 µg/l (Table 17). The compounds have not been detected in deeper monitoring screens. These compounds also leached 1 m b.g.s. at the Silstrup and Faardrup sites, reaching both the drainage system (Table 17 and 18) and groundwater monitoring screens (Table 19 and 20). 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 at both Silstrup and Faardrup (see Kjær *et al.*, 2002 and Kjær *et al.*, 2004 for details). The above leaching was observed following an application of 345 g/ha of ethofumesate and 2,100 g/ha of met amitron in 2000 and 2003. Since then, ethofumesate has been regulated and the leaching risk related to the new admissible dose of 70 g/ha was evaluated with the two recent applications (2008 at Silstrup and 2009 at Faardrup). Although met amitron has not been regulated, a reduced dose of 1400 g/ha was applied at the two recent applications. The leaching following these recent applications (2008 at Silstrup and 2009 at Faardrup) with reduced dose of both ethofumesate and met amitron was minor. Apart from a few samples from the drainage system and groundwater monitoring wells containing less than 0.1 µg/l,

neither ethofumesate nor metamitron was found in any of the analysed water samples (see section 4.2.3 and 6.2.3).

- Fluazifop-P-butyl has several times been included in the monitoring programme at Jyndevad, Tylstrup, Silstrup, and Faardrup. As fluazifop-P-butyl rapidly degrades, until July 2008 monitoring has focused only on its degradation product fluazifop-P (free acid). Except for one detection below 0.1 µg/l in groundwater at Silstrup and 17 detections with eight exceeding 0.1 µg/l (four drains, three vadose zone, one groundwater, Table 18 and 20) at Faardrup, leaching was not evident. TFMP, the degradation product of fluazifop-P-butyl, was included in the monitoring programme at Silstrup in July 2008 following an application of fluazifop-P-butyl. After approximately one month, TFMP was detected in the groundwater monitoring wells, where concentrations at or above 0.1 µg/l were detected within a ten-month period following application (Figure 22, Tables 19 and 20). At the onset of drainage flow in September, TFMP was detected in all the drainage water samples at concentrations exceeding 0.1 µg/l (Figure 22). The leaching pattern of TFMP indicates pronounced preferential flow also in periods with a relatively dry vadose zone.
- Glyphosate and AMPA was found to leach through the root zone at high average concentrations on loamy soils. At the loamy sites Silstrup and Estrup, glyphosate has been applied two (in 2001 and 2003) and four (in 2000, 2002, 2005, and 2007) times within the monitoring period, respectively. All six autumn applications have resulted in detectable leaching of glyphosate and AMPA from the upper meter into the drainage water, often at concentrations exceeding 0.1 µg/l several months after application. Higher leaching levels of glyphosate and AMPA have mainly been confined to the depth of the drainage system and have rarely been detected in monitoring screens located below the depth of the drainage systems, although it should be noted that detections of particularly glyphosate in groundwater monitoring wells at Estrup seem to increase over the years (Figure 33D). This increase may be underestimated for the period June 2007 to July 2010 as external quality assurance of analytical methods in this period indicates that the true concentration of glyphosate may be underestimated (see section 7.2.2 ). On two occasions heavy rain events and snowmelt triggered leaching to the groundwater monitoring wells in concentrations exceeding 0.1 µg/l more than two year after the application (Figure 33D). Numbers of detections exceeding 0.1 µg/l in groundwater monitoring wells are, however, very limited (only three samples). Glyphosate and AMPA were also detected in drainage water at the loamy site of 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 on loamy soils, whereas the leaching risk was negligible on the coarse sandy soil of Jyndevad. Here, 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).
- Two degradation products of metribuzin – metribuzin-diketo and metribuzin-desamino-diketo – leached 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 seen as late as three years after application (Table 17). Evidence was also found that their degradation products might be present in the groundwater several

years after application, meaning that metribuzin and its degradation products have long-term sorption and dissipation characteristics (Rosenbom *et al.*, 2009). At both sandy sites (Tylstrup and Jyndevad), previous applications of metribuzin has caused marked groundwater contamination with its degradation products (Kjær *et al.*, 2005b).

- At Estrup, CL153815 (degradation product of picolinafen) leached through the root zone upper meter into the drainage water in average concentrations exceeding 0.1 µg/l (Appendix 5). CL153815 has not been detected in deeper monitoring screens (Table 20). Leaching of CL153815 have not been observed on the sandy soil at Jyndevad, (Table 17, Table 20, and Appendix 5).
- Pirimicarb together with its two degradation products pirimicarb-desmethyl and pirimicarb-desmethyl-formamido has been included in the monitoring programme for all five sites. All of the three compounds have been detected, but only pirimicarb-desmethyl-formamido leached through the root zone (1 m b.g.s.) entering the drainage system in average concentrations exceeding 0.1 µg/l (Table 17) at Estrup. Comparable high levels of leaching of pirimicarb-desmethyl-formamido have not been observed with any of the previous applications of pirimicarb at the other PLAP sites (Table 17 and Kjær *et al.*, 2004). Both degradation products (pirimicarb-desmethyl and pirimicarb-desmethyl-formamido) have been detected in deeper monitoring screens at Faardrup (Table 19 and 20).
- Propyzamide leached through the root zone (1 m b.g.s.) at the loamy Silstrup and Faardrup sites, entering the drainage system at average concentrations exceeding 0.1 µg/l (Table 17 and 18). Propyzamide was also detected in the monitoring screens situated beneath the drainage system. Apart from a few samples at Silstrup, the concentrations in the groundwater from the screens were always less than 0.1 µg/l (Appendix 5, Table 19 and 20).
- 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. 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 (Tables 17 and 18). In groundwater PPU was occasionally detected and twice exceeded 0.1 µg/l at Jyndevad, whereas it was only detected once (and at a low concentration) at Tylstrup (Table 19 and 20). At both sites, PPU was relatively stable and persisted in the soil water for several years, with relatively little further degradation into PPU-desamino. E.g. average leaching concentrations reaching 0.1 µg/l were seen as much as three years after application at Jyndevad. With an overall transport time of about four years, PPU reached the downstream monitoring screens. Thus, the concentration of PPU-desamino was much lower and apart from four samples at Jyndevad, never exceeded 0.1 µg/l. It should be noted that the concentration of PPU is likely to be underestimated by up to 22-47%. Results from the field-spiked samples thus indicate that PPU is unstable and may have further degraded to PPU-desamino during analysis (Rosenbom *et al.*, 2010a).
- Terbutylazine as well as its degradation products leached through the root zone (1 m b.g.s.) at high average concentrations on loamy soils. At the three loamy soil sites Silstrup, Estrup, and Faardrup, desethyl-terbutylazine leached from the upper meter



entering the drainage water in average concentrations exceeding 0.1 µg/l (Table 17 and 18). Four years after application at Estrup, both terbuthylazine and desethyl-terbuthylazine were detected in drainage water, but not exceeding 0.1 µg/l. At Silstrup (Kjær *et al.*, 2007) and Faardrup (Kjær *et al.*, 2009), desethyl-terbuthylazine was frequently detected in the monitoring screens situated beneath the drainage system (Table 19 and 20) at concentrations exceeding 0.1 µg/l 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 desethyl-terbuthylazine was also seen at the two sandy sites Jyndevad and Tylstrup, where desethyl-terbuthylazine was detected in low concentrations (<0.1 µg/l) in the soil water sampled 1 m b.g.s. While desethyl-terbuthylazine was not detected in the groundwater monitoring screens at Tylstrup, it was frequently detected in low concentration (< 0.1 µg/l) at Jyndevad (Table 20, Kjær *et al.*, 2004). Marked leaching of terbuthylazine was also seen at two of the three loamy sites (Estrup and Faardrup), the leaching pattern being similar to that of desethyl-terbuthylazine. 2-hydroxy-desethyl-terbuthylazine and 2-hydroxy-terbuthylazine leached at both Faardrup and Estrup and at the latter site the average drainage concentration exceeded 0.1 µg/l. Leaching of these two degradation products was at both sites confined to the drainage system. None of the two degradation products were detected in groundwater monitoring screen at Estrup, whereas at Faardrup both were found, but at low frequencies of detection and concentrations.

