

The Danish Pesticide Leaching Assessment Programme

Monitoring results May 1999–June 2009

Annette E. Rosenbom, Walter Brusch, Rene K. Juhler, Vibeke Ernstsen, Lasse Gudmundsson, Jeanne Kjær, Finn Plauborg, Ruth Grant, Per Nyegaard, and Preben Olsen

Geological Survey of Denmark and Greenland
Ministry of Climate and Energy

Faculty of Agricultural Sciences
Aarhus University

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Aarhus University

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

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Preface

In 1998, the Danish Parliament initiated the Danish Pesticide Leaching Assessment Programme (PLAP), an intensive monitoring programme aimed at evaluating the leaching risk of pesticides under field conditions. The Danish Government funded the first phase of the programme from 1998 to 2001. 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 Faculty of Agricultural Sciences (DJF) at Aarhus University and the National Environmental Research Institute (NERI), Aarhus University under the direction of a management group comprising Jeanne Kjær (GEUS), Annette E. Rosenbom (GEUS), Walter Brüsch (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 2009. Results covering part of the period May 1999–June 2008 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, and Kjær *et al.*, 2009). 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 2007.

The report was prepared jointly by Annette E. Rosenbom, Walter Brüsch, Vibeke Ernstsén, Rene K. Juhler, Jeanne Kjær, Per Nyegaard, 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:

- Pesticide and bromide leaching: Walter Brüsch, Preben Olsen, and Annette E. Rosenbom.
- Soil water dynamics and water balances: Annette E. Rosenbom, Finn Plauborg, and Ruth Grant.
- Pesticide analysis quality assurance: Rene K. Juhler.
- Sampling procedure and geochemical analysis: Vibeke Ernstsén.

Annette E. Rosenbom
August 2010

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 41 pesticides and 40 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.). The results of the period 1999-2009 show that regarding:

Yearly average concentration 1 m b.g.s.

- Of the 41 pesticides applied, **12 pesticides** and/or their degradation product(-s) (clopyralid, chlormequat, desmedipham, fenpropimorph, florasulam, iodosulfuron-methyl-sodium, linuron, mancozeb, metsulfuron-methyl, phenmedipham, thiamethoxam, tribenuronmethyl, and triasulfuron) **did not leach** during the 1999-2009 monitoring period.
- **13 of the applied pesticides** exhibited **pronounced leaching of the pesticide** and/or their degradation product(-s) 1 m b.g.s. in yearly average concentrations exceeding 0.1 µg/l (maximum allowable concentration). Thus:
 - azoxystrobin and its degradation product CyPM
 - bentazone
 - ethofumesate
 - TFMP (degradation product of fluazifop-P-butyl)
 - glyphosate and its degradation product AMPA
 - metamitron and its degradation product metamitron-desamino
 - metribuzin-desamino-diketo and metribuzin-diketo (degradation products of metribuzine)
 - CL153815 (degradation product of picolinafen)
 - pirimicarb-desmethyl-formamido (degradation product of pirimicarb)
 - propyzamide
 - PPU and PPU-desamino (degradation products of rimsulfuron)
 - terbuthylazine and its degradation products: desethyl-terbuthylazine, desiospropyl-atrazine, 2-hydroxy-desethyl-terbuthylazine, and 2-hydroxy-terbuthylazine
 - tebuconazole

were frequently detected in samples from suction cups and drainage systems.

- The monitoring data also indicate **leaching of an additional 16 pesticides, but in low concentrations**. Although concentrations exceeded 0.1 µg/l in several samples, average leaching concentrations on a yearly basis did not.

Detections in groundwater monitoring screens

- Of the 41 pesticides applied, **16 pesticides and/or their degradation products** (picolinafen, amidosulfuron, bromoxynil, clomazone, epoxiconazole, mesosulfuron-methyl, triflurosulfuron-methyl, clopyralid, chlormequat, florasulam, iodosulfuron-methyl-sodium, linuron, metsulfuron-methyl, thiamethoxam, tribenuronmethyl, and triasulfuron) **were not detected** during the 1999-2009 monitoring period.
- **9 of the pesticides and/or their degradation products:**
 - bentazone
 - ethofumesate
 - TFMP and fluazifop-P (degradation products of fluazifop-P-butyl)
 - glyphosate and its degradation product AMPA
 - metamitron and its degradation product metamitron-desamino
 - metribuzin-desamino-diketo and metribuzin-diketo (degradation products of metribuzin)
 - propyzamide
 - PPU (degradation product of rimsulfuron)
 - terbuthylazine and its degradation product desethyl-terbuthylazine.

were in some instances detected in the groundwater monitoring wells **in concentrations exceeding 0.1 µg/l**. Consequently, the Danish Environmental Protection Agency banned the use of metribuzin and enforced considerable restrictions on the use of terbuthylazine, which has now been totally banned. In the autumn 2008, the Danish Environmental Protection Agency enforced considerable restrictions on the application of fluazifop-P-butyl, which, given the pronounced leaching of its degradation product TFMP have proven highly needed. Leaching of TFMP relating to the present-day more restrictive terms is now being evaluated via PLAP. For the rest of the compounds it is assessed by the Danish Environmental Protection Agency that no restriction is needed given a yearly average concentration not exceeding 0.1 µg/l. New results from one of PLAP-field-sites show that late summer periods with several pronounced rain events (more than 50 mm/day) can generate leaching of the herbicide glyphosate through drained, clayey soils into the groundwater – also this will be evaluated further via PLAP.

- Additional **16 pesticides were detected**, however, **in low concentrations** not 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).

Pesticides were applied in the maximum permitted dose. In order to describe water transport, a bromide tracer was applied to the fields. Bromide and pesticide concentrations are measured monthly in both the unsaturated and the saturated zones, and weekly in the drainage water. This report covers the period May 1999–June 2009 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 2007.

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. Udvaskningsrisikoen for 41 pesticider og 40 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.). De hidtidige resultater for perioden 1999-2009 viser følgende vedrørende:

Årlige gennemsnitskoncentrationer 1 m u.t.

- Af de 41 pesticider, der er blevet udbragt, blev **12 pesticider eller nedbrydningsprodukter heraf** (clopyralid, chlormequat, desmedipham, fenpropimorph, florasulam, iodosulfuron-methyl-natrium, linuron, mancozeb, metsulfuron-methyl, phenmedipham, thiamethoxam, tribenuronmethyl og triasulfuron) **ikke fundet udvasket** i løbet af perioden 1999–2009.
- **13 af de udbragte pesticider gav anledning til en væsentlig udvaskning** enten af pesticidet og/eller dets nedbrydningsprodukt(-er) i 1 meters dybde i årlige gennemsnitskoncentrationer over 0,1 µg/l. Disse stoffer:
 - azoxystrobin og dets nedbrydningsprodukt CyPM
 - bentazon
 - ethofumesat
 - TFMP (nedbrydningsprodukt af fluazifop-P-butyl)
 - glyphosat og dets nedbrydningsprodukt AMPA
 - metamitron og dets nedbrydningsprodukt metamitron-desamino
 - metribuzin-desamino-diketo og metribuzin-diketo (nedbrydningsprodukter af metribuzin)
 - CL153815 (nedbrydningsprodukt af picolinafen)
 - pirimicarb-desmethyl-formamido (nedbrydningsprodukt af pirimicarb)
 - propyzamid
 - PPU and PPU-desamino (nedbrydningsprodukter af rimsulfuron)
 - terbuthylazin og dets nedbrydningsprodukter desethyl-terbuthylazin, desiospropyl-atrazin, 2-hydroxy-desethyl-terbuthylazin og 2-hydroxy-terbuthylazin
 - tebuconazol

blev hyppigt fundet i prøver udtaget med sugeceller og fra drænrør.

- Andre **16 stoffer gav anledning til mindre udvaskning**. Selv om flere af disse stoffer ofte blev fundet i koncentrationer over 0,1 µg/l, var der ikke tale om, at udvaskningen som årsmiddel oversteg 0,1 µg/l.

Fund i grundvandsmoniteringsfiltre

- Af de 41 pesticider, der er blevet udbragt, blev **16 pesticider** og/eller nedbrydningsprodukt(-er) heraf (picolinafen, amidosulfuron, bromoxynil, clomazon, epoxiconazol, mesosulfuron-methyl, triflusaluron-methyl, clopyralid, chlormequat, florasulam, iodosulfuron-methyl-natrium, linuron, metsulfuron-methyl, thiamethoxam, tribenuronmethyl og triasulfuron) **ikke fundet udvasket** i løbet af perioden 1999–2009.
- **9 af de udbragte pesticider** og/eller dets nedbrydningsprodukt(-er):
 - bentazon
 - ethofumesat
 - TFMP og fluazifop-P (nedbrydningsprodukter af fluazifop-P-butyl)
 - glyphosat og dets nedbrydningsprodukt AMPA
 - metamitron og dets nedbrydningsprodukt metamitron-desamino
 - metribuzin-desamino-diketo og metribuzin-diketo (nedbrydningsprodukter af metribuzin)
 - propyzamid
 - PPU (nedbrydningsprodukt af rimsulfuron)
 - terbuthylazin og dets nedbrydningsprodukt desethyl-terbuthylazin.

blev i nogle tilfælde fundet i koncentrationer over 0,1 µg/l. Som følge heraf har Miljøstyrelsen forbudt metribuzin og lagt meget væsentlige restriktioner på anvendelsen af terbuthylazin, som efterfølgende ligeledes er blevet forbudt. At Miljøstyrelsen i efteråret 2008 lagde væsentlige restriktioner på anvendelsen af fluazifop-P-butyl har nu vist sig at være berettiget p.g.a. markant udvaskning af nedbrydningsproduktet TFMP med de tidligere mere lempeligere krav til anvendelse. Udvasning af TFMP, med de nye restriktive krav til anvendelsen, bliver nu undersøgt i VAP-regi. For de øvrige stoffer har Miljøstyrelsen vurderet, at der ikke har været behov for indgreb, idet den årlige gennemsnitskoncentration ikke overskrider grænseværdien. Nye tal fra én af VAP-forsøgsmarkerne viser, at sensommerperioder med flere markante regnhændelser (mere end 50 mm/dag) kan generere udvaskning af ukrudtsmidlet glyphosat igennem drænet lerjord til grundvandet – dette vil ligeledes blive undersøgt nærmere.

- Andre **16 pesticider** og/eller dets nedbrydningsprodukt(-er) **blev fundet i koncentrationer under 0,1 µg/l.**

VAP-programmet omfattede oprindeligt seks marker placeret, så de repræsenterer forskellige typer geologi og tillige tager hensyn til de klimatiske variationer i Danmark, specielt hvad angår nedbørforhold. Monitering på den ene forsøgsmark (Slæggerup) stoppede den 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 2009 primært med fokus på pesticider udbragt i 2007. 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, Annex 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, 40 pesticides and 40 degradation products are included in the PLAP. All the compounds analysed are listed in Appendix 1.

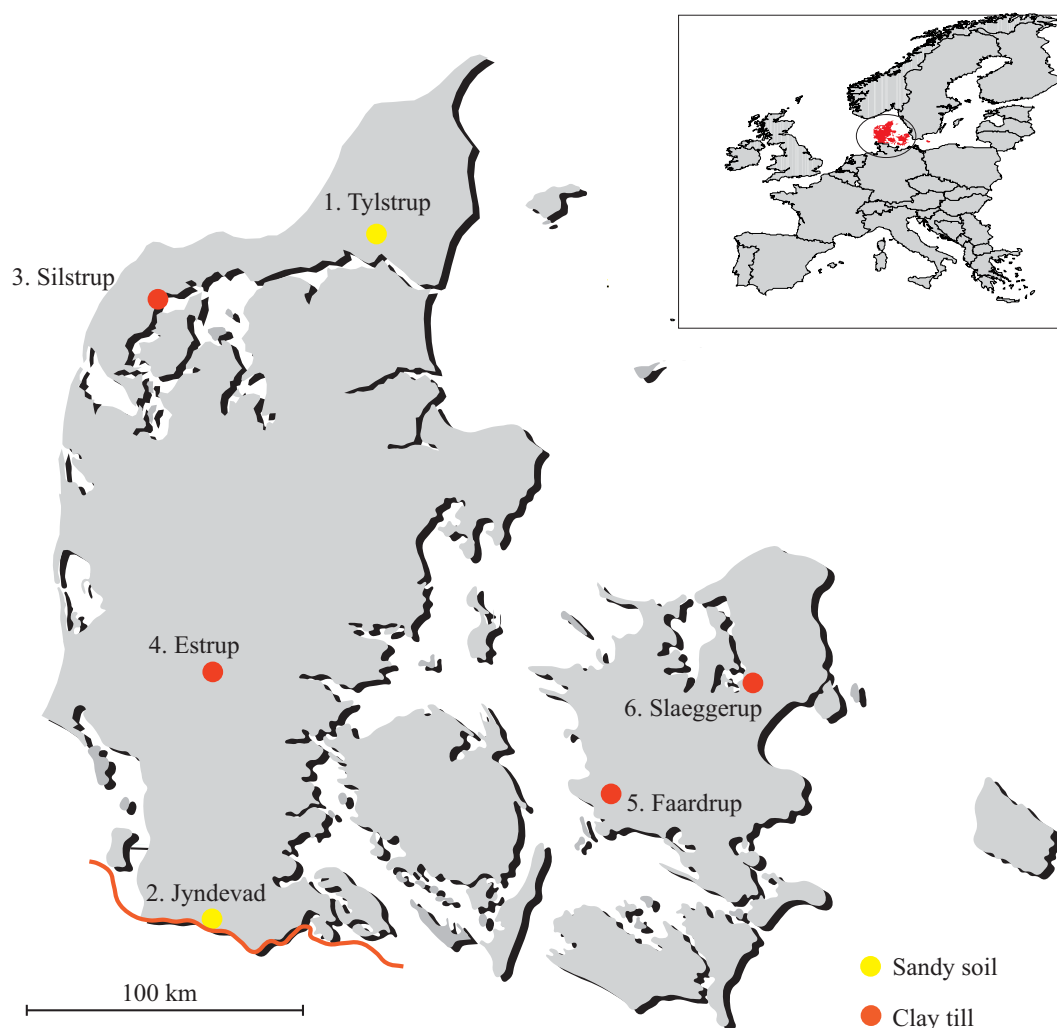


Figure 1. Location of the PLAP sites **Tylstrup**, **Jynde vad**, **Silstrup**, **Estrup**, and **Faardrup**. Monitoring at Slaeggerup was terminated on 1 July 2003.