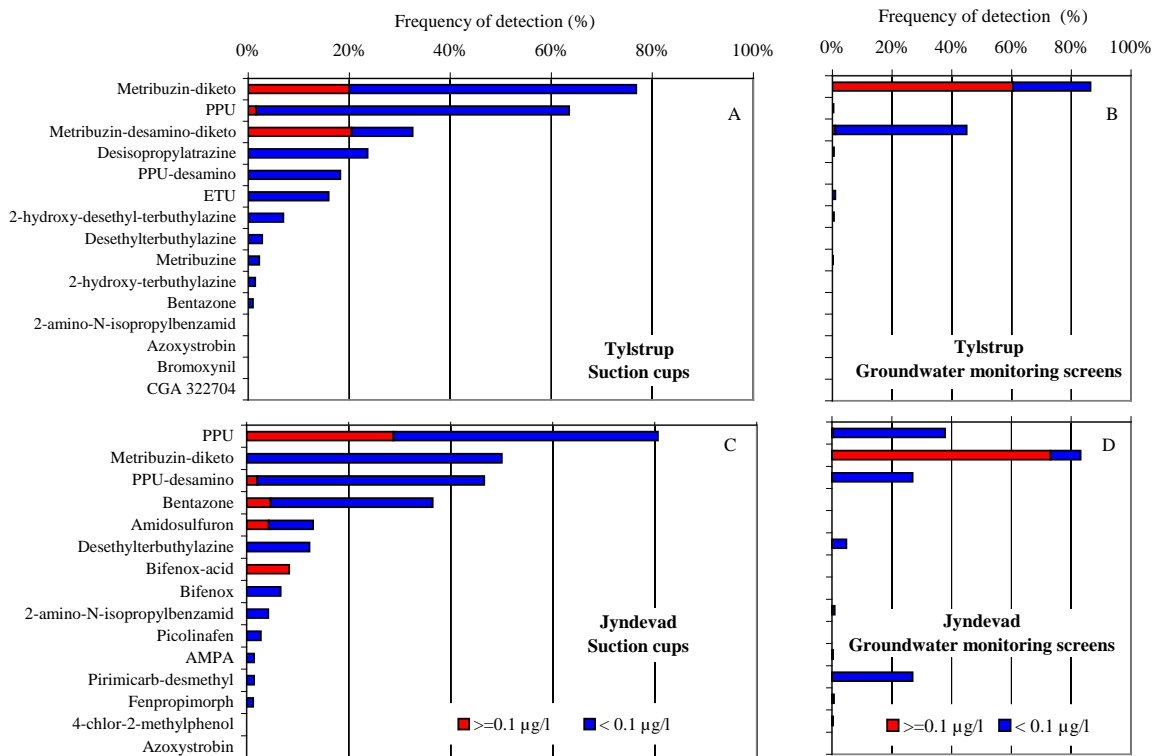
- Tebuconazole has been applied in autumn 2007 at Tylstrup, Jyndevad, Estrup and Faardrup. Only on the loamy soil of Estrup did it leach through the root zone (1 m b.g.s.) and into the drainage water in average concentrations exceeding 0.1 µg/l (Table 17 and 18). Leaching was mainly confined to the depth of the drainage system, although the snow melt occurring in March 2011 (more than two years after application) induced leaching of tebuconazole to the groundwater monitoring well in concentrations exceeding 0.1 µg/l (Tables 19 and 20). None of the applications at the three other PLAP sites caused tebuconazole to be detected in similarly high concentrations in the vadose zone, though concentrations below 0.1 µg/l have been detected in a few samples from the groundwater monitoring screens (Table 19 and 20).

The monitoring data also indicate leaching 1 m b.g.s. of a further 17 pesticides (or their degradation products), but often in low concentrations. Although the concentrations detected 1 m b.g.s. 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, within this group of 16 pesticides (or their degradation products) leaching from 1 meter 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 vadose zone. It should be noted that the findings regarding amidosulfuron are of very limited use since the degradation products – with which the leaching risk is probably mainly associated – are not included, as methods for their analysis are not yet available.

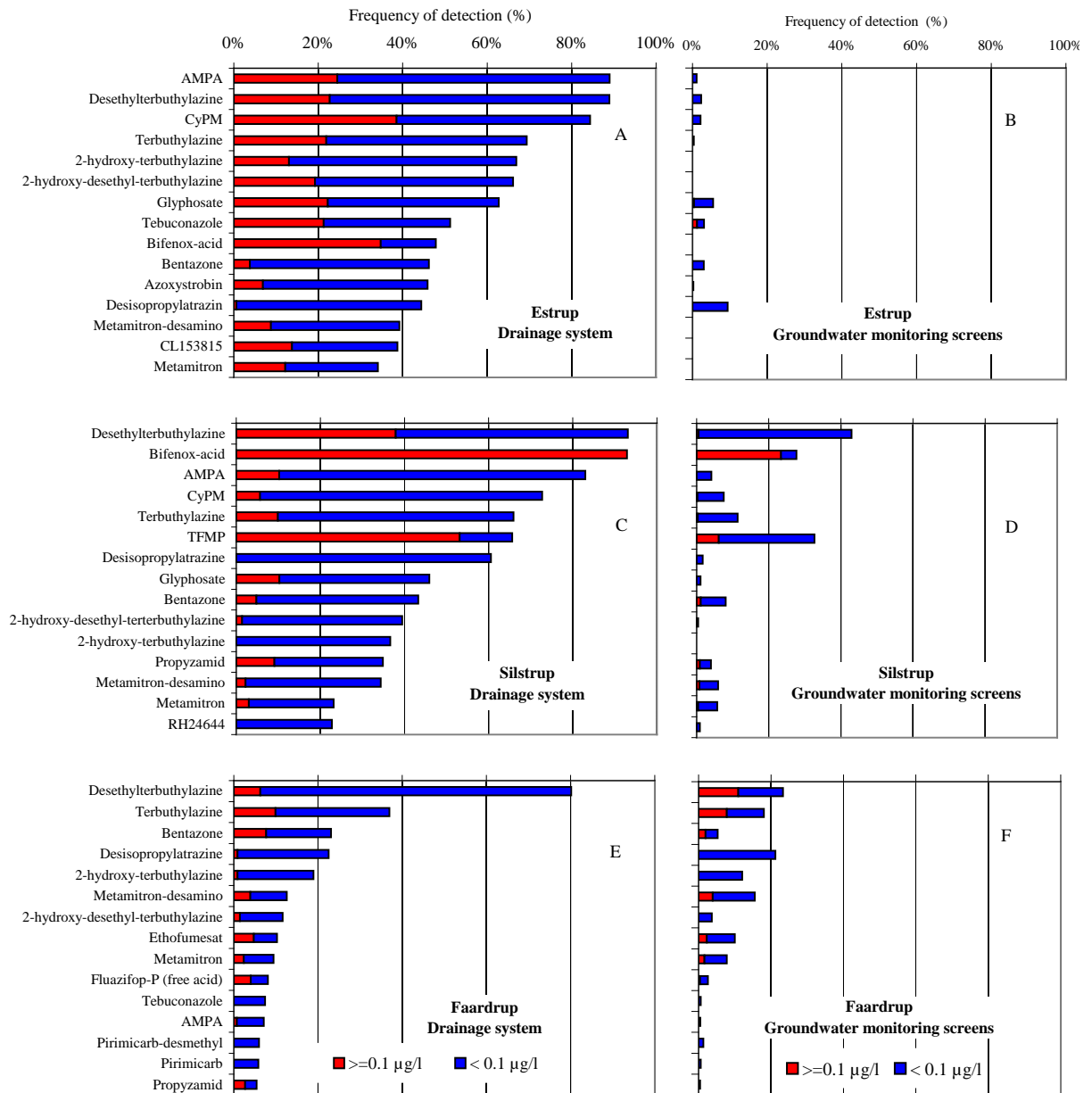
Eleven of the 42 pesticides applied – about 26% – did not leach at all from 1 m b.g.s. during the monitoring period (Table 17). Four of the 11 were, however, detected in the

groundwater monitoring screens (Table 19). The group of 11 includes the three different sulfonylureas – metsulfuron-methyl, triasulfuron, iodosulfuron-methyl-sodium and tribenuron-methyl applied at several sites. For example, tribenuron-methyl was applied at four different sites under different hydrological conditions, with percolation (1 m b.g.s.) during the first month after application ranging from 0 to 114 mm. The monitoring results give no indication of leaching for any of the compounds or their degradation products. It should, however, be noted, that the leaching risk associated with an autumn application of tribenuron-methyl, where preferential transport is likely to occur, has not yet been evaluated for the loamy soils.

The leaching patterns of the sandy and loamy sites are further illustrated in Figure 40 and 41, 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.



**Figure 40.** 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: **Tylstrup** (A, B) and **Jyndevad** (C, D). Frequency is estimated for the entire monitoring period and the length of 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 fifteen 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.



**Figure 41.** 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: **Estrup** (A, B), **Silstrup** (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 15 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.

On the sandy soils the number of leached pesticides as well as the frequency of detection was much lower than on loamy soils (Figure 40 and 41), 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 the loamy types 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 frequency of detection in the monitoring screens situated beneath the drainage system was lower and varied considerably between the three sites (Figure 41). 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 captures 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 39, 27 and 16 samples containing glyphosate, desisopropyl-atrazine, and bentazone respectively, pesticides have only occasionally 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 the risk of transport to deeper soil layers. An indication thereof are the long periods with groundwater table beyond drainage depth in which an increasing lateral transport to the drainage system and decreased leaching to the deeper groundwater will occur.