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, Jyndevad and Faardrup in 1999 and at Silstrup and Estrup in 2000 (Table 1).

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

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

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

²⁾ Large variation within the field.

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

Site characterization and monitoring design are described in detail in Lindhardt *et al.* (2001). The present report presents the results of the monitoring period May 1999–June 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 2006), see Kjær *et al.*, (2002), Kjær *et al.* (2003), Kjær *et al.* (2004), Kjær *et al.* (2005c), Kjær *et al.* (2006), Kjær *et al.* (2007), Kjær *et al.* (2008), and Kjær *et al.* (2009).

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 2009. The five site models have been calibrated for the monitoring period May 1999–June 2004 and validated for the monitoring period July 2004–June 2009.

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 characterized 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).

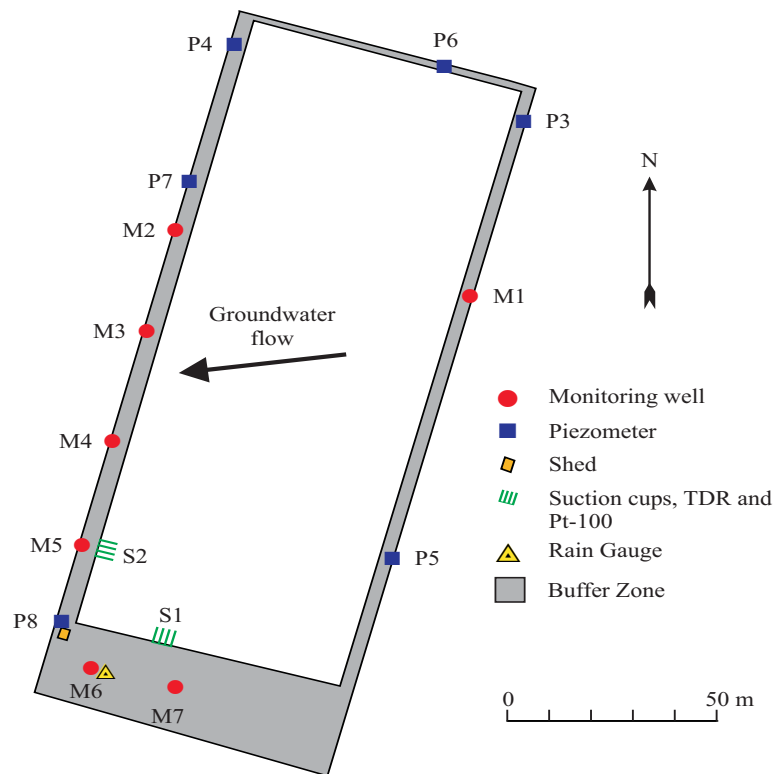


Figure 2. Overview of the Tylstrup site. The innermost white area indicates the cultivated land, while the grey area indicates the surrounding buffer zone. The positions of the various installations are indicated, as is the direction of groundwater flow (by an arrow).

2.1.2 Agricultural management

Management practice during the 2007 and 2008 growing seasons is briefly summarized below and detailed in Appendix 3 (Table A3.1). For information about management practice during the previous monitoring periods, see Kjær *et al.* (2002, 2003, 2004, 2005c, 2007, 2008, and 2009).

The field was rotary-cultivated twice on 3 August and 7 September 2007 in order to incorporate the rape residues. Ploughing on 12 September was followed by the sowing of winter wheat (cv. Smuggler) on 24 September, which emerged on 5 October. The herbicide pendimethalin was applied on 18 October at the stage of one unfurled leaf. The fungicide tebuconazol was used on 16 November, at which time three leaves were unfurled. On both 22 and 29 May 2008, 32 mm of irrigation was applied and on both 5 and 13 June, 30 mm was applied. The fungicide azoxystrobin was applied on 17 June at the end of flowering, but not included in the monitoring. The winter wheat was harvested on 18 August, yielding 92.1 hkg/ha of grain (85% dry matter), which was 40% above the average for this soil type and year (Plantedirektoratet, 2008), and 18.5 hkg/ha of straw (100% dry matter).

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) 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% dry matter) was removed from the field.

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 2009 and to establish an annual water balance.

Compared to Kjær *et al.* (2009), 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 2009. 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) and Rosenbom *et al.* (*In prep.*).

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

	Normal precipitation ²⁾	Precipitation	Irrigation	Actual evapotranspiration	Groundwater recharge ³⁾
1.5.99–30.6.99 ¹⁾	120	269	0	112	156
1.7.99–30.6.00	773	1073	33	498	608
1.7.00–30.6.01	773	914	75	487	502
1.7.01–30.6.02	773	906	80	570	416
1.7.02–30.6.03	773	918	23	502	439
1.7.03–30.6.04	773	758	0	472	287
1.7.04–30.6.05	773	854	57	477	434
1.7.05–30.6.06	773	725	67	488	304
1.7.06–30.6.07	773	1147	59	591	615
1.7.07–30.6.08	773	913	126	572	467
1.7.08–30.6.09	773	1269	26	600	695

¹⁾ Accumulated for a two-month period.

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

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

2.2 Results and discussion

2.2.1 Soil water dynamics and water balances

The model simulations were generally consistent with the observed data, thus indicating a good model description of the overall soil water dynamics in the unsaturated zone (Figure 3). The overall trends in soil water saturation were modelled successfully, with the model capturing soil water dynamics at all depths (Figure 3C-E). The initial decrease in water saturation observed during the summer periods at 25, 60 and 110 cm b.g.s. was, however, less well captured. The dynamics of groundwater table were captured with some exceptions, but as with previous simulations the amplitude of the fluctuations was less well described (Figure 3B).

The resulting annual water balance is shown for each hydraulic year of the monitoring period (July–June) in Table 2. Values for precipitation and actual evapotranspiration for the most recent hydraulic year, July 2008–June 2009, were the highest observed since monitoring began at the site, and the monthly precipitation pattern for this year was medium to high compared with earlier years. Especially August and March were very wet (Appendix 4). Artificial irrigation was therefore minimal and the groundwater recharge/percolation was the highest of all monitored years. The simulated percolation 1 m b.g.s. in June was, however, not observed (Figure 3A).

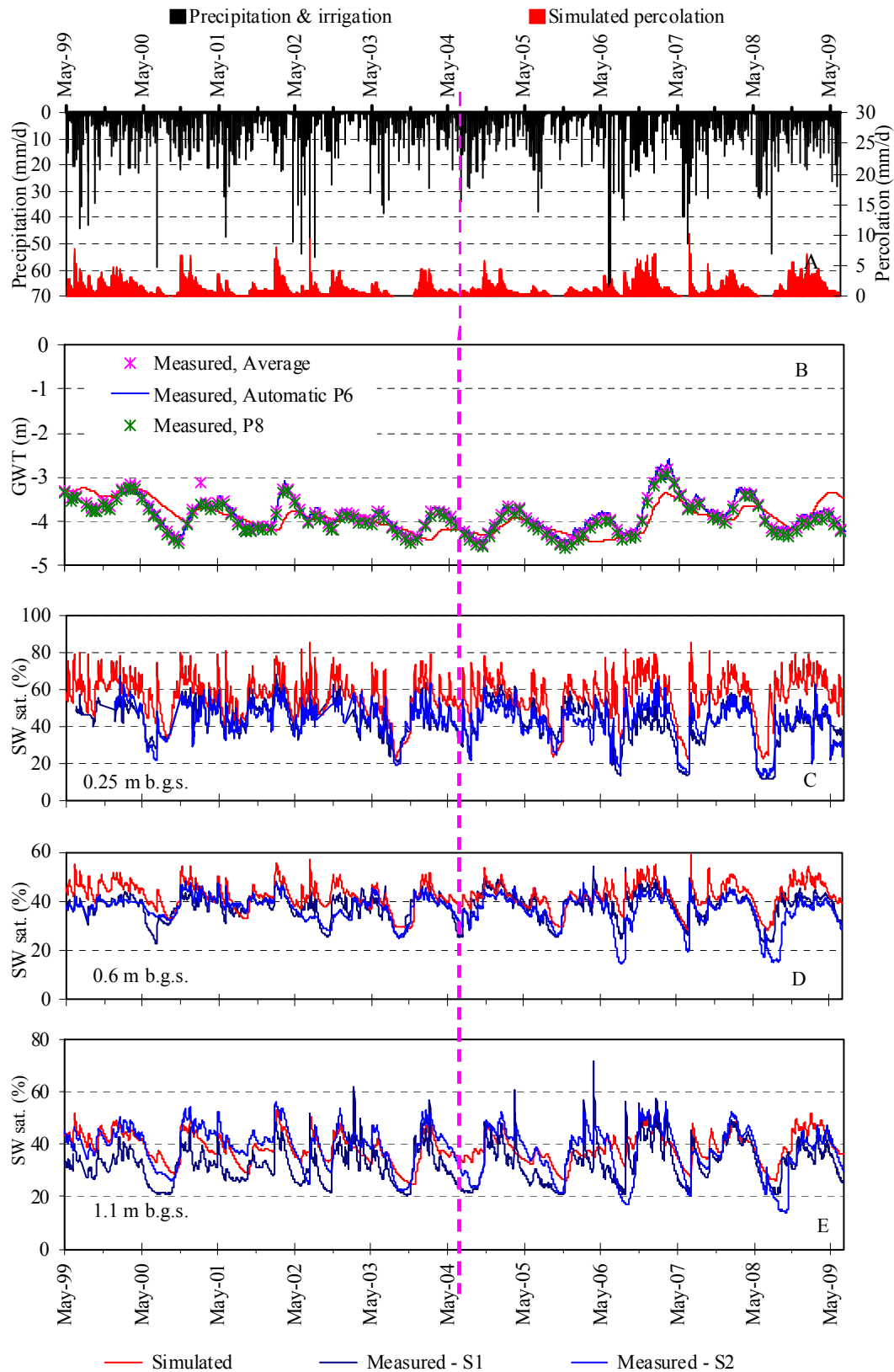


Figure 3. Soil water dynamics at Tylstrup: Measured precipitation, irrigation and simulated percolation 1 m b.g.s. (A), simulated and measured groundwater level GWT (B), and simulated and measured soil water saturation (SW sat.) at three different soil depths (C, D and E). The measured data in B derive 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 2009).

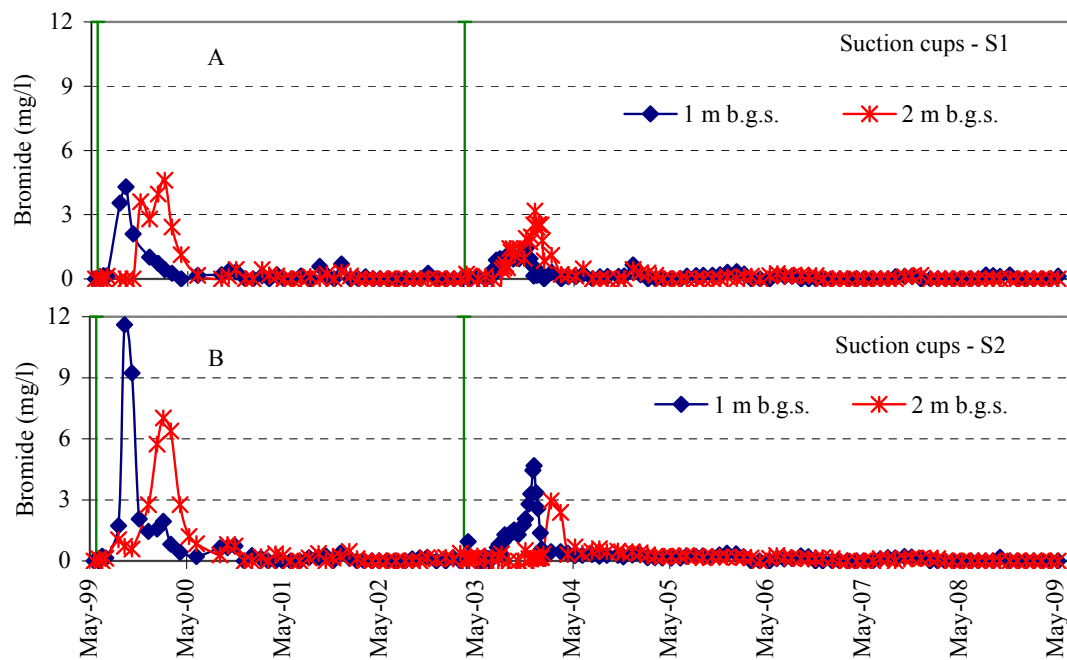


Figure 4. Measured bromide concentration in the unsaturated zone at **Tylstrup**. The measured data derive from suction cups installed 1 m b.g.s. and 2 m b.g.s. at locations S1 (A) and S2 (B) indicated in Figure 2. The green vertical lines indicate the dates of bromide applications.