Comparing the loamy sites, the number of drainage water samples containing pesticides/degradation products was markedly higher at Silstrup and Estrup than at Faardrup, which is largely attributable to the differences in the hydrological conditions. The occurrence of precipitation and subsequent percolation within the first month after application were, generally, higher at Silstrup and Estrup than at Faardrup (Table 9, Table 11, and Table 13).

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

Parameter	Systematic chemical nomenclature
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
- <i>CyPM</i>	E-2-(2-[6-cyanophenoxy]-pyrimidin-4-yloxy)-phenyl) – 3-methoxyacrylic acid
Bentazone	3-(1-methylethyl)-1H-2,1,3-benzothiadiazin-4(3H)-one 2,2 dioxide
- <i>AIBA</i>	2-amino-N-isopropyl-benzamid
Bromoxynil	3,5-dibromo-4-hydroxybenzoxitrile
Bifenox	methyl 5-(2,4-dichlorophenoxy)-2-nitrobenzoate
- <i>Bifenox acid</i>	5-(2,4-dichlorophenoxy)-2-nitrobenzoic acid
- <i>Nitrofen</i>	2,4-dichlorophenyl 4'-nitrophenyl ether
Chlormequat	2-chloroethyltrimethylammonium chloride
Clomazone	2-[(2-chlorophenyl)methyl]-4,4-dimethyl-3-isoxazolidione
- <i>FMC65317 (Propanamide-clomazone)</i>	(N-[2-chlorophenol)methyl]-3-hydroxy-2,2-dimethyl propanamide
Clopyralid	3,6-Dichloropyridine-2-carboxylic acid
Desmedipham	Ethyl 3-(phenylcarbamoyloxy)phenylcarbamate
- <i>EHPC</i>	Carbamic acid, (3-hydroxyphenyl)-ethyl ester
Dimethoate	O,O-dimethyl S-methylcarbamoylmethyl-phosphorodithioate
Ethofumesate	(±)-2-ethoxy-2,3-dihydro-3,3-dimethylbenzofuran-5-yl-methanesulfonate
- <i>Fluazifop-P<sup>2)</sup></i>	(R)-2-(4-((5-(trifluoromethyl)-2-pyridinyl)oxy)phenoxy)propanoic acid
- <i>TFMP<sup>2)</sup></i>	5-trifluoromethyl-pyridin-2-ol
Epoxiconazole	(2RS, 3SR)-1-(2-(2-chlorophenyl)-2,3-epoxy-2-(4-fluorophenyl)propyl)-1H-1,2,4-triazol
- <i>ETU<sup>1)</sup></i>	Ethylenethiourea
Fenpropimorph	Cis-4-[3-[4-(1,1-dimethylethyl)-phenyl]-2-methylpropyl]-2,6-imethylmorpholine
- <i>Fenpropimorphic acid</i>	Cis-4-[3-[4-(2-carboxypropyl)-phenyl]-2-methylpropyl]-2,6-dimethylmorpholine
Flamprop-M-isopropyl	Isopropyl N-benzoyl-N-(3-chloro-4-fluorophenyl)-D-alaninate
- <i>Flamprop (free acid)</i>	N-benzoyl-N-(3-chloro-4-fluorophenyl)-D-alanine
Florasulam	2',6',8'-Trifluoro-5-methoxy-s-triazolo [1,5-c]pyrimidine-2-sulfonanilide
- <i>Florasulam-desmethyl</i>	N-(2,6-difluorophenyl)-8-fluoro-5-hydroxy[1,2,4]triazolo[1,5-c]pyrimidine-2-sulfonamide
Fluroxypyr	(4-amino-3,5-dichloro-6-fluoro-2-pyridinyl)oxy]acetic acid
Glyphosate	N-(phosphonomethyl)glycine
- <i>AMPA</i>	Amino-methylphosphonic acid
Iodosulfuron-methyl-sodium	sodium salt of methyl 4-iodo-2-[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl]amino]sulfonyl]benzoate
- <i>Triazinamine</i>	2-amino-4-methoxy-6-methyl-1,3,5-triazine
- <i>Metsulfuron-methyl</i>	Methyl 2-[[[(4-methoxy-6-methyl-1,3,5-triazine-2-yl)amino]=carbonyl]amino]-sulfonyl]benzoic acid
Ioxynil	4-hydroxy-3,5-diiodobenzonitrile
Linuron	3-(3,4-dichlorophenyl)-1-methoxy-1-methylurea
MCPA	(4-chloro-2-methylphenoxy)acetic acid
- <i>4-chlor-2-methylphenol</i>	4-chlor-2-methylphenol
Mesosulfuron-methyl	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
- <i>Metamitron-desamino</i>	4,5-dihydro-3-methyl-6-phenyl-1,2,4-triazine-5-one
Metribuzin	4-amino-6-tert-butyl-4,5-dihydro-3-methylthio-1,2,4-triazine-5-one
- <i>Metribuzin-desamino</i>	6-(1,1-dimethylethyl)-3-(methylthio)-1,2,4-triazin-5-(4H)-one
- <i>Metribuzin-desamino-diketo</i>	6-tert-butyl-4,5-dihydro-3-methylthio-1,2,4-triazine-3,5-dione
- <i>Metribuzin-diketo</i>	4-amino-6-tert-butyl-4,5-dihydro-1,2,4-triazine-3,5-dione
Metsulfuron-methyl	Methyl 2-[[[(4-methoxy-6-methyl-1,3,5-triazine-2-yl)amino]=carbonyl]amino]-sulfonyl]benzoic acid
- <i>Mesosulfuron</i>	2-[[[(4,6-dimethoxy-2-pyrimidinyl)amino]carbonyl]amino]sulfonyl]-4-[[methylsulfonyl]amino]methyl]benzoic acid
Pendimethalin	N-(1-ethyl)-2,6-dinitro-3,4-xynile
Phenmedipham	3-[(methoxycarbonyl)amino]phenyl (3-methylphenyl)carbamate
- <i>MHPC</i>	Methyl-N-(3-hydroxyphenyl)-carbamate
- <i>3-aminophenol</i>	1-amino-3-hydroxybenzene
- <i>PHCP<sup>3)</sup></i>	3-phenyl-4-hydroxy-6-chloropyridazine

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

Parameter	Systematic chemical nomenclature
Picolinafen	4'-fluoro-6-( $\alpha,\alpha,\alpha$ -trifluoro-m-tolyloxy)pyridine-2-carboxanilide
- <i>CL153815</i>	6-(3-trifluoromethylphenoxy)-2-pyridine carboxylic acid
Pirimicarb	2-(dimethylamino)-5,6-dimethyl-4-pyrimidinyl dimethylcarbamate
- <i>Pirimicarb-desmethyl</i>	2-(dimethylamino)-5,6-dimethyl-4-pyrimidinylmethylcarbamate
- <i>Pirimicarb-desmethyl-formamido</i>	2-methylformamido-5,6-dimethylpyrimidine-4-yl dimethylcarbamate
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
- <i>RH-24644</i>	2-(3,5-dichlorophenyl)-4,4-dimethyl-5-methylene-oxazolone
- <i>RH-24580</i>	N-(1,1-dimethylacetyl)-3,5-dichlorobenzamide
- <i>RH-24655</i>	3,5-dichloro-N-(1,1-dimethylpropenyl)benzamide
Prosulfocarb	N-[[3-(4-methoxy-6-methyl-1,3,5-triazin-2-yl)-3-[2-(3,3,3-trifluoro=propyl)phenylsulfonyl]urea
Rimsulfuron	N-[[[(4,6-dimethoxy-2-pyrimidinyl)amino]carbonyl]-3-(ethylsulfonyl)-2-pyridinesulfonamide
- <i>PPU</i>	N-(4,6-dimethoxy-2-pyrimidinyl-N-((3-ethylsulfonyl)-2-pyridinyl)urea (IN70941)
- <i>PPU-desamino</i>	N-((3-(ethylsulfonyl)-2-pyridinyl)-4,6-dimethoxy-2-pyrimidinamine (IN70942)
Terbuthylazine	6-chloro-N-(1,1-dimethylethyl)-N-ethyl-1,3,5-triazine-2,4-diamine
- <i>Desethyl-terbuthylazine</i>	6-chloro-N-(1,1-dimethylethyl)-1,3,5-triazine-2,4-diamine
- <i>Desisopropyl-atrazine</i>	6-chloro-N-ethyl-1,3,5-triazine-2,4-diamine
- <i>2-hydroxy-desethyl-terbuthylazine</i>	6-hydroxy-N-(1,1-dimethylethyl)-1,3,5-triazine-2,4-diamine
- <i>2-hydroxy-terbuthylazine</i>	6-hydroxy-N-(1,1-dimethylethyl)-N'-ethyl-1,3,5-triazine-2,4-diamine
Tebuconazole	a-[2-(4-chlorophenyl)ethyl]-a-(1,1-dimethylethyl)-1H-1,2,4-triazole-1-ethanol
Thiamethoxam	3-(2-chloro-thiazol-5-ylmethyl)-5-methyl[1,3,5]oxadiazinan-4-ylidene-N-nitroamine
- <i>CGA 322704</i>	[C(E)]-N-[(2-chloro-5-thiazolyl)methyl]-N'-methyl-N'-nitroguanidine
- <i>Triazinamin-methyl<sup>4)</sup></i>	4-methoxy-6-methyl-1,3,5-triazin-methylamine
Triflurosulfuron	methyl 2-[4-dimethylamino-6-(2,2,2-trifluoroethoxy)-1,3,5-triazin-2-ylcarbamoylsulfamoyl]-m-toluate
- <i>IN-E7710</i>	N-methyl-6-(2,2,2-trifluoroethoxy)-1,3,5-triazine-2,4-diamine
- <i>IN-D8526</i>	N,N-dimethyl-6-(2,2,2-trifluoroethoxy)-1,3,5-triazine-2,4-diamine
- <i>IN-M7222</i>	6-(2,2,2-trifluoroethoxy)-1,3,5-triazine-2,4-diamine
Triasulfuron	1-[2-(2-chloroethoxy)phenylsulfonyl]-2-(4-methoxy-6-methyl-1,3,5-triazine-2-yl)-urea