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

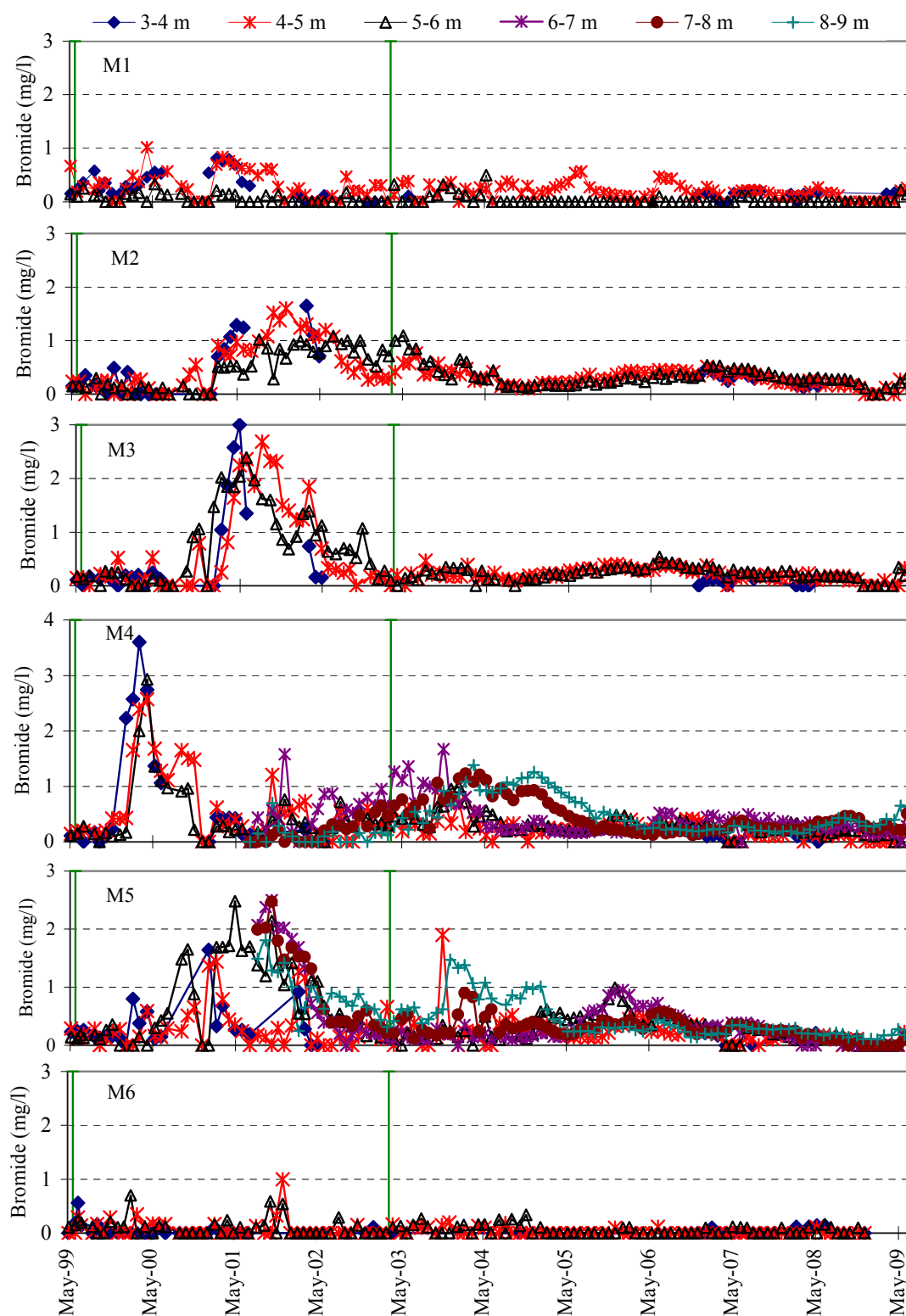


Figure 5. Bromide concentration in the groundwater at **Tylstrup**. The data derive from monitoring wells M1–M6. Monitoring at well M6 was suspended September 2008 (Appendix 2). Screen depth is indicated in m b.g.s. The green vertical lines indicate the dates of bromide applications.

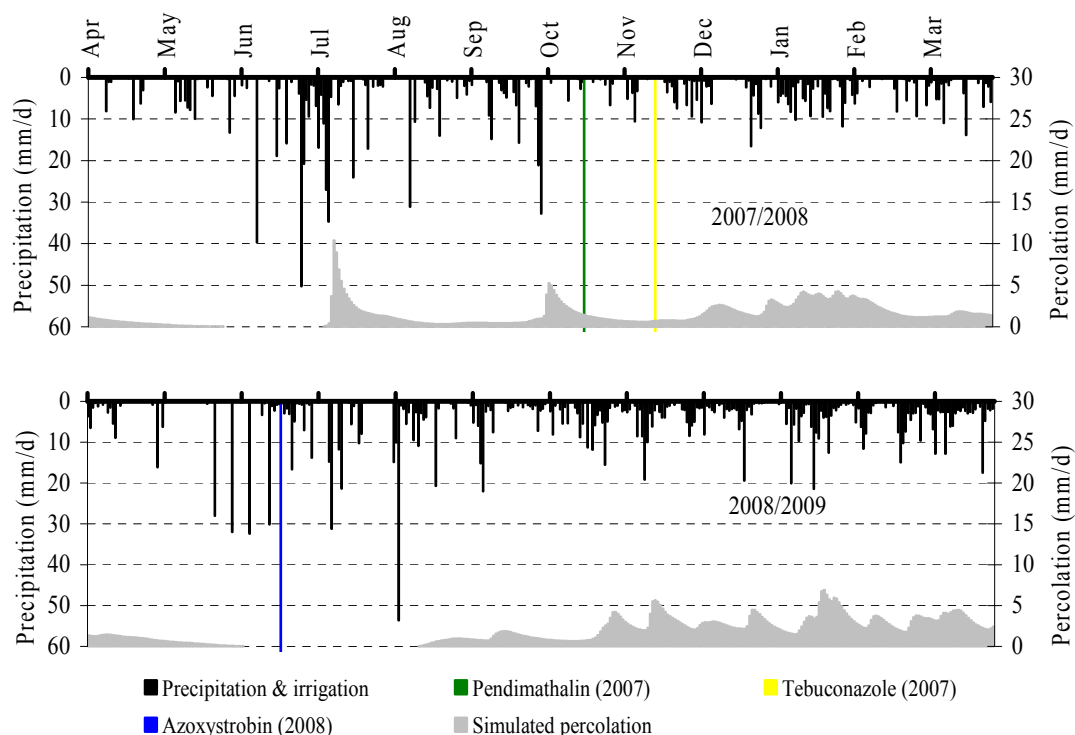


Figure 6. Application of pesticides included in the monitoring programme, precipitation and irrigation (primary axis) together with simulated percolation 1 m b.g.s. (secondary axis) at **Tylstrup** in 2007/2008 (upper) and 2008/2009 (lower).

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), rimsulfuron (applied here as Titus), and propyzamide (Kerb 500 SC). The risk of leaching is therefore associated with their respective degradation products: ETU, triazinamin-methyl, PPU, PPU-desamino and RH-24644, RH-24580 and RH-24655 rather than the parent compounds. This is why the degradation products and not the parent compounds are monitored in PLAP (Table 3). Pesticides applied later than April 2009 are not evaluated in this report and hence are not included in Table 3 and Figure 6.

The leaching risk of pesticides applied from 2000 to 2008 has been evaluated in Kjær *et al.* (2002, 2003, 2004, 2005c, 2007, 2008, and 2009). The leaching of metribuzin is further detailed in Kjær *et al.* (2005b) and Rosenbom *et al.* (2009).

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

Crop and analysed pesticides	Application date	End of monitoring	Prec. (mm)	Perc. (mm)	1 st month perc. (mm)	C _{mean} (µg/L)
Potatoes 1999						
Linuron (Afalon)	May 99	Jul 01	2550	1253	87	<0.01 (0)
- <i>ETU</i> ¹⁾ (Dithane DG)	Jun 99	Oct 01	2381	1169	73	<0.01(9)
Metribuzin (Sencor WG)	Jun 99	Jul 03	4223	2097	85	<0.01 (3)
- <i>metribuzin-diketo</i>		Jul 09 [†]	10227	4907	85	0.05–0.36(678)
- <i>metribuzin-desamino</i>		Jul 03	4223	2097	85	<0.02 (0)
- <i>metribuzin-desamino-diketo</i>		Jul 09 [†]	8689	4192	85	0.14–0.97 (317)
Spring barley 2000						
Triasulfuron (Logran 20 WG)	May 00	Apr 03	2740	1283	13	<0.02 (0)
- <i>triazinamin</i>						<0.02 (0)
Propiconazole (Tilt Top)	Jun 00	Jul 03	2948	1341	11	<0.01 (0)
Fenpropimorph (Tilt Top)	Jun 00	Jul 03	2948	1341	11	<0.01 (0)
- <i>fenpropimorphic acid</i>						<0.02 (0)
Pirimicarb (Pirimor G)	Jun 00	Apr 03	2622	1263	17	<0.01 (0)
- <i>pirimicarb-desmethyl</i>						<0.02 (0)
- <i>pirimicarb-desmethyl-formamido</i>						<0.02 (0)
Winter rye 2001						
Pendimethalin (Stomp SC)	Nov 00	Apr 03	2271	1219	109	<0.01 (0)
<i>Triazinamin-methyl</i> ²⁾ (Express)	Nov 00	Apr 03	2271	1219	109	<0.02 (0)
Propiconazole (Tilt Top)	May 01	Jul 03	2948	1341	11	<0.01 (0)
Fenpropimorph (Tilt Top)	May 01	Jul 03	2948	1341	11	<0.01 (0)
- <i>fenpropimorphic acid</i>						<0.01 (0)
Winter rape 2002						
Clomazone (Command CS)	Sep 01	Jul 04	2534	1194	9	<0.01 (0)
- <i>propanamide-clomazone</i>						<0.02 (0)

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

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

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

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

Degradation products of rimsulfuron, which was applied in June 2004, continued to leach also in 2008/2009. The results of this 2004 application are summarised below and in Rosenbom *et al.* (2010).

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 at S1, 10 months after the application of rimsulfuron (Figure 7B), whereafter PPU was found in 62 out of 79 analysed samples with concentrations ranging between 0.017 and 0.150 µg/l. At S1, PPU-desamino has been found in 27 out of 97 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 34 out of 84 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 slowly decreased, 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. 1st month perc. refers to accumulated percolation within the first month after the application. C_{mean} refers to average leachate concentration at 1 m b.g.s. the first year after application. The number of pesticide-positive samples is indicated in parentheses.

Crop and analysed pesticides	Application date	End of monitoring	Prec. (mm)	Perc. (mm)	1 st month perc. (mm)	C _{mean} (µg/l)
Winter wheat 2003						
Bromoxynil (Oxitril CM)	Oct 02	Apr 05	2082	995	53	<0.01 (0)
Ioxynil (Oxitril CM)	Oct 02	Apr 05	2082	995	53	<0.01 (0)
Fluroxypyr (Starane 180)	May 03	Jul 05	1867	787	50	<0.02 (0)
Flamprop-M-isopropyl (Barnon Plus 3)	May 03	Jul 05	2635	1031	42	<0.01 (0)
- <i>Flamprop-M (free acid)</i>						
Dimethoate (Perfekthion 500 S)	Jul 03	Jul 05	1629	722	14	<0.01 (0)
Potatoes 2004						
- <i>Fluazifop-P (free acid)</i> ¹⁾ (Fusilade X-tra)	May 04	Jul 06	1754	704	16	<0.01 (0)
- PPU ²⁾ (Titus)	Jun 04	Jul 09 [†]	5296	2528	13	<0.01 (97) ³⁾
- PPU-desamino ²⁾ (Titus)	Jun 04	Jul 09 [†]	5296	2528	13	<0.01 (30) ³⁾
Maize 2005						
Terbuthylazine (Inter-Terbutylazin)	May 05	Jul 07	2145	933	16	<0.01 (0)
- <i>desethyl-terbuthylazine</i>						<0.01 (2)
- <i>2-hydroxy-terbuthylazine</i>						<0.01 (1)
- <i>desisopropyl-atrazine</i>						<0.01 (18) ³⁾
- <i>2-hydroxy-desethyl-terbuthylazine</i>						<0.01 (6)
Bentazone (Laddok TE)	Jun 05	Jul 07	2061	927	33	<0.01 (1 [*])
- AIBA						<0.01 (0)
Spring barley 2006						
- <i>triazinamin-methyl</i> ⁴⁾ (Express ST)	Jun 06	Jul 08	2349	1184	43	<0.02 (0)
Epoxiconazole (Opus)	Jul 06	Jul 08	2233	1148	24	<0.01 (0)
Winter rape 2007						
Thiamethoxam (Cruiser RAPS) ⁵⁾	Aug 06	Apr 08	2030	1123	57	<0.01 (0)
- CGA 322704						<0.02 (0)
Propyzamide (Kerb 500 SC)	Feb 07	Apr 09	2400	1172	40	<0.01 (0)
- RH-24644						<0.01 (0)
- RH-24580						<0.01 (0)
- RH-24655						<0.01 (0)
Clopyralid (Matrigon)	Mar 07	Apr 09	2317	1112	24	<0.01 (0)
Winter wheat 2008						
Pendimethalin (Stomp)	Oct 07	Jul 09 [†]	1936	1029	27	<0.01 (0)
Tebuconazole (Folicur EC250)	Nov 07	Jul 09 [†]	1900	1004	46	<0.01 (1)
Azoxystrobin (Amistar)	Jun 08	Jul 09 [†]	1350	671	0	<0.01(0)
- CyPM						
Spring barley 2009						
Bentazone (Basagran M75)	May 09	Jul 09 [†]	169	32	22	<0.01 (1 [*])

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

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

²⁾ Degradation product of rimsulfuron. The parent compound degrades too rapidly to be detected by monitoring. rimsulfuron has, however, been analyzed in more than 200 water samples after its application without any detections.

³⁾ Leaching increased the second year after application (see Figure 7).

⁴⁾ Degradation product of tribenuron-methyl. The parent compound degrades too rapidly to be detected by monitoring.

⁵⁾ 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.

[†] Monitoring will continue during the following year. The values for prec. and perc. are accumulated up to July 2009.

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

PPU was found in a single groundwater sample (0.045 µg/l on 7 December 2005 in the monitoring screen of M4 located 4.4-5.4 m b.g.s.). PPU-desamino has not been detected in the groundwater (Table A5.1 in Appendix 5).

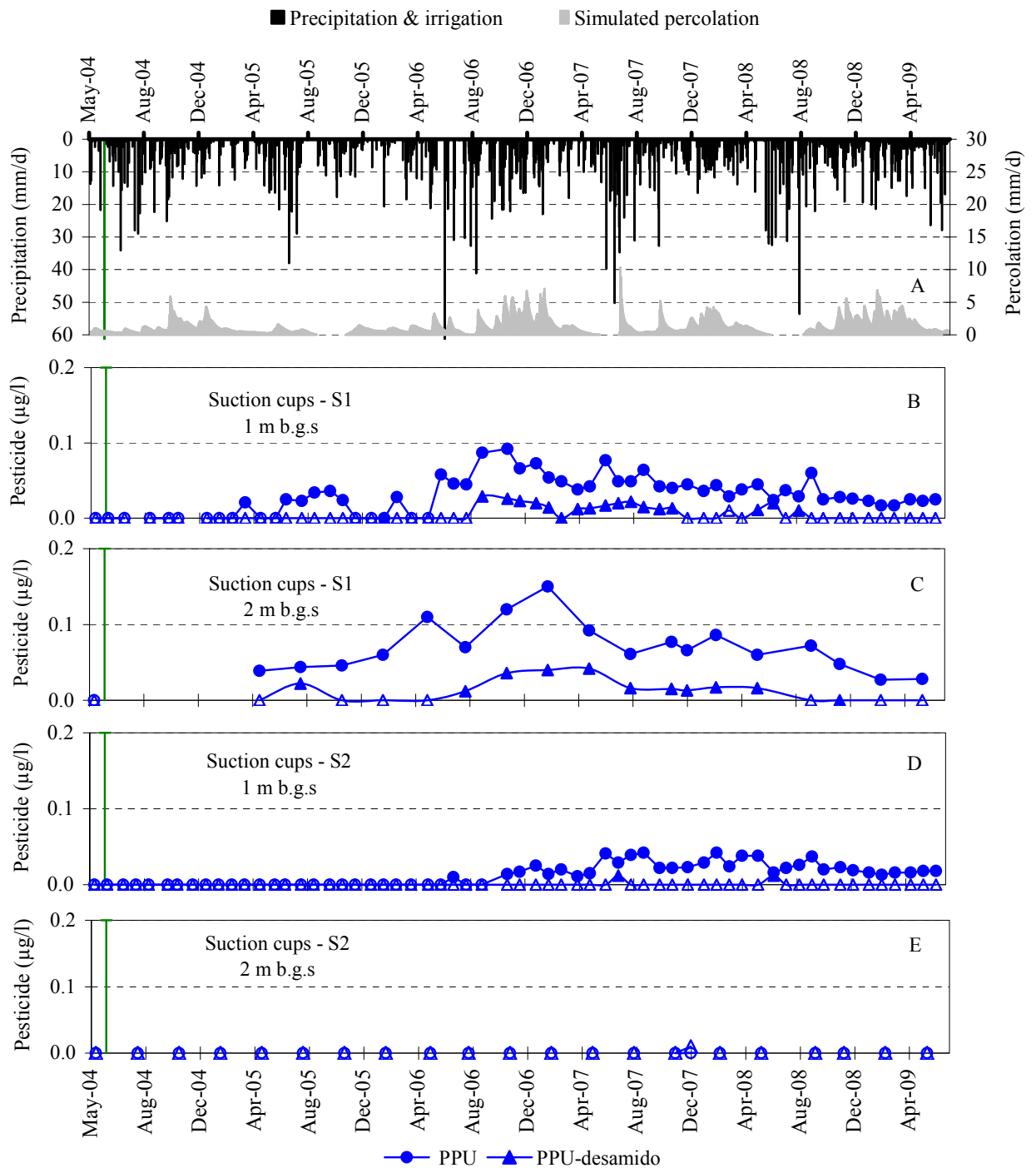


Figure 7. Precipitation, irrigation and simulated percolation 1 m b.g.s. (A) together with measured concentration of PPU and PPU-desamino (µg/l) in suction cups installed at location S1 at 1 m b.g.s. (B) and 2 m b.g.s. (C) and location S2 at 1 m b.g.s. (D) and 2 m b.g.s. (D) at Tylstrup. The green vertical line indicates the date of pesticide application. Open symbols indicate concentrations below the limit of detection (0.02 µg/l prior to July 2006 and 0.01 µg/l thereafter).

Table 4. Percolation together with estimated average concentration (µg/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

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.*, 2010; 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-desamido is likely to be overestimated.

In June 2006 tribenuron-methyl and epoxiconazole were applied to spring barley. Tribenuron-methyl degrades rapidly and therefore only the degradation product triazineamine-methyl is monitored. No trace of epoxiconazole or its degradation product triazineamine-methyl was found in water samples taken from groundwater or suction cups in the monitoring period 2006 to June 2008 (Table 3).

The pesticides applied on winter rape 2007 and winter wheat 2008 and their degradation products (Table 3) have not been found in any of the analysed water samples from suction cups, but tebuconazole has been found in one sample from groundwater (M4.2, 09-04-2008) at a concentration of 0.011 µg/l.

In May 2009 bentazone was applied to spring barley. So far bentazone has been found in one sample (10 April 2006, at S1 1 m b.g.s.) originating from the application in 2005. The final evaluation awaits an additional year of monitoring.

3 Pesticide leaching at Jynde vad

3.1 Materials and methods

3.1.1 Site description and monitoring design

Jynde vad 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 2007-2008 growing seasons is briefly summarized below and detailed in Appendix 3 (Table A3.2). For information about management practice during the previous monitoring periods see Kjær *et al.* (2002, 2003, 2004, 2005c, 2007, 2008, and 2009).

Having been sprayed with glyphosate (not included in the monitoring) on 13 September 2007, the field was ploughed on 28 September and sown with winter wheat (cv. Ambitron) on 1 October. The crop emerged on 12 October. The herbicide picolinafen was applied on 29 October and the fungicide tebuconazol on 3 December. In both instances, the crop had two unfurled leaves. Due to the very dry growing season of 2008, the field was irrigated on seven occasions: 7 May (42 mm), 14 May (27 mm), 21 May (27 mm), 30 May (30 mm), 5 June (35 mm), 25 June (35 mm), and 8 July (30 mm). The fungicide azoxystrobin was applied on 11 June at full flowering, but was not included in the monitoring (Figure 12, Table A3.2). Harvest took place on 30 August, yielding 68.1 hkg/ha grain (85% dry matter) and 28.1 hkg/ha straw (100% dry matter), grain yield being similar to the average for this soil type for that year (Plantedirektoratet, 2008).

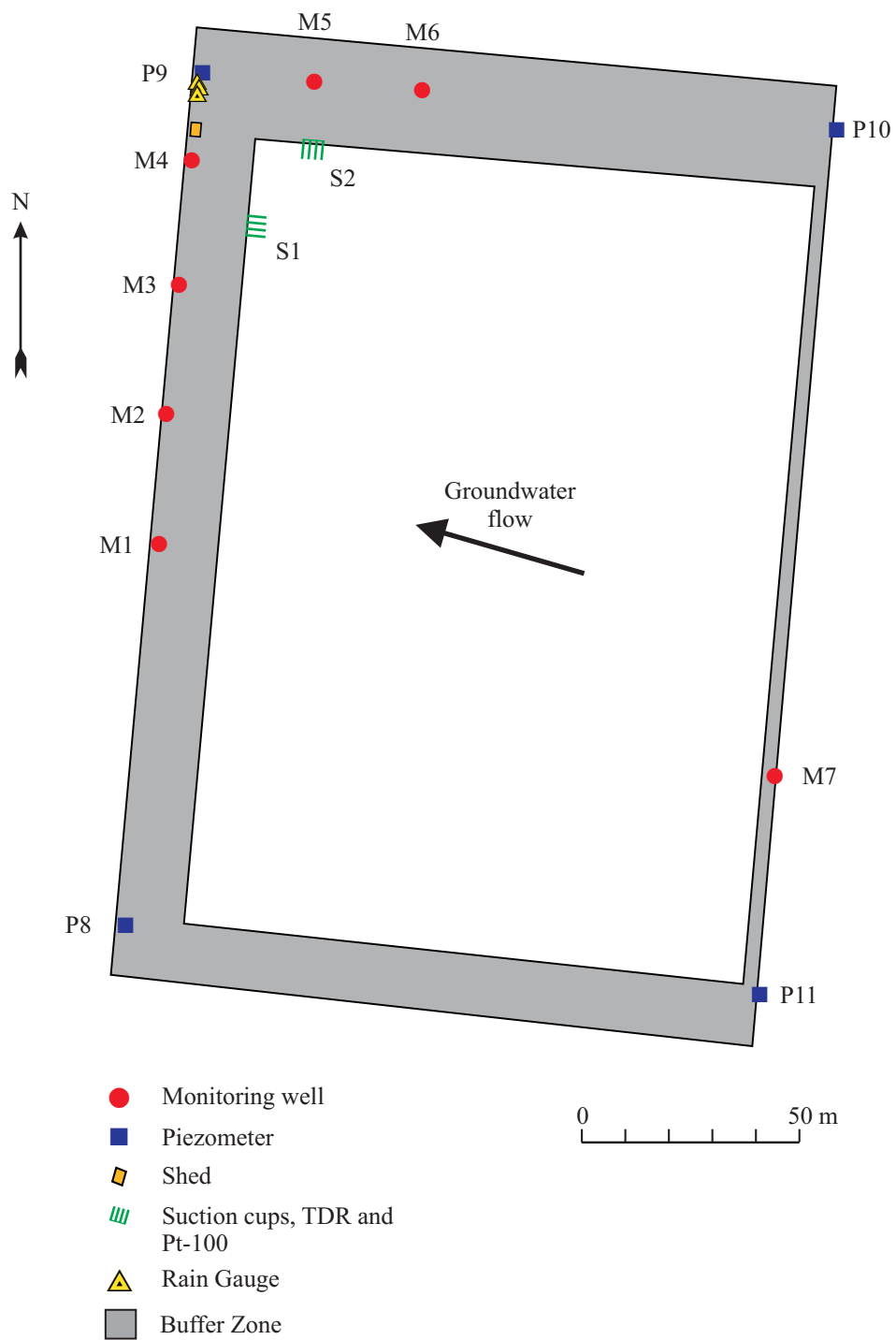


Figure 8. Overview of the **Jynde vad** site. The innermost white area indicates the cultivated land, while the grey area indicates the surrounding buffer zone. The positions of the various installations are indicated, as is the direction of groundwater flow (by an arrow).

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

	Normal Precipitation ¹⁾	Precipitation	Irrigation	Actual Evapotranspiration	Groundwater recharge ²⁾
1.7.99–30.6.00	995	1073	29	500	602
1.7.00–30.6.01	995	810	0	461	349
1.7.01–30.6.02	995	1204	81	545	740
1.7.02–30.6.03	995	991	51	415	627
1.7.03–30.6.04	995	937	27	432	531
1.7.04–30.6.05	995	1218	87	578	727
1.7.05–30.6.06	995	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) Normal values based on time series for 1961 – 1990.

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

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% dry matter, respectively), grain yield being nearly 30% above the average for the soil type and year (Plantedirektoratet, 2009).

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 2009 and to establish an annual water balance.

Compared with the setup in Kjær *et al.* (2009), 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 2009. 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) and Rosenbom *et al.* (*In prep.*).

3.2 Results and discussion

3.2.1 Soil water dynamics and water balances

The model simulations were generally consistent with the observed data, thus indicating a good model description of the overall soil water dynamics in the unsaturated zone (Figure 9). The dynamics of the simulated groundwater table were well described with MACRO 5.1 (Figure 9B). As noted earlier (Kjær *et al.*, 2009), the model had some difficulty in capturing the degree of soil water saturation 1.1 m b.g.s. – a difference that is still apparent (Figure 9E). As in the Tylstrup scenario, the decrease in water saturation observed during the summer periods at 25 and 60 cm b.g.s. was less well captured.

The resulting water balance for Jyndevad for the ten monitoring periods is shown in Table 5. Compared with the previous nine years, the latest hydraulic year July 2008-June 2009 was characterised by having the third highest precipitation, the fourth highest simulated actual evapotranspiration and the third highest irrigation values. Precipitation in the latest hydraulic year was characterized by August and October being very wet, and December to February and April being very dry (Appendix 4). Continuous percolation 1 m b.g.s. was, however, simulated throughout the year.