<sup>1)</sup>Degradation product of mancozeb.<sup>2)</sup>Degradation product of fluazifop-P-butyl.<sup>3)</sup>Degradation product of pyridate.<sup>4)</sup>Degradation product of Tribenuron-methyl.

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 four 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).

On the sandy soils, the analysis of a number of pesticides in water from the monitoring wells had to be further reduced, due to economical constraints imposed by the high prices on pesticide analysis. This reduction was based on results from the suction cups implying that leaching risk of certain pesticides was negligible, why analysis of a limited number of groundwater samples would be reasonable (see Table A5.1 and Table A5.2 in Appendix 5).

In March 2008, a new revision of the monitoring programme was completed resulting in an optimization of the programme including an additional reduction in the sampling programme (Table A2.1). On the loamy sites, sampling from the suction cups for inorganic analysis, from one-two monitoring wells per site, and one horizontal well at Silstrup (H2) and Faardrup (H1) was suspended. On the sandy sites, only sampling from the monitoring well M6 at Tylstrup has been suspended (see Rosenbom *et al.*, 2010b for details).

**Table A2.1.** Pesticide monitoring programme in suction cups (S), horizontal monitoring wells (H) and vertical monitoring wells (M) as of March 2009. Water sampling places (S, H, and M) from where sampling stopped in 2008 and 2009 are given in bold. Well M10 at Silstrup was included in the programme on 5 February 2009.

Site	Monthly monitoring (Intensive)	Half-yearly monitoring (Extensive)	Not Monitored
Tylstrup	M4, M5, S1a, S2a	M1, M3, M4, M5, S1a, S2a, S1b*, S2b*	M2, <b>M6</b> , M7
Jyndevad	M1, M4, S1a, S2a	M1, M2, M4, M5, M7, S1a, S2a	M3, <b>M6</b> , S1b, S2b
Silstrup	M5, H1.2	M5, M9, M10, M12, H1.1, H1.2, H1.3	M1, M2, M4, <b>M6</b> , M8, M7, M11, <b>M13</b> , <b>H2.1, H2.2, H2.3</b>
Estrup	M4, H1.2	M1, M4, M5, M6, H1.1, H1.2, H1.3	M2, <b>M3</b> , <b>M7</b> ,
Faardrup	M4, M5, H2.3	M4, M5, M6, H2.1, H2.3, H2.5	M1, <b>M2</b> , <b>M3</b> , <b>M7</b> , <b>H1.1</b> , H1.2, <b>H1.3</b>

*S1a and S1b refer to suction cups installed 1 and 2 m b.g.s., respectively, at location S1, whereas S2a and S2b refer to suction cups installed 1 and 2 m b.g.s., respectively, at location S2.\* At Tylstrup suction cups installed 2 m b.g.s. are monitored four times a year(see text).*

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 over 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<sub>i</sub> = Weekly accumulated drainage runoff (mm/week).

C<sub>i</sub> = 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:

$$M_i = C_{t_i} \cdot V_i \quad \text{If no flow event occurs within the } i\text{'th week}$$

$$M_i = C_{f_i} \cdot V_{f_i} \quad \text{If a flow event occurs within the } i\text{'th week and if } C_{f_i} \cdot V_{f_i} > C_{t_i} \cdot V_i$$

where:

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

V<sub>i</sub> = Weekly accumulated drainage runoff (mm/week).

V<sub>f<sub>i</sub></sub> = Drainage runoff accumulated during a “flow event” (mm/storm event).

C<sub>f<sub>i</sub></sub> = Pesticide concentration in the “event samples” collected by means of the flow-proportional sampler (µg/l).

C<sub>t<sub>i</sub></sub> = Pesticide concentration in the weekly samples collected by means of the time-proportional sampler (µg/l).

Tables 9, 11, and 13 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, as pesticides are usually present in the first drainage runoff occurring after application of pesticide.

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 cups S1 and 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.

Tables 3 and 6 report the weighted average leachate concentration. In these tables this calculation period is defined as the period from the date of first detection until 1 July the following year. On sandy soils the transport of pesticides down to the suction cups situated at 1 m depth may take some time. In most cases the first detection of pesticides occurs around 1 July, why the reported concentration represents the yearly average concentration. In a few cases the first detection of pesticides occurs later, but this later occurrence does not affect the weighted average calculation. E.g. the reported average concentration using a calculation period from the first detection until 1 July the following year is equal to that using a calculation period of a year (1 July – 30 June) the following year). Unless noted the concentrations listed in Tables 3 and 6 can therefore be considered as yearly average concentrations. In the few cases where reported concentrations are either not representative for an annual average concentration or not representative for the given leaching pattern (leaching increases the second or third year after application) a note is inserted in the table.



**Table A3.1** Management practice at **Tylstrup** during the 2007 to 2010 growing seasons. The active ingredients of the various pesticides are indicated in parentheses.

Date	Management practice
09.02.07	Herbicide - 1.0 l/ha Kerb 500 SC (propyzamide)
27.03.07	Herbicide - 0.8 l/ha Matrigon (clopyralid)
08.06.07	Irrigation 30 mm
01.08.07	Direct harvest and simultaneous shredding of straw (seed yield 24.5 hkg/ha 91% DM, straw yield)
03.08.07	Rotary cultivated - depth 3.0 cm (straw incorporation)
07.09.07	Rotary cultivated - depth 7.0 cm (straw incorporation)
12.09.07	Ploughed - 22 cm depth
12.09.07	Winter wheat sown - cv. Smuggler.
18.10.07	Herbicide - 5.0 l/ha Stomp (pendimethalin)
16.11.07	Herbicide - 1.0 l/ha Folicur EC250 (tebuconazole)
22.05.08	Irrigation - 32 mm
29.05.08	Irrigation - 32 mm
05.06.08	Irrigation - 32 mm
13.06.08	Irrigation - 30 mm
17.06.08	Fungicide – 1.0 l/ha Amistar (azoxystrobin)
18.08.08	Winter wheat harvested (seed yield 92.1 hkg/ha 85% DM)
31.08.08	Straw yield (18.5 hkg/ha 100% DM)
10.04.09	Ploughed - 24 cm depth
10.04.09	Rolled with a concrete roller
14.04.09	Spring barley sown - cv. Keops
15.05.09	Herbicide - 1.5 l/ha Basagran M75 (bentazone + MCPA)
23.06.09	Fungicide - 1.0 l/ha Amistar (azoxystrobin) – fungi
29.06.09	Irrigation - 26 mm
08.07.09	Mavrik (tau-fluvalinate) - pests - 0.1 l/ha (not analysed)
08.07.09	Irrigation – 27 mm
20.08.09	Harvest of spring barley. Grain yield 53.4 hkg/ha, 85% DM
28.08.09	Straw removed, yield 17.4 hkg/ha 100% DM
04.04.10	Ploughed - 24 cm depth
26.04.10	Rolled with concrete roller
04.05.10	Seedbed preparation - 10 cm depth
06.05.10	Planting of potatoes - cv. Kuras
17.05.10	Ridging
26.05.10	Herbicides - 1.0 l/ha Fenix (aclonifen) + 10 g/ha Titus WSB (rimsulfuron)
08.06.10	Herbicide - 20 g/ha Titus WSB (rimsulfuron)
15.06.10	Fungicide - 0.2 l/ha Ranman (cyazofamid)
24.06.10	Fungicide - 0.2 l/ha Ranman (cyazofamid)
01.07.10	Fungicide - 0.2 l/ha Ranman (cyazofamid)

**Table A3.2** Management practice at **Jynde vad** during the 2007 to 2010 growing seasons. The active ingredients of the various pesticides are indicated in parentheses.