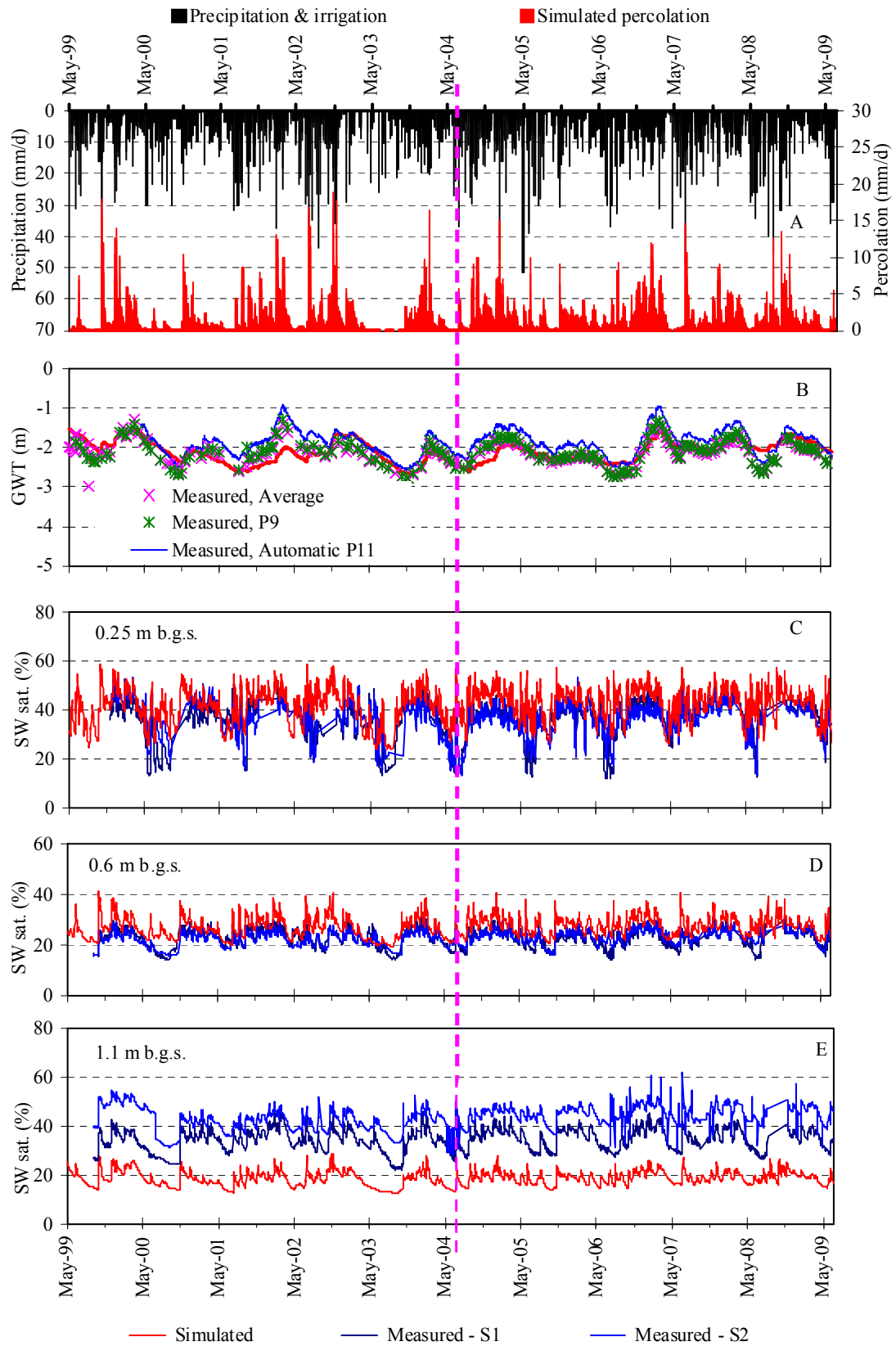


Figure 9. Soil water dynamics at Jyndevid: Measured precipitation, irrigation and simulated percolation 1 m b.g.s. (A), simulated and measured groundwater level (B), and simulated and measured soil water saturation (SW sat.) at three different soil depths (C, D and E). The measured data in B derive from 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 2009).

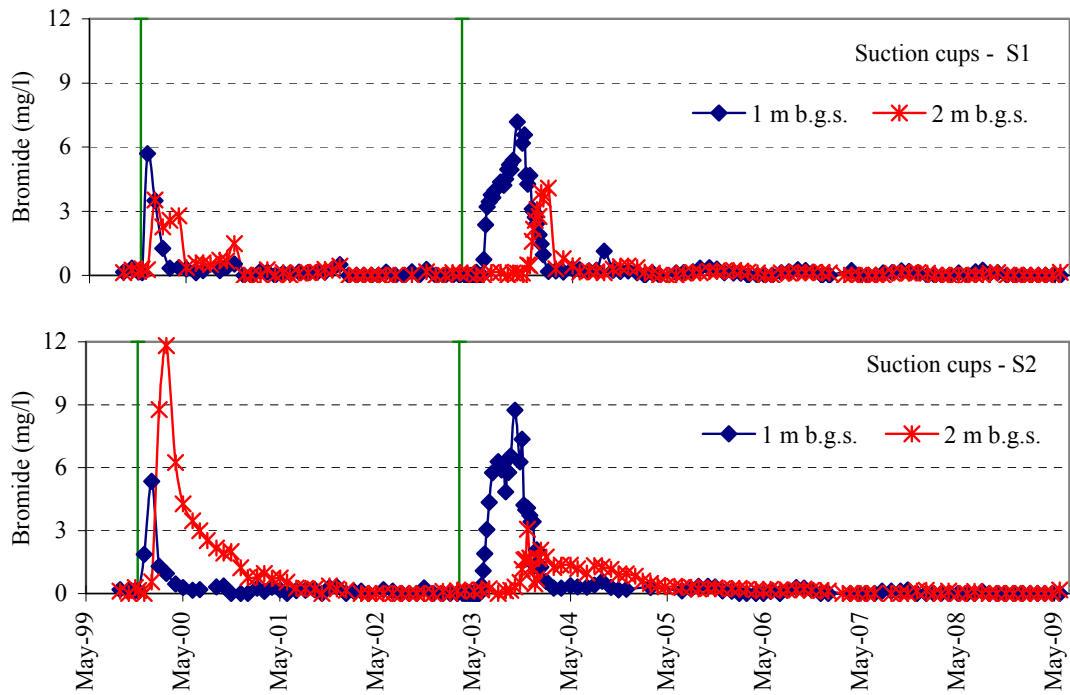


Figure 10. Bromide concentration in the unsaturated zone at **Jynde vad**. The measured data derive from suction cups installed (A) 1 m b.g.s. and (B) 2 m b.g.s. at locations S1 and S2 (Figure 8). The green vertical lines indicate the dates of bromide applications.

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

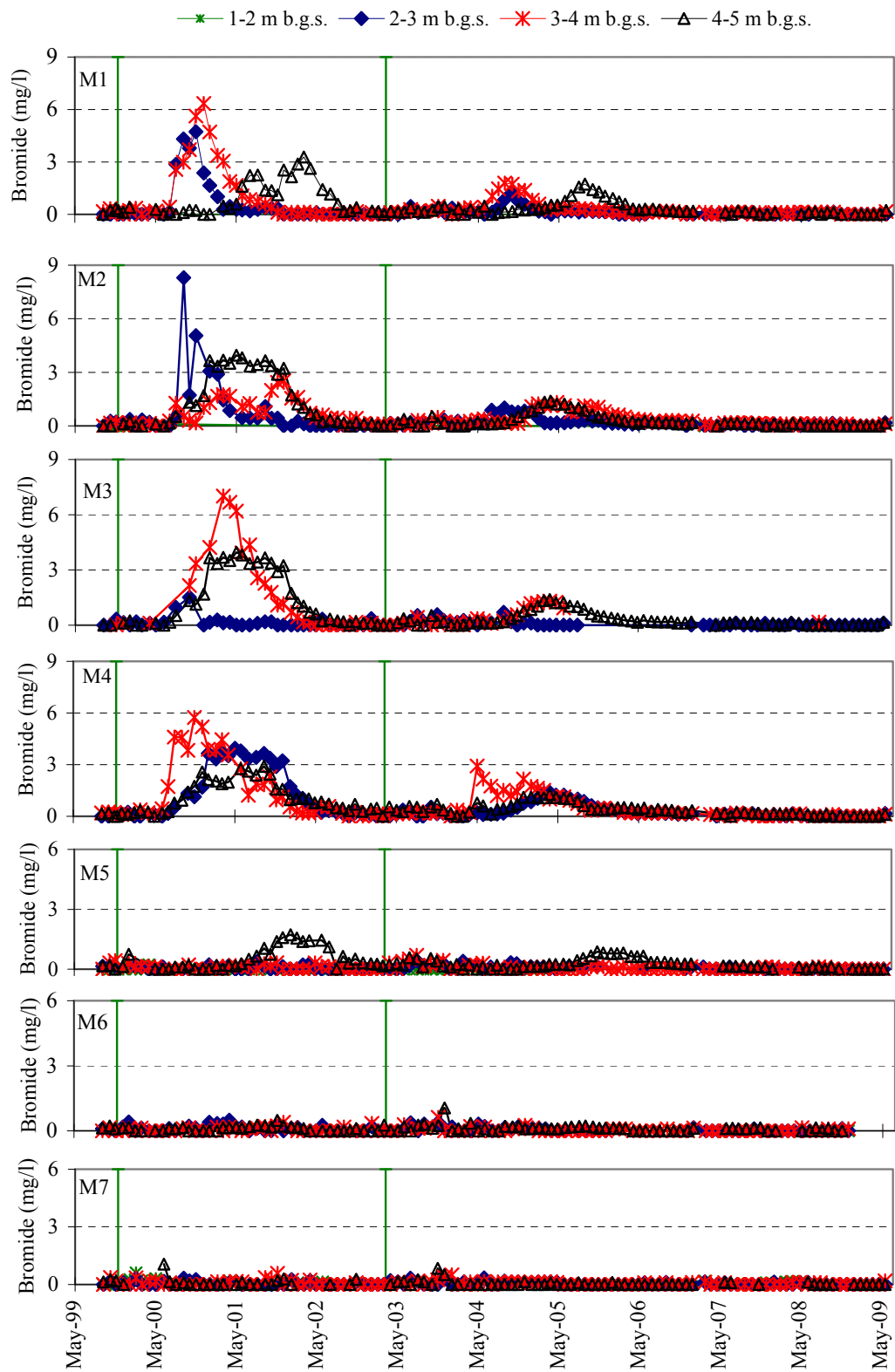


Figure 11. Bromide concentration in the groundwater at **Jynde vad**. The data derive from monitoring wells M1–M7. Monitoring at well M6 was suspended September 2008 (Appendix 2). Screen depth is indicated in m b.g.s. The green vertical lines indicate the dates of bromide applications.

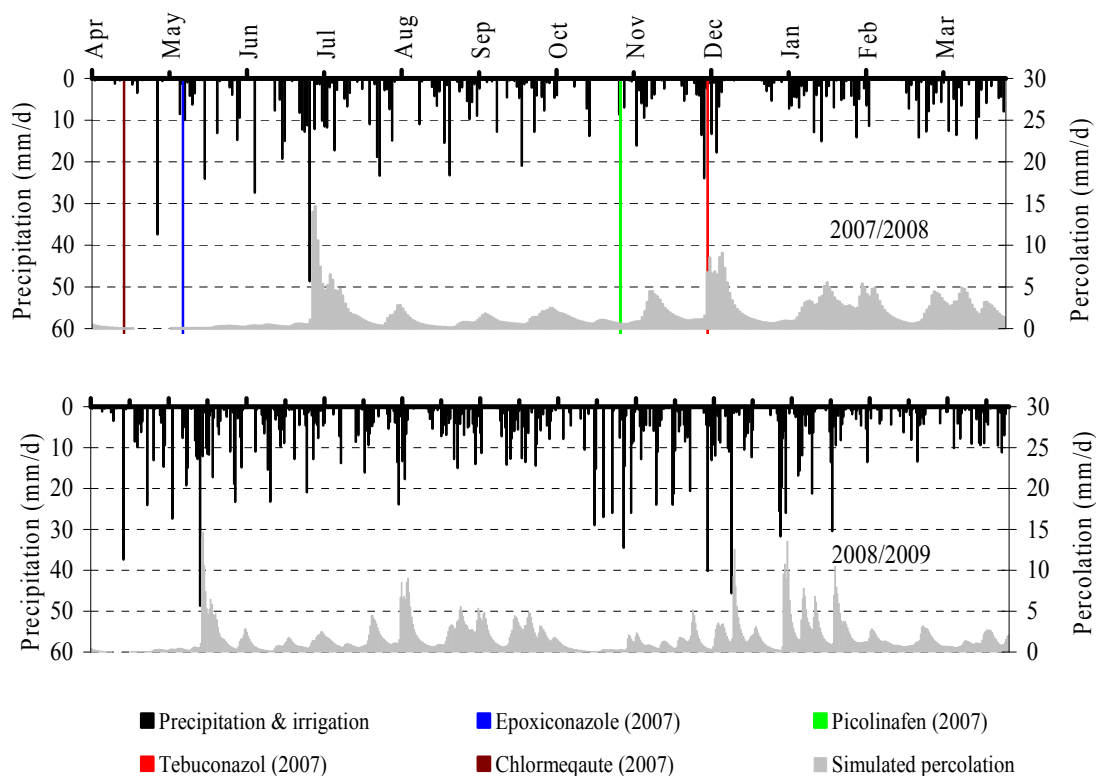


Figure 12. Application of pesticides included in the monitoring programme, precipitation and irrigation (primary axis) together with simulated percolation 1 m b.g.s. (secondary axis) at **Jyndevad** in 2007/2008 (upper) and 2008/2009 (lower).

3.2.3 Pesticide leaching

Monitoring at Jyndevad began in September 1999 and presently encompasses several pesticides and their degradation products, as indicated in Table 6. Pesticide application during the two most recent growing seasons is shown together with precipitation and simulated precipitation in Figure 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). Bifenox (Fox 480 SC) as well its two degradation products bifenox-acid and nitrofen are all monitored. The product Basagran M75 contains two active substances, bentazone and MCPA, but only bentazone is monitored. Pesticides applied later than April 2009 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. 1st month perc. refers to accumulated percolation within the first month after application. C_{mean} refers to average leachate concentration 1 m b.g.s the first year after application. The number of pesticide-positive samples is indicated in parentheses.

Crop and analysed pesticides	Application date	End of monitoring	Prec. (mm)	Perc. (mm)	1 st month perc. (mm)	C _{mean} (µg/l)
Winter rye 2000						
Glyphosate (Roundup 2000)	Sep 99	Apr 02	2759	1607	139	<0.01 (0)
- AMPA						<0.01 (3)
Triazinamin-methyl ¹⁾ (Express)	Nov 99	Apr 02	2534	1451	86	<0.02 (0)
Propiconazole (Tilt Top)	Apr 00	Jul 02	2301	1061	3	<0.01 (0)
Fenpropimorph (Tilt Top)	Apr 00	Apr 02	2015	1029	3	<0.01 (2)
- fenpropimorphic acid						<0.01 (0)
Maize 2001						
Terbutylazine (Lido 410 SC)	May 01	Apr 04	3118	1809	4	<0.01 (0)
- desethyl-terbutylazine	May 01	Apr 07	6742	3826	4	<0.01–0.02 (42)
PHCP ²⁾ (Lido 410 SC)	May 01	Jul 03	2413	1366	4	<0.02 (0)
Potatoes 2002						
- PPU (Titus) ³⁾	May 02	Jul 09 [†]	8247	4526	11	0.06 ⁴⁾ –0.13 (376)
- PPU-desamino (Titus)		Jul 09 [†]	8247	4526	11	0.01–0.03 (150)
Spring barley 2003						
MCPA (Metaxon)	Jun 03	Jul 05	2340	1233	0	<0.01 (0)
- 4-chlor-2-methylphenol						<0.01 (0)
Dimethoate (Perfekthion 500 S)	Jun 03	Jul 05	2278	1232	1	<0.01 (0)
Pea 2004						
Bentazone (Basagran 480)	May 04	Jul 07	3888	2044	4	0.02 (30*)
- AIBA						<0.01 (2)
Pendimethalin (Stomp SC)	May 04	Apr 07	3557	1996	4	<0.01 (0)
Pirimicarb (Pirimor G)	Jun 04	Apr 07	3493	1993	27	<0.01 (0)
- pirimicarb-desmethyl						<0.01 (1)
- pirimicarb-desmethyl-formamido						<0.02 (0)
- fluazifop-P(free acid) ⁵⁾	Jun 04	Jul 06	2395	1233	27	<0.01 (0)
(Fusilade X-tra)						
Winter wheat 2005						
Ioxynil (Oxitril CM)	Oct 04	Apr 07	2955	1791	81	<0.01 (0)
Bromoxynil (Oxitril CM)	Oct 04	Apr 07	2955	1791	81	<0.01 (0)
Amidosulfuron (Gratil 75 WG)	Apr 05	Jul 07	1070	515	33	<0.01 (3)
Fluroxypyr (Starane 180 S)	May 05	Jul 07	2683	1360	37	<0.02 (0)
Azoxystrobin (Amistar)	May 05	Apr 07	2274	1283	49	<0.01 (0)
- CyPM						<0.02 (0)
Spring barley 2006						
Florasulam (Primus)	May 06	Jul 08	2779	1487	34	<0.01 (0)
- florasulam-desmethyl						<0.03 (0)
Epoxiconazole (Opus)	Jun 06	Jul 09 [†]	3890	2119	31	<0.01 (1)
Triticale 2007						
Mesosulfuron-methyl (Atlantis WG)	Oct 06	Jul 09 [†]	2206	1291	73	<0.01 (0)
- mesosulfuron						<0.01 (0)
Chlormequat (Cycocel 750)	Apr 07	Jul 08	1548	689	1	<0.01 (0)
Epoxiconazole (Opus)	May 07	Jul 09 [†]	2657	1342	6	<0.01 (1)
Winter wheat 2008						
Picolinafen (Pico 750 WG)	Oct 07	Jul 09 [†]	1998	1116	55	<0.01 (1)
- CL153815						<0.01 (0)
Tebuconazole (Folicur EC 250)	Dec 07	Jul 09 [†]	1871	1056	97	<0.01 (1)
Spring barley 2009						
Bifenox (Fox 480 SC)	Apr 09	Jul 09 [†]	235	47	3	<0.01 (0)
- bifenox-acid						<0.01 (0)
- nitrofen						<0.01 (0)
Bentazone (Basagran M75)	May 09	Jul 09 [†]	187	47	14	<0.01 (30*)

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

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

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

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

⁴⁾ Leaching increased the second year after application (see Figure 13).

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

[†] Monitoring will continue for an additional year. The values for prec. and perc. are accumulated up to July 2009.

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

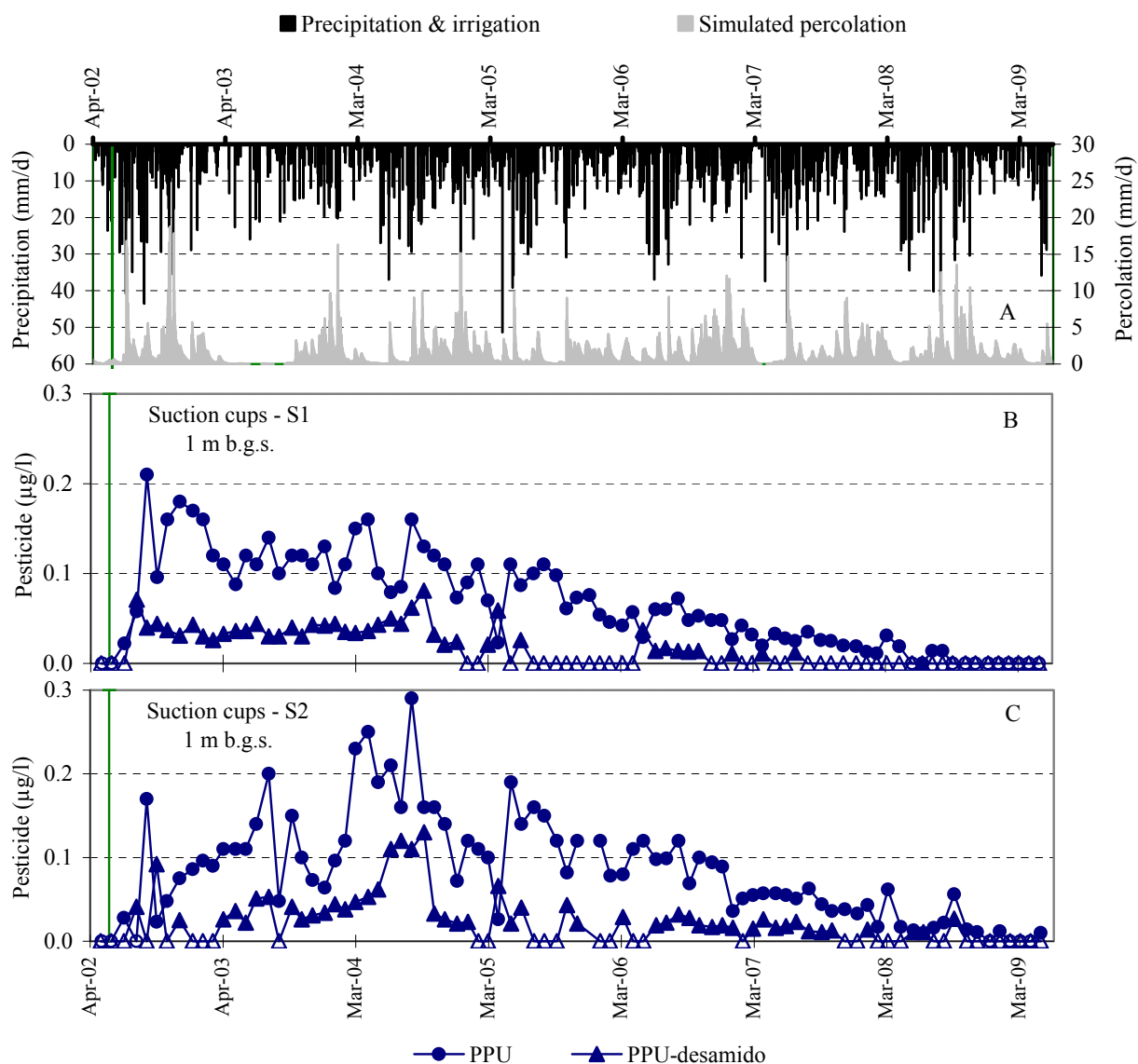


Figure 13. Precipitation, irrigation and simulated percolation 1 m b.g.s. (A) together with measured concentrations of PPU and PPU-desamino (µg/l) in suction cups installed 1 m b.g.s. at location S1 (B) and S2 (C) at Jyndeved. The green vertical line indicates the date of pesticide application. Open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

The leaching risk of pesticides applied during 2000, 2001, 2002, 2003, 2004, 2005, 2006, 2007, and 2008 has been evaluated in Kjær *et al.* (2002, 2003, 2004, 2005c, 2007, 2008, and 2009). 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.* (2010). For a detailed description of the leaching pattern, including primary data and climatic conditions characterising the monitoring periods, see Kjær *et al.* (2005c).

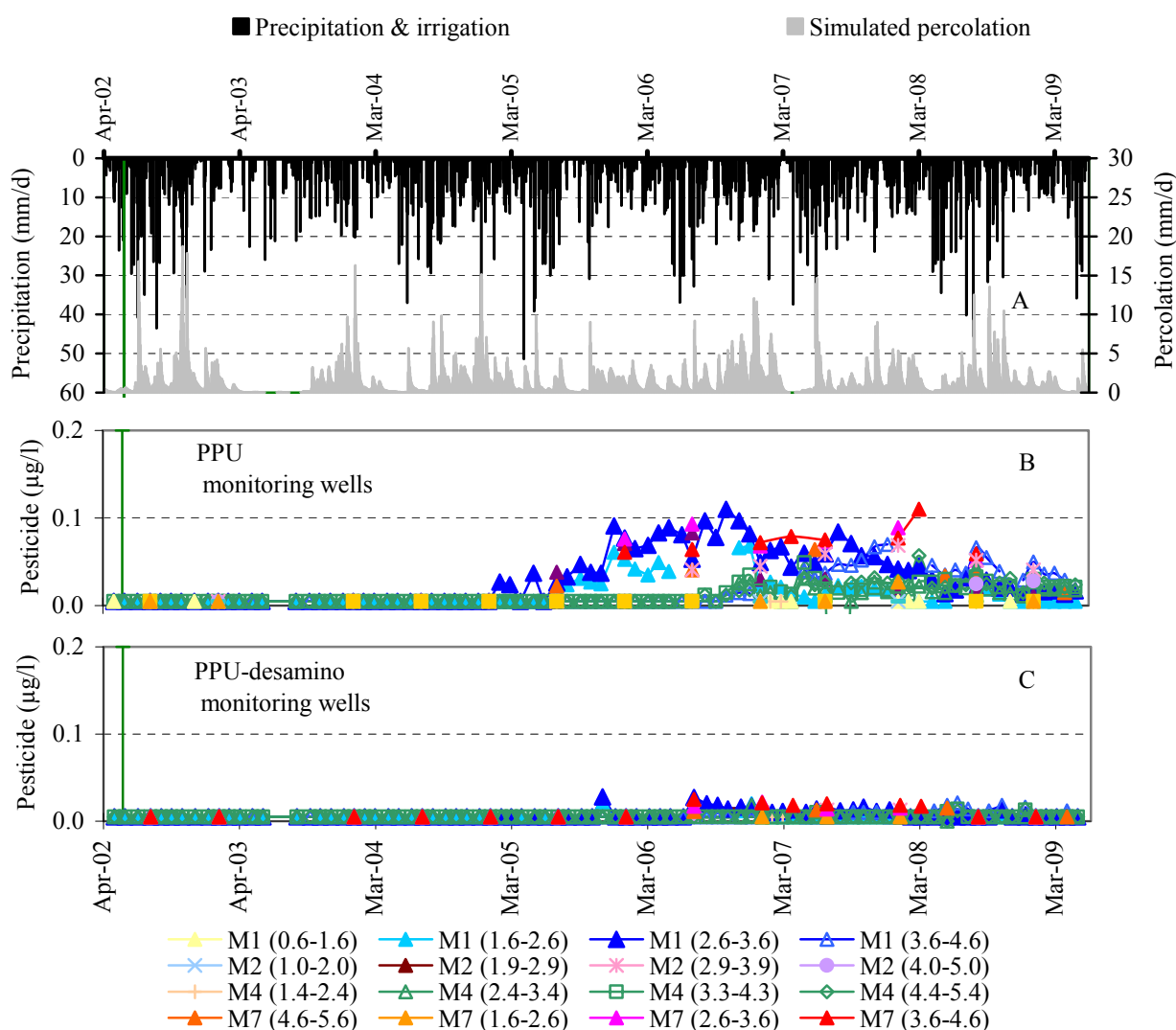


Figure 14. Precipitation, irrigation and simulated percolation 1 m b.g.s. (A) together with measured concentrations ($\mu\text{g/l}$) in downstream (M1, M2, M4) and upstream monitoring wells (M7) of PPU (B) and PPU-desamino (C) at Jyndeved. The numbers in parentheses indicate the depths of the analysed 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 characterized by continuous leaching over a long period of time. Although the concentration decreased during the last monitoring year, PPU was still detected towards the end of 2008/2009, i.e. seven 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). Elevated concentrations of PPU were seen in M1 (sampled monthly), M2 (sampled half-yearly) and from 2006 in M4 (sampled monthly). PPU was also found in low concentrations in M7, which receives water from the upstream neighbouring field (Figure 9 and Figure 15). This is because the tracer test suggested that water sampled in M7 had not infiltrated at the PLAP site, and because rimsulfuron was also applied in the neighbouring upstream area (Kjær *et al.*, 2007).