Date	Management practice
13.04.07	Plant growth inhibitor – 1.0 l/ha Cycocel 750 (Chlormequat-chloride)
27.04.07	Irrigation - 27 mm
07.05.07	Herbicide - 1.0 l/ha Opus (epoxiconazole)
05.06.07	Irrigation - 27 mm
07.08.07	Harvest of triticale (seed yield 38.7 hkg/ha 85% DM, straw yield 38.3 hkg/ha 100% DM)
13.09.07	Herbicide - 2.0 l/ha Roundup (glyphosate, not monitored)
28.09.07	Ploughed - 22 cm depth
29.09.07	Rolled with a concrete roller
01.10.07	Winter wheat sown – cv. Ambition
29.10.07	Herbicide - 0.133 g/ha Pico 750 WG (picolinafen)
03.12.07	Fungicide - 1.0 l/ha Folicur EC 250 (tebuconazole)
07.05.08	Irrigation - 42 mm
14.05.08	Irrigation - 27 mm
21.05.08	Irrigation - 27 mm
30.05.08	Irrigation - 30 mm
05.06.08	Irrigation - 35 mm
11.06.08	Fungicide - 1.0 l/ha Amistar (azoxystrobin)
25.06.08	Irrigation - 35 mm
08.07.08	Irrigation - 30 mm
30.08.08	Winter wheat harvested (seed yield 68.1 hkg/ha 85% DM, straw yield 28.1 hkg/ha 100% DM)
17.03.09	Ploughed - 22 cm depth
18.03.09	Rolled with a concrete roller
18.03.09	Spring barley sown cv. Simba
27.04.09	Herbicide - 1.2 l/ha Fox 480 SC (bifenox)
11.05.09	Herbicide - 1.5 l/ha Basagran M75 (bentazone+ MCPA )
26.05.09	Fungicide - 1.5 l/ha Bell (boscalide + epoxiconazole)
27.05.09	Irrigation - 30 mm
05.06.09	Irrigation - 27 mm
29.06.09	Irrigation - 27 mm
07.08.09	Harvest of spring barley. Grain yield 64.0 hkg/ha 85% DM, straw yield 19.5 hkg/ha 100% DM
14.04.10	Ploughed. Depth 24 cm
15.04.10	Rolled with concrete roller
22.04.10	Seedbed preparation - 9 cm depth
04.05.10	Planting of potatoes - cv. Kuras
04.05.10	Ridging
27.05.10	Herbicides - 1.0 l/ha Fenix (aclonifen) + 10 g/ha Titus WSB (rimsulfuron)
08.06.10	Herbicide - 20 g/ha Titus WSB (rimsulfuron)
24.06.10	Irrigation - 25 mm
28.06.10	Fungicide - 0.2 l/ha Ranman (cyazofamid)
30.06.10	Irrigation - 25 mm



**Table A3.3** Management practice at **Silstrup** during the 2007 to 2010 growing seasons. The active ingredients of the various pesticides are indicated in parentheses.

Date	Management practice
13.04.07	Herbicide - 100 ml/ha Hussar OD (iodosulfuron)
13.04.07	Growth retardant - 1.2 l/ha Cycocel 750 (chlormequat-chloride)
07.06.07	Fungicide - 1.0 l/ha Opus (epoxiconazole)
24.08.07	Winter wheat harvested (seed yield 100.7 hkg/ha 85% DM, straw yield 40.8 hkg/ha 100% DM, shredded at harvest)
29.08.07	Stubble harrowed, heavy disk harrow (Dalbo) - 5 cm depth
12.11.07	Ploughed - 27 cm depth
07.05.08	Fodder beet sown - cv. Kyros
22.05.08	Herbicide - 30 g/ha Safari (triflusaluron) + 0.5 l/ha Goliath (metamitron) + 1.5 l/ha Betanal (phenmedipham)
30.05.08	Herbicide - 30 g/ha Safari (triflusaluron) + 0.5 l/ha Goliath (metamitron) + 1.5 l/ha Betanal (phenmedipham) + 0.07 l/ha Trammat 500 SC (ethofumesate)
17.06.08	Herbicide - 30 g/ha Safari (triflusaluron) + 0.5 l/ha Goliath (metamitron) + 1.5 l/ha Betanal (phenmedipham) + 0.07 l/ha Trammat 500 SC (ethofumesate)
26.06.08	Insecticide - 0.30kg/ha Pirimor G (pirimicarb)
01.07.08	Herbicide - 3.0 l/ha Fusilade Max (fluazifop-P-butyl)
04.07.08	Herbicide - 30 g/ha Safari (triflusaluron) + 0.5 l/ha Goliath (metamitron) + 1.5 l/ha Betanal (phenmedipham)
09.07.08	Insecticide - 0.300 kg/ha Pirimor G (pirimicarb)
27.10.08	Fodder beet harvested. Yield of root 17.3 t/ha 100% DM, yield of top 5.15 t/ha 100% DM
15.12.08	Ploughed - 23 cm depth
02.04.09	Tracer - 31.5 kg/ha potassium bromide
11.04.09	Rolled with Cambridge roller
11.04.09	Spring barley sown - cv. Keops; undersown red fescue cv. Jasperina
19.05.09	Herbicide -1.25 l/ha Fighter 480 (bentazone)
24.06.09	Fungicide - 1.0 l/ha Amistar (azoxystrobin)
16.07.09	Wholecrop harvest of spring barley - 94.6 hkg/ha 100% DM
24.08.09	Herbicide - 0.020 l/ha Hussar OD (iodosulfuron)
09.09.09	Herbicide - 1.5 l/ha Fox 480 SC (bifenox)
02.05.10	Herbicide - 1.5 l/ha Fusilade Max (fluazifop-P-butyl)
05.05.10	Herbicides - 0.1 l/ha Hussar OD (iodosulfuron) + 0.7 l/ha SweDane MCPA 750 (not analyzed)

**Table A3.4** Management practice at **Estrup** during the 2007 to 2010 growing seasons. The active ingredients of the various pesticides are indicated in parentheses.

Date	Management practice
11.04.07	Growth retardant - 1.2 l/ha Cycocel 750 (chlormequat-chloride)
31.05.07	Fungicide - 1.0 l/ha Opus (epoxiconazole)
07.08.07	Winter wheat harvested (seed yield 81.5 hkg/ha, 85% DM)
08.08.07	Straw shredded (47.4 hkg/ha, 100% DM)
14.09.07	Herbicide - 1.5 l/ha Roundup Max (glyphosate)
02.10.07	Ploughed - depth 20 cm (packed with a ring roller)
03.10.07	Winter wheat sown – cv. Frument.
30.10.07	Herbicide - 0.133 g/ha Pico 750 WG (picolinafen)
22.11.07	Fungicide - 1.0 l/ha Folicur EC 250 (tebuconazole)
13.06.08	Fungicide - 1.0 Amistar (azoxystrobin)
16.08.08	Winter wheat harvested (seed yield 83.8 hkg/ha 85% DM)
16.08.08	Straw shredded - 40.7 hkg/ha 100% DM
12.03.09	Ploughed - depth 18 cm - packed with a ring roller
06.04.09	Tracer - 30 kg/ha potassium bromide
08.04.09	Spring barley sown - cv. Keops
08.04.09	Rolled with a cambridge roller
01.05.09	Herbicide - 1.2 l/ha Fox 480 SC (bifenox)
14.05.09	Herbicide - 1.5 l/ha Basagran M75 (bentazone/MCPA)
04.06.09	Fungicide - 1.0 l/ha Amistar (azoxystrobin)
07.08.09	Spring barley harvested. Grain yield 71.4 hkg/ha, 85% DM
07.08.09	Straw shredded. 39.9 hkg/ha, 100% DM
24.08.09	Ploughed - 20 cm depth - packed with a ring roller
24.08.09	Rotor harrowed - 4 cm depth
24.08.09	Winter rape sown - cv. Cabernet
25.08.09	Herbicide - 0.33 l/ha Command CS (clomazone)
30.09.09	Herbicide - 0.75 l/ha Fox 480 SC (bifenox)
09.10.09	Insecticide - 0.15 l/ha Cyperb (cypermethrin) (not analysed)
20.04.10	Field partially resown with spring rape - cv. Pluto
10.05.10	Insecticide - 0.3 l/ha Biscay OD 240 (thiacloprid)

**Table A3.5** Management practice at **Faardrup** during the 2007 to 2010 growing seasons. The active ingredients of the various pesticides are indicated in parentheses.