Table 7. Percolation together with estimated average concentrations ($\mu\text{g/l}$) of PPU and PPU-desamino 1 m b.g.s. at **Jynde vad**. Leached mass refers to the total mass (% of applied rimsulfuron) leached during the monitoring period 1.7.02–30.6.09.

	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

In addition to the leaching observed at the PLAP site, this result thus indicates that leaching also occurred in the neighbouring upstream field. Furthermore, PPU-desamino was detected in monitoring wells, 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 Section 2.2.3 and section 7.2.2.

Of the four pesticides (tebuconazole, chlormequat, epoxiconazole, picolinafen and its degradation products CL153815) applied during the 2007/08 growing season only picolinafen and tebuconazol were detected in concentrations of 0.015 and 0.014 $\mu\text{g/l}$, respectively. 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).

The pesticides used in spring barley 2009 have not been found in any of the analysed water samples. The final evaluation awaits an additional year of monitoring.

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 2006–2007 growing seasons is briefly summarized below and detailed in Appendix 3 (Table A3.3). For information about management practice during the previous monitoring periods see Kjær *et al.* (2002, 2003, 2004, 2005c, 2007, 2008, and 2009).

The field was ploughed on 20 September 2006 and two days later sown with winter wheat (cv. Skalmeye) as well as sprayed with the herbicide pendimethalin. Eight days later the wheat emerged. At the beginning of stem elongation on 13 June 2007 the plant growth inhibitor chlormequat and the herbicide iodosulfuron were applied. On 7 June, at the end of heading, the fungicide epoxiconazole was applied. The winter wheat was harvested on 24 August, yielding 100.7 hkg/ha of grain and 40.8 hkg/ha straw – 85 and 100% of dry matter, respectively. The straw was shredded at harvest. Straw and stubble were incorporated on 29 August using a disk harrow and the field was ploughed on 12 November. Grain yield was some 0.5 t/ha larger than on a similar soil for this year (Plantedirektoratet, 2008).

Having been harrowed, levelled and rolled between 21 April and 5 May 2008 the field was sown with fodder beet (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-methyl, metatiron, and phenmedipham. A second spraying of weeds took place on 30 May, the crop having three leaves unfurled, using triflusaluron-methyl, metatiron, ethofumesate, and phenmedipham.

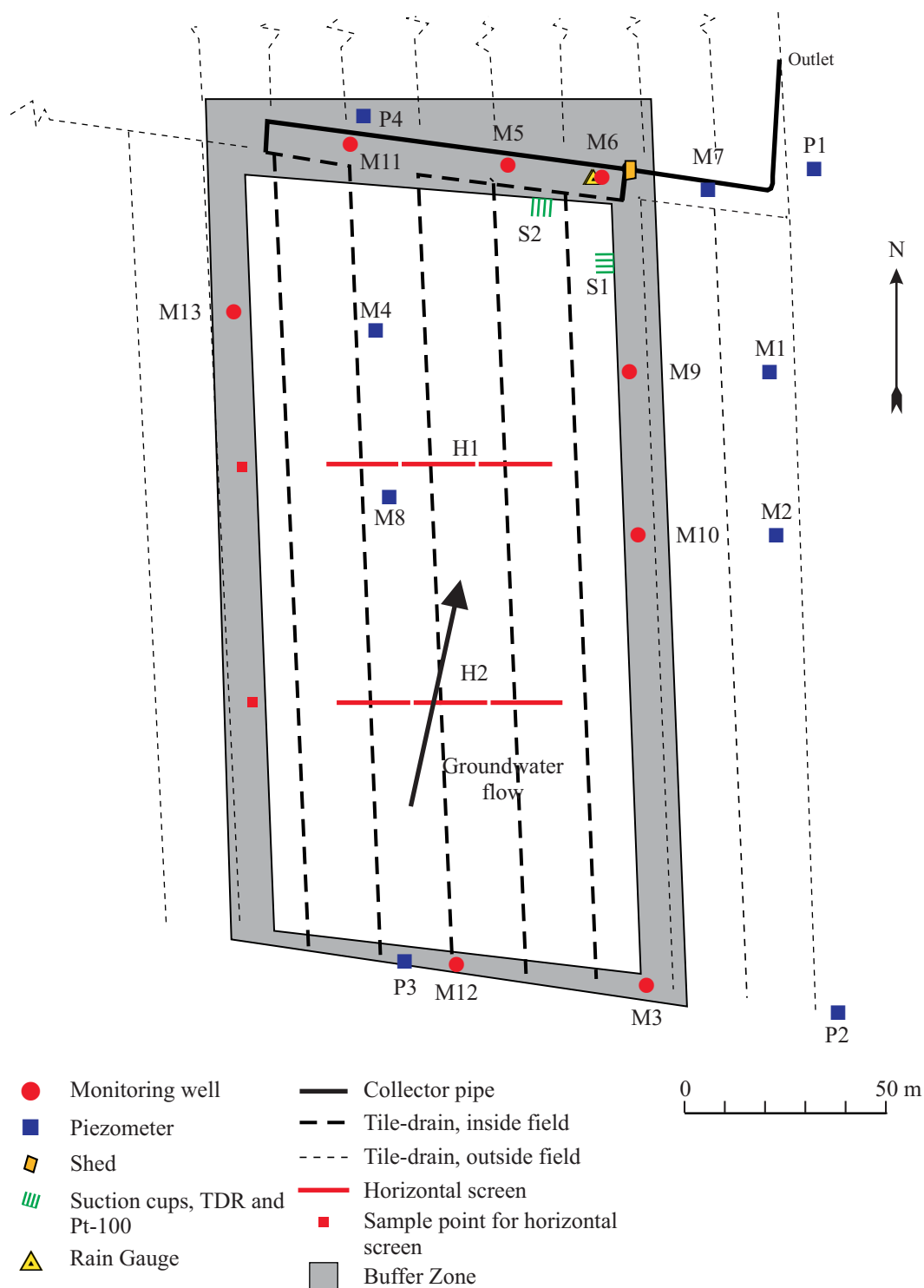


Figure 15. Overview of the **Silstrup** site. The innermost white area indicates the cultivated land, while the grey area indicates the surrounding buffer zone. The positions of the various installations are indicated, as is the direction of groundwater flow (by an arrow).

A third spraying of weeds took place on 17 June, at the stage of five unfurled leaves, using triflurosulfuron-methyl, 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-methyl, 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% dry matter. All beet tops (5.2 t/ha) were shredded and ploughed into the soil on 15 December.

4.1.3 Model setup and calibration

The numerical model MACRO (version 5.1, Larsbo *et al.*, 2005) was applied to the Silstrup site covering the soil profile to a depth of 5 m b.g.s., always including the groundwater table. The model is used to simulate the water flow in the unsaturated zone during the full monitoring period April 2000–June 2009 and to establish an annual water balance.

Compared with the setup in Kjær *et al.* (2009), 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 2009. 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) and Rosenbom *et al.* (*In prep.*). 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.

4.2 Results and discussion

4.2.1 Soil water dynamics and water balances

The model simulations were largely consistent with the observed data, thus indicating a reasonable model description of the overall soil water dynamics in the unsaturated zone (Figure 16). As in Kjær *et al.* (2009), 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 16B and 16C). The earlier reported delay in the initial increase in simulated drainage flow was still present in October and January (Figure 16C). As in the previous monitoring periods, the overall trends in soil water content were described reasonably well (Figure 16D, 16E, and 16F), 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 16E and 16F).

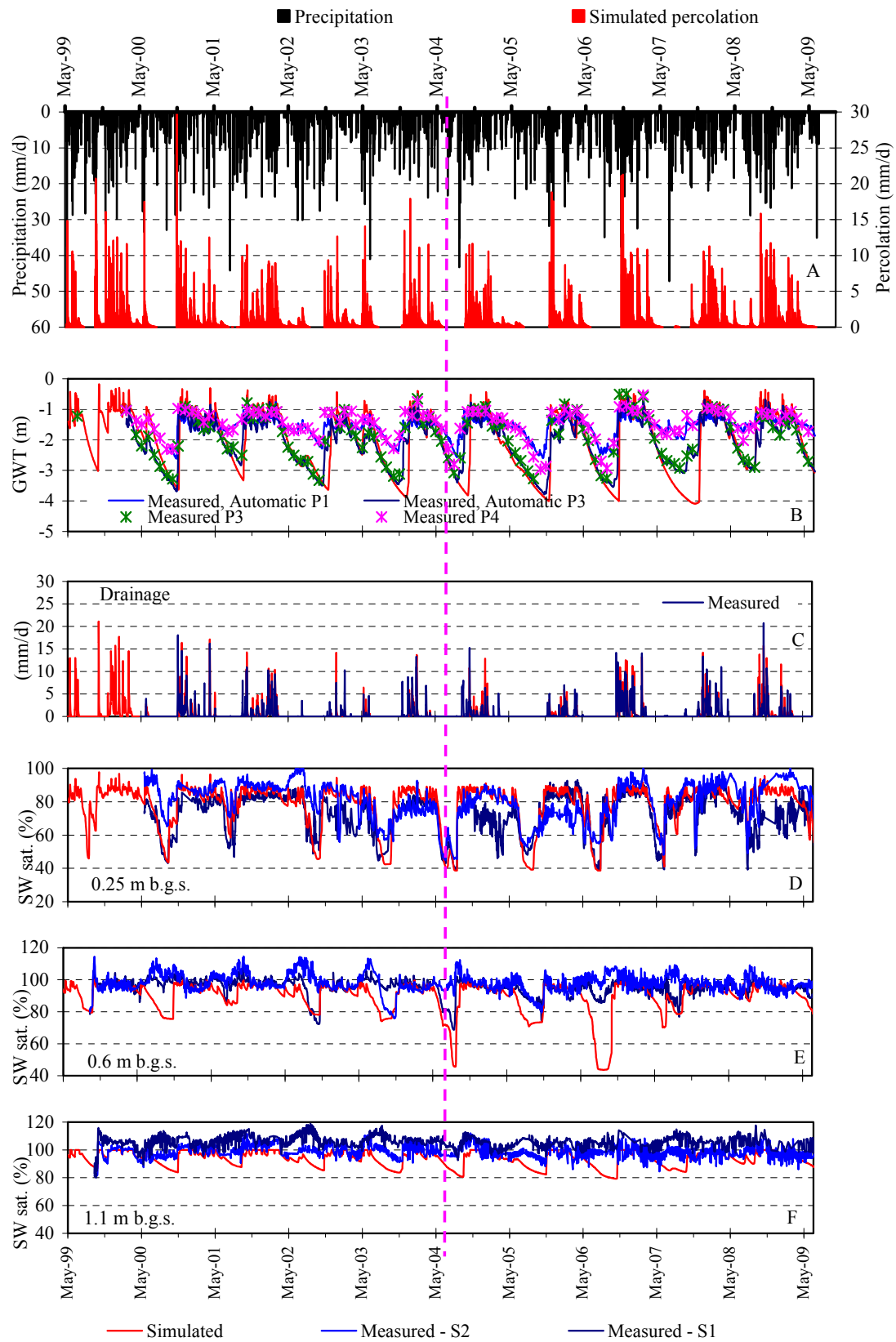


Figure 16. Soil water dynamics at **Silstrup**: Measured precipitation and simulated percolation 1 m b.g.s. (A), simulated and measured groundwater level GWT (B), simulated and measured drainage flow (C), and simulated and measured soil water saturation (SW sat.) at three different soil depths (D, E, and F). The measured data in B derive from piezometers located in the buffer zone. The measured data in D, E, and F derive from TDR probes installed at S1 and S2 (Figure 15). The broken vertical line indicates the beginning of the validation period (July 2004-June 2009).

Table 8. Annual water balance for **Silstrup** (mm/year). Precipitation is corrected to the soil surface according to the method of Allerup and Madsen (1979).

	Normal precipitation ²⁾	Precipitation	Actual evapotranspiration	Measured drainage	Simulated drainage	Groundwater recharge ³⁾
1.7.99–30.6.00 ¹⁾	976	1175	457	–	443	275 ⁴⁾
1.7.00–30.6.01	976	909	413	217	232	279
1.7.01–30.6.02	976	1034	470	227	279	338
1.7.02–30.6.03	976	879	537	81	74	261
1.7.03–30.6.04	976	760	517	148	97	94
1.7.04–30.6.05	976	913	491	155	158	267
1.7.05–30.6.06	976	808	506	101	95	201
1.7.06–30.6.07	976	1150	539	361	307	249
1.7.07–30.6.08	976	877	434	200	184	242
1.7.08–30.6.09	976	985	527	161	260	296

¹⁾ The monitoring started in April 2000.

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

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

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

Hydraulic conductivity and water content were measured downstream of the field (close to P1 and P4), but no such data were available upstream, where P3 was located. As mentioned above, the calibration showed that the hydraulic conditions around P3 affected the measurements considerably. In order to model the measured values, the calibrated hydraulic conductivity curves were fitted less well to the measured data from P1 and P4 than from the other sites (Barlebo *et al.*, 2007).

The resulting water balance for Silstrup for the entire monitoring period is shown in Table 8. Compared with the previous nine years, the latest hydraulic year July 2008–June 2009 was characterised by having the fourth highest precipitation, the third highest simulated actual evapotranspiration, and the fifth highest measured drainage. Precipitation in this year was characterized by the period from July to October being very wet, and December and April being very dry (Appendix 4). Due to this precipitation pattern, the simulated percolation pattern of the year July 2008–June 2009 was represented by continuous percolation (Figure 16A). The climatic setting of this year gave rise to periods with the groundwater table above the drainage level, causing the fifth largest measured drainage since monitoring started in July 2000 (Figure 16B and 16C). Apart from differences in the measured and simulated yearly amounts of drainage, the overall pattern of drainage levels in the hydraulic years was captured.

4.2.2 Bromide leaching

The bromide concentrations shown in Figure 17 and Figure 18 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 Rosenbom *et al.* (*In prep.*) and 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.

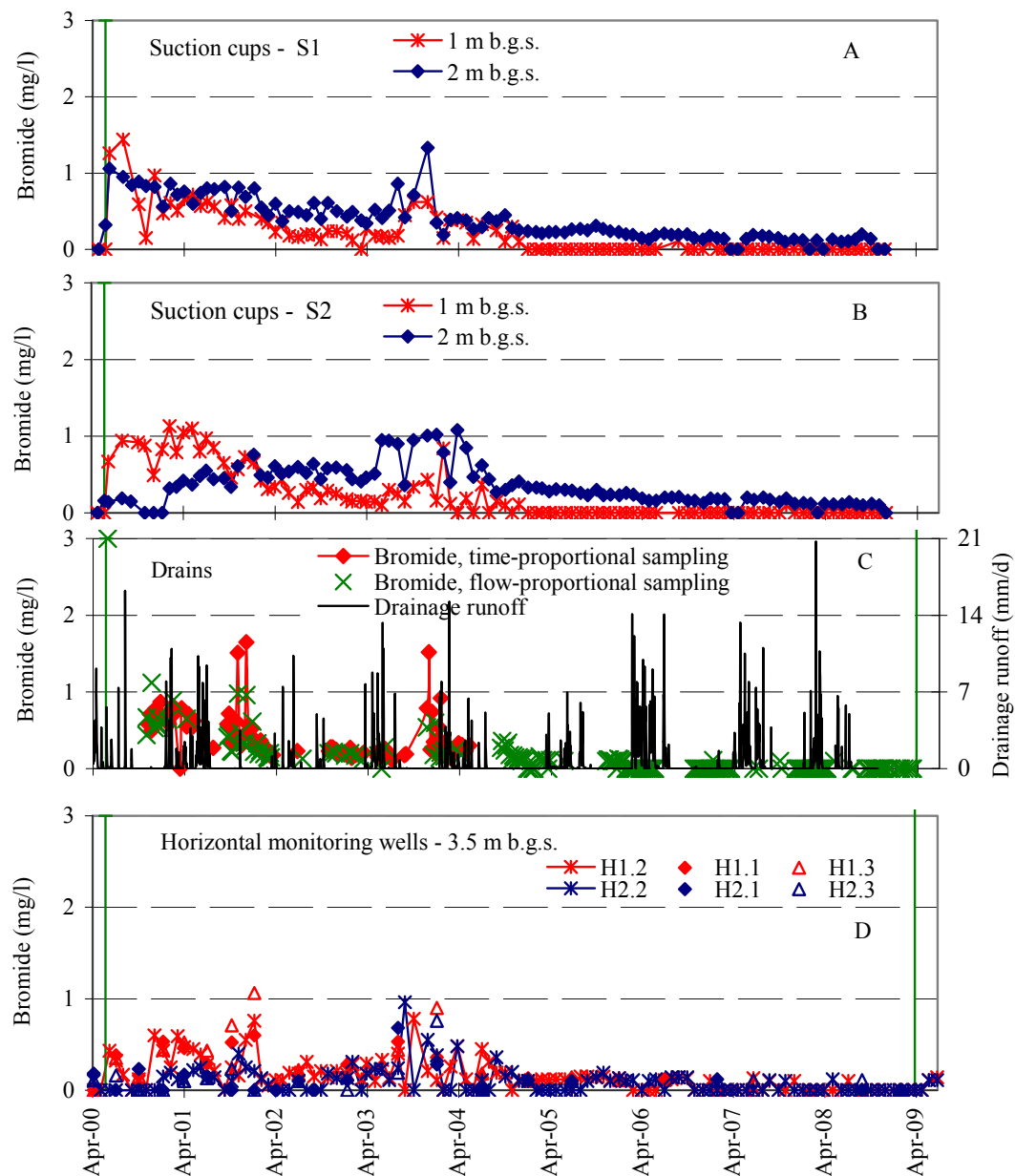


Figure 17. Bromide concentration at **Silstrup**. A and B refer to suction cups located at S1 and S2. The bromide concentration is also shown for drainage runoff (C) and the horizontal monitoring wells H1 and H2 (D). In Marts 2009, bromide measurements in the suction cups were suspended (Appendix 2). The green vertical lines indicate the date of bromide applications.

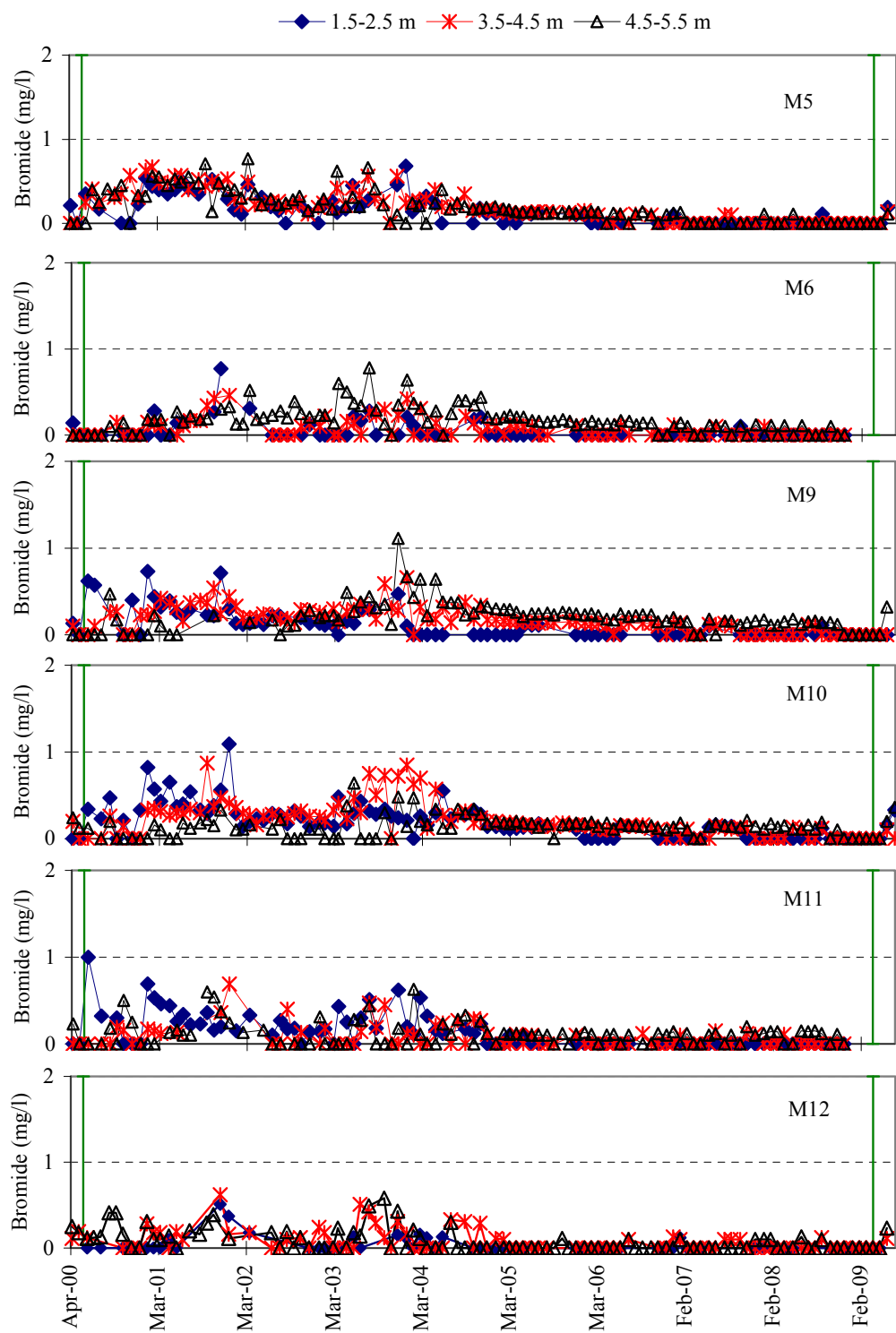


Figure 18. Bromide concentration at **Silstrup**. The data derive from the vertical monitoring wells (M5–M12). In September 2008, monitoring wells M6 and M11 were suspended (Appendix 2). Screen depth is indicated in m b.g.s. The green vertical lines indicate the date of bromide applications.

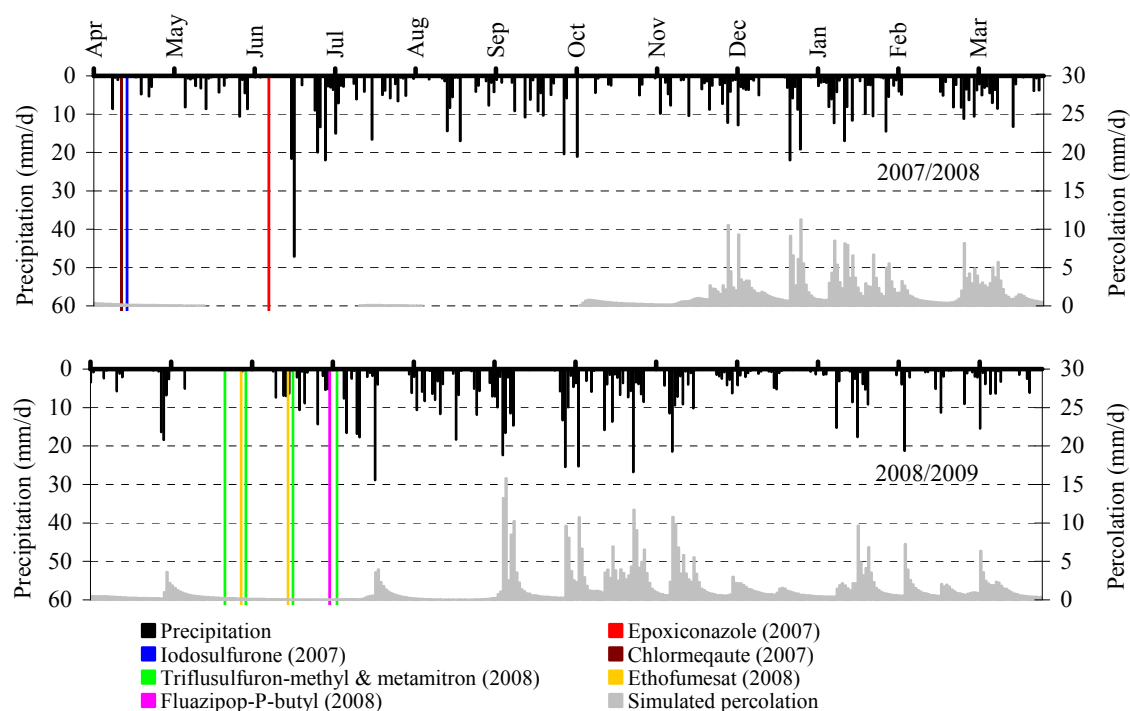


Figure 19. Application of pesticides included in the monitoring programme, precipitation, and irrigation (primary axis) and simulated percolation 1 m b.g.s. (secondary axis) at **Silstrup** in 2007/2008 (upper) and 2008/2009 (lower).

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 2009 are not evaluated in this report and hence not included in Table 9. 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. 1st month perc. refers to accumulated percolation within the first month after application. C_{mean} refers to average leachate concentration in the drainage water within the first drainage season after application (See Appendix 2 for calculation methods). The number of pesticide-positive samples is indicated in parentheses.

Crop and analysed pesticides	Application date	End of monitoring	Prec. (mm)	Perc. (mm)	1 st month perc. (mm)	C _{mean} (µg/l)
Fodder beet 2000						
Metamitron (Goltix WG)	May 00	Apr 03	2634	1328	53	0.05 (69)
- <i>metamitron-desamino</i>						0.06 (61)
Ethofumesate (Betanal Optima)	May 00	Apr 03	2634	1328	53	0.03 (24)
Desmedipham (Betanal Optima)	May 00	Apr 03	2634	1328	53	<0.01 (1)
- <i>EHPC</i>						<0.02 (0)
Phenmedipham (Betanal Optima)	May 00	Apr 03	2634	1328	53	<0.01 (0)
- <i>MHPC</i>						<0.02 (0)
- <i>3-aminophenol</i>						<0.02 (0)
Fluazifop-P-butyl (Fusilade X-tra)	Jun 00	Jul 02	1953	1019	5	<0.01 (0)
- <i>fluazifop (free acid)</i>						<0.02 (1)
Pirimicarb (Pirimor G)	Jul 00	Jul 07	6452	2825	1	<0.01 (17 [*])
- <i>pirimicarb-desmethyl</i>						<0.01 (1 [*])
- <i>pirimicarb-desmethyl-formamido</i>						<0.02 (0)
Spring barley 2001						
Triazinamin-methyl ¹⁾ (Express)	May 01	Jul 03	1941	951	10	<0.02 (0)
Flamprop-M-isopropyl (Barnon Plus 3)	Jun 01	Jul 03	1928	944	3	<0.01 (13)
- <i>flamprop (free acid