Date	Management practice
10.08.07	Stubble cultivation - 15 cm depth
22.08.07	Stubble cultivation - 15 cm depth
18.09.07	Ploughed and packed - 25 cm depth
18.09.07	Winter wheat sown – cv. Ambition
09.10.07	Herbicide - 5.0 l/ha Stomp (pendimethalin)
20.11.07	Fungicide - 1.0 l/ha Folicur 250 (tebuconazole)
20.08.08	Winter wheat harvested (seed yield 89.6 hkg 85% DM, straw yield 65.2 hkg/ha 100% DM)
26.08.08	Tracer - 30 kg/ha potassium bromide
01.12.08	Ploughing - 23 cm depth
05.04.09	Sugar beet sown - cv. Palace
24.04.09	Herbicide - 1.5 l/ha Betanal (phenmedipham) + 1.0 l/ha Goliath (metamitron)
30.04.09	Herbicide - 10 g/ha Safari (triflusalufuron) + 1.5 l/ha Betanal (phenmedipham) + 1.0 l/ha Goliath
11.05.09	Herbicide - 10 g/ha Safari (triflusalufuron) + 1.5 l/ha Betanal (phenmedipham) + 1.0 l/ha Goliath
14.05.09	Herbicide - 1.0 l/ha Focus Ultra (cycloxydim)
17.06.09	Herbicide - 1.0 l/ha Focus Ultra (cycloxydim)
06.10.09	Harvest of sugar beet. Root yield 147.9 hkg/ha 100% DM, top yield 40.1 hkg/ha 100% DM
01.11.09	Ploughing - 20 cm depth
07.04.10	Seedbed preparation - 6 cm depth
22.04.10	Spring barley sown - mixture of varieties. Undersown red fescue – cv. Maximum
01.06.10	Herbicide - 1.25 l/ha Fighter 480 (bentazone)



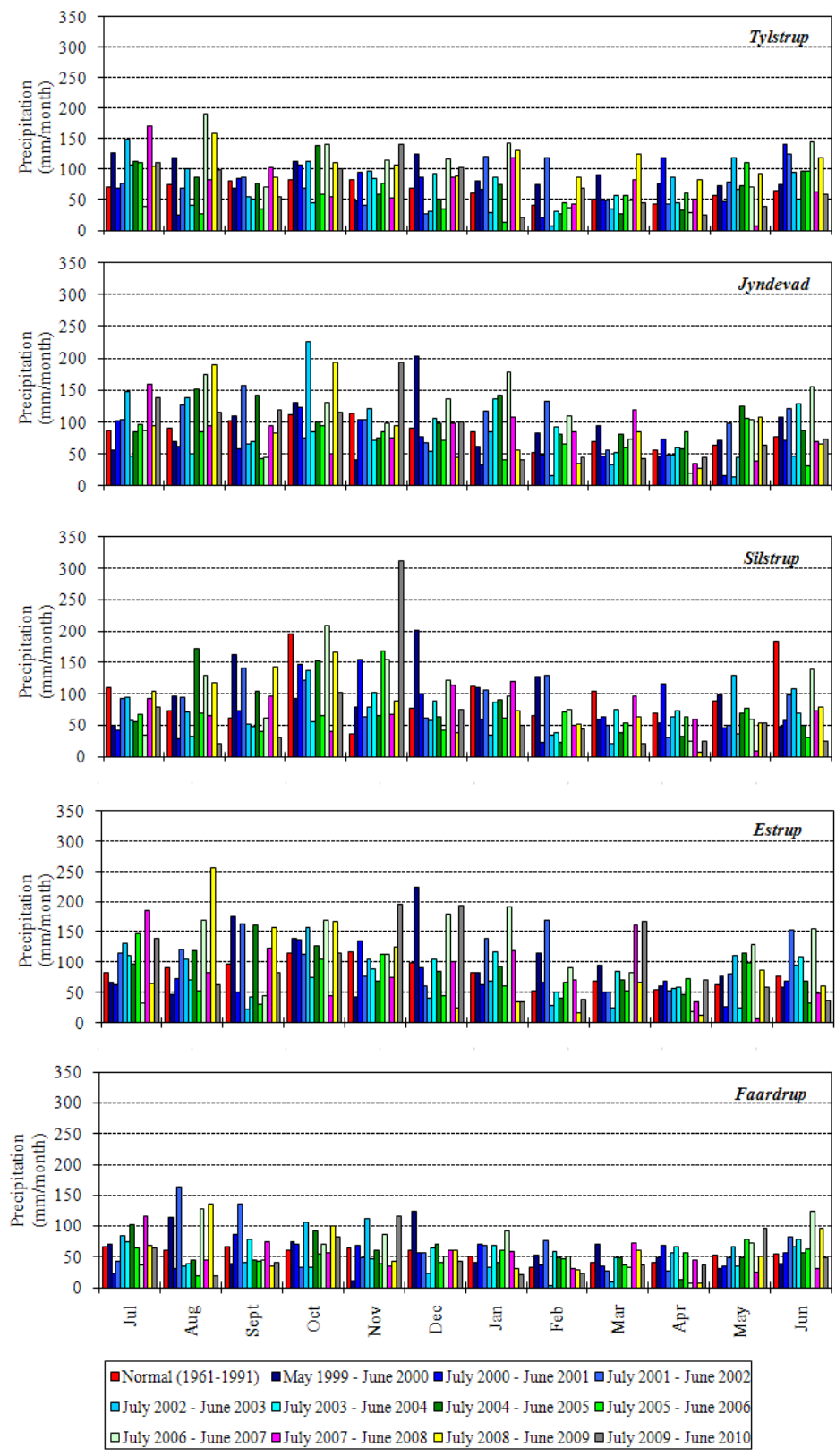


Figure A4.1. Monthly precipitation at all localities for the monitoring period July 2000 – June 2010. Normal values (1961 – 1990) are included for comparison.



**Appendix 5. Pesticide detections in samples from drainage system, suction cups and monitoring wells**

**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
AIBA	191			72		
2-hydroxy-desethyl-terbuthylazine	190	1		67	5	
2-hydroxy-terbuthylazin	191			71	1	
Azoxystrobin	163			67		
Bentazone	277			108	1	
Bromoxynil	192			72		
CGA 322704	175			64		
Clomazone	224			82		
Clopyralid*	6			63		
CyPM	163			67		
Desethyl-terbuthylazine	191			70	2	
Desisopropyl-atrazine	190	1		55	17	
Dimethoate	176			65		
Epoxiconazole	199			74		
ETU	198	2		37	7	
Fenpropimorph	307			89		
Fenpropimorph-acid	276			73		
Flamprop-M (free acid)	176			65		
Flamprop-M-isopropyl	176			65		
Fluazifop-P (free acid)	178			65		
Fluroxypyr	194			70		
FMC65317	208			74		
PPU	507	2		70	119	3
PPU-desamino	509			157	35	
Ioxynil	198			72		
Linuron	270			67		
Metribuzin	386	1		89	2	
Metribuzin-desamino	365			85		
Metribuzin-desamino-diketo	289	231	5	168	30	51
Metribuzin-diketo	71	136	317	73	179	63
Pendimethalin	430			144		
Pirimicarb	295			82		
Pirimicarb-desmethyl	295			81		
Pirimicarb-desmethyl-formamido	167			52		
Propiconazole	307			89		
Propyzamide	221			82		
RH24580	221			82		
RH24644	221			82		
RH24655	157			58		
Rimsulfuron	178			65		
Tebuconazole	195	1		77		
Terbuthylazine	179			72		
TFMP	3					
Thiamethoxam	175			64		
Triasulfuron	295			82		
Triazinamin	285			75		
Triazinamin-methyl	440			137		

\*Number of analysed samples collected from the monitoring wells was reduced (see Appendix 2 for explanation).

**Appendix 5. Pesticide detections in samples from drainage system, suction cups and monitoring wells**

**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 **Jynde vad**. 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
AIBA	178			45	2	
4-chlor-2-methylphenol	189			52		
Amidosulfuron	88			20	2	1
AMPA	221	2		68	1	
Azoxystrobin	233			65		
Bentazone	377			68	34	5
Bifenox	98	2		28	2	
Bifenox acid	48			11		1
Bromoxynil	218			61		
CL153815*	35			36		
Chlormequat*	14			28		
CyPM	233			65		
Desethyl-terbuthylazine	472	24		128	18	
Desmethyl-amidosulfuron	88			23		
Dimethoate	169			48		
Epoxiconazole	323	1		90		
Fenpropimorph	246	1		76	1	
Fenpropimorph-acid	259			79		
Flamprop-M (free acid)	12			4		
Flamprop-M-isopropyl	12			4		
Florasulam	191			54		
Florasulam-desmethyl				28		
Fluazifop-P (free acid)	190			51		
Fluroxypyr	193			55		
Glyphosate	223			69		
PPU	402	282	2	37	99	55
PPU-desamino	616	71		102	85	4
Ioxynil	218			61		
MCPA	189			52		
Mesosulfuron*	12			45		
Mesosulfuron-methyl	285			78		
Metribuzin	26			6		
Metribuzin-desamino	26			4		
Metribuzin-desamino-diketo	6	7	13	6		
Metribuzin-diketo		7	19	3	3	
Nitrofen	100			30		
Pendimethalin	257			71		
PHCP	184			59		
Picolinafen*	35			35	1	
Pirimicarb	251			69		
Pirimicarb-desmethyl	251			68	1	
Pirimicarb-desmethyl- formamido	251			69		
Propiconazole	230			73		
Pyridate	116			39		
Rimsulfuron	168			48		
Tebuconazole	213	1		58		
Terbuthylazine	239			75		
TFMP	3					
Triazinamin-methyl	247			77		

\*Number of analysed samples collected from the monitoring wells was reduced (see Appendix 2 for explanation).



**Appendix 5. Pesticide detections in samples from drainage system, suction cups and monitoring wells**
**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 period, and pesticides monitored for less than one year are not included.

	Drainage			Horizontal			Vertical screens			Suction cups		
	n.d.	det <0.1 µg/l	det >=0.1 µg/l	n.d.	det <0.1 µg/l	det >=0.1 µg/l	n.d.	det <0.1 µg/l	det >=0.1 µg/l	n.d.	det <0.1 µg/l	det >=0.1 µg/l
AIBA	64			74			131					
2-hydroxy-desethyl-terbuthylazine	43	27	1	84			151	1				
2-hydroxy-terbuthylazin	45	26		84			152					
3-aminophenol	53			70			170			36		
4-chlor-2-methylphenol	51			66			124					
AMPA	25	107	15	123	5		226	10		8		
Azoxystrobin	55	10		91			168					
Bentazone	59	40	5	117	8	1	213	17	3			
Bifenox	14	1		16			27	4	1			
Bifenox acid	1		13	11	1	4	23	1	7			
Clopyralid	44			63			118					
Chlormequat	20	1		36			66					
CyPM	24	59	5	120	8		223	19	1			
Desethyl-terbuthylazine	8	64	44	101	32		113	127	2			
Desisopropyl-atrazine	28	43		84			148	4				
Desmedipham	101			107	1		240			58		
Dimethoate	81		1	73	1		147			27		
EHPC	68			62			118			20		
Epoxiconazole	36			62			117					
Ethofumesate	119	14	1	162	2		339	3		54	3	2
Fenpropimorph	82			74			148			27		
Fenpropimorph-acid	81	1		74			147			27		
Flamprop-M (free acid)	73	7		74			148			26		
Flamprop-M-isopropyl	70	11	1	73	1		148			27		
Fluazifop-P (free acid)	106			133	1		283			56		
Fluroxypyr	50			74			142					
Glyphosate	79	52	15	128			232	4		8		
IN-D8526	33			56			102					
IN-E7710	28	5		56			102					
IN-M7222	33			55	1		102					
Iodosulfuron-methyl-MCPA	52			78			149					
Metamitron	51			66			123					
Metamitron-desamino	103	27	4	154	10		323	17	2	40	9	9
Metsulfuron methyl	88	43	3	158	3	3	318	23	1	40	15	4
MHPC	52			78			149					
Nitrofen	100			106			234			55		
Pendimethalin	14	1		16			32					
PHCP	90	14		121			223					
Phenmedipham	62		4	66	2		109	8	4			
Pirimicarb	101			108			240			59		
Pirimicarb-desmethyl	160	14		209			433	3		59		
Pirimicarb-desmethyl-formamido	173	1		209			436			59		
Propiconazole	141			159			308			20		
Propyzamide	76	6		74			148			27		
Prosulfocarb	43	17	6	75	2	1	143	5	1			
RH24580	69	4	1	78	1		147					
RH24644	64	2		78			149					
RH24655	51	15		77	1		148	1				
Terbuthylazine	66			78			149					
TFMP	31	51	9	107	5		173	30	1			
Triazinamin	11	4	17	42	10		57	29	9			
Triazinamin-methyl	41			72			135					
Triflurosulfuron	82			74			148			27		
	33			56			102					

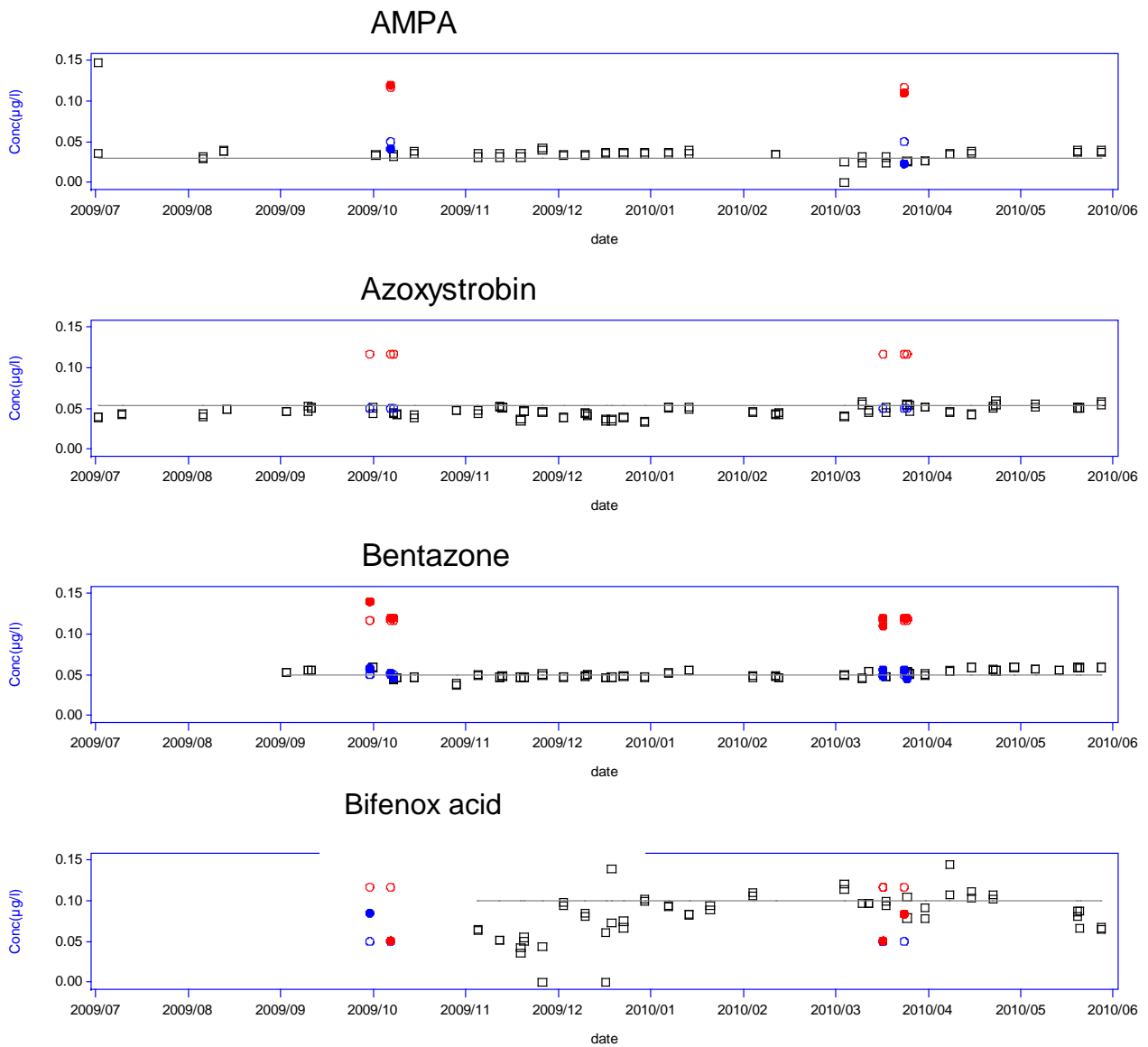
**Appendix 5. Pesticide detections in samples from drainage system, suction cups and monitoring wells**
**Table A5.4** Number of samples where pesticides were either not detected (n.d), detected in concentrations below 0.1 µg/l (det<0.1 µg/l) or detected in concentrations above 0.1 µg/l (det>=0.1µg/l) at **Estrup**. Numbers are accumulated for the entire monitoring period, 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
AIBA	235	1		79	1		271			5		
2-hydroxy-desethyl-terbuthylazine	44	61	25	50			180					
2-hydroxy-terbuthylazine	43	70	17	50			180					
4-chlor-2-methylphenol	101	1		34			112					
Amidosulfuron	98			34			109					
AMPA	44	258	98	158	1		546	7		23		
Azoxystrobin	118	85	15	96			323	1				
Bentazone	169	133	12	107	15		408	1		3	2	2
Bifenox	23	2	1	19			50					
Bifenox acid	12	3	8	18			51					
Bromoxynil	135	1	2	41			125			3		
CL153815	49	20	11	40			118					
Clopyralid	1											
Chlormequat	44	1		18			56					
CyPM	34	100	84	92	4		319	5				
Desethyl-terbuthylazine	18	108	37	59	7		232					
Desisopropyl-atrazine	89	70	1	62	1		197	26				
Dimethoate	88			42			159			23		
Epoxiconazole	35	11	2	19			69					
Ethofumesate	91	27	8	46			158					
Fenpropimorph	82	1		39			150			23		
Fenpropimorph-acid	82			34			124			17		
Flamprop-M (free acid)	118	13		55			208			23		
Flamprop-M-isopropyl	111	20		55			208			23		
Florasulam	91			35			125					
Florasulam-desmethyl	80			30			100					
Fluroxypyr	87	1	2	34			120	1				
Glyphosate	149	162	89	155	2		514	34	3	23		
Ioxynil	118	14	6	41			125			3		
MCPA	91	9	2	34			111	1				
Mesosulfuron	73			24			83					
Mesosulfuron-methyl	61	13		27			99					
Metamitron	81	27	15	46			158					
Metamitron-desamino	76	38	11	46			157					
Metsulfuron methyl	130			55			208			22	1	
Nitrofen	26			19			50					
Picolinafen	63	17		40			118					
Pirimicarb	159	39		67			225	1		6		
Pirimicarb-desmethyl	191			66			223			6		
Pirimicarb-desmethyl-formamido	198	13	13	76			261			5		
Propiconazole	192	22	3	86			309	2		23		
Tebuconazole	39	24	17	39			118	3	2			
Terbuthylazine	49	76	35	63			222	1				
Triazinamin	125			52			195	1		22		
Triazinamin-methyl	1											

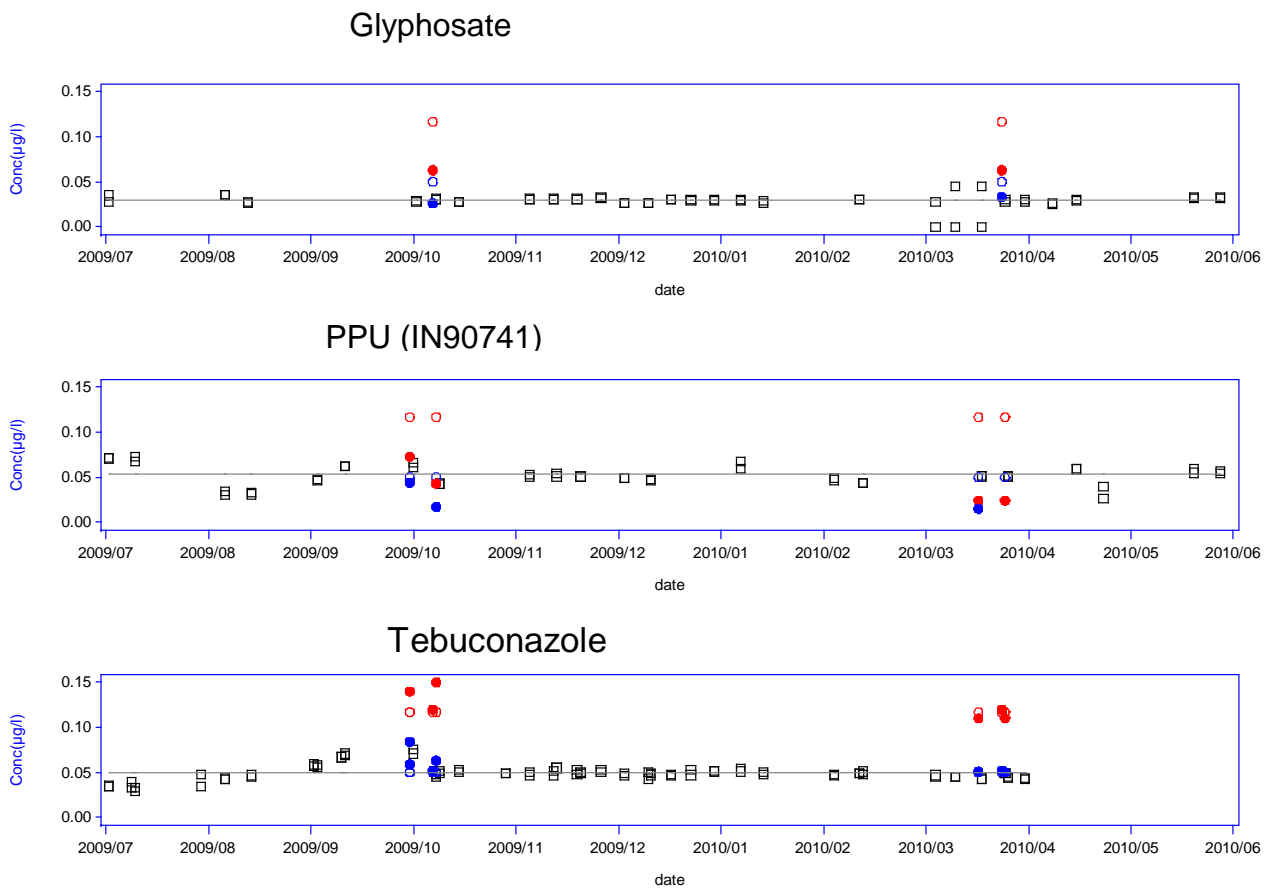
**Appendix 5. Pesticide detections in samples from drainage system, suction cups and monitoring wells**
**Table A5.5** Number of samples where pesticides were either not detected (n.d), detected in concentrations below 0.1 µg/l (det<0.1 µg/l) or detected in concentrations above 0.1 µg/l (det>=0.1µg/l) at **Faarstrup**. Numbers are accumulated for the entire monitoring period, 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
AIBA	68	1		61			132					
2-hydroxy-desethyl-	61	7	1	60	1		126	6				
2-hydroxy-terbuthylazine	90	20	1	85	4		164	30				
4-chlor-2-methylphenol	143		1	109			254					
AMPA	131	9	1	110			282	2		57	5	
Azoxystrobin	107			92			194					
Bentazone	60	12	6	62	3	1	136	4	3			
Bromoxynil	101			81			225			73		
CGA 322704	68			58			126					
Clomazone	84		1	69			166					
CyPM	103	4		92			194					
Desethyl-terbuthylazine	22	82	7	68	21		149	14	31			
Desisopropyl-atrazine	86	24	1	57	32		166	28				
Desmedipham	99			66			165			29		
Dimethoate	77			58			148					
EHPC	83			52			123			16		
Epoxiconazole	81			66			143					
Ethofumesate	114	7	6	90			188	24	7	27	2	
Fenpropimorph	70			58	1		156			54		
Fenpropimorph-acid	70			59			156			54		
Flamprop-M (free acid)	76	1		58			148					
Flamprop-M-isopropyl	70	1		56			142					
Fluazifop-P (free acid)	91	4	4	66			159	5	1	26	3	
Fluazifop-P-butyl	99			66			165			29		
Fluroxypyr	155		1	128	1		305			55		
FMC65317	84		1	69			166					
Glyphosate	137	4		109	1		282	2		61	1	
IN-D8526	27			24			54					
IN-E7710	27			24			54					
IN-M7222	27			24			54					
Ioxynil	99	1		81			224	1		73		
MCPA	142	1	1	109			255					
Metamitron	115	9	3	90			195	19	5	29		
Metamitron-desamino	111	11	5	90			171	36	12	29		
MHPC	97	1	1	66			163	1		29		
Pendimethalin	55	2		55			125					
Phenmedipham	99			66			163	2		29		
Pirimicarb	113	7		90			243	2		52		
Pirimicarb-desmethyl	94	6		66			162	3		29		
Pirimicarb-desmethyl-	97	3		66			163	2		29		
Propiconazole	147			116			303	1		54		
Propyzamide	70	2	2	68	1		155					
Prosulfocarb	79			61			126					
RH24580	74			69			155					
RH24644	70	4		69			155					
RH24655	73	1		69			155					
Tebuconazole	50	4		53			120	1				
Terbuthylazine	70	30	11	83	5	1	149	24	21			
TFMP				1			2					
Thiamethoxam	68			58			126					
Triazinamin-methyl	77			57			147					
Triflurosulfuron	27			24			54					





**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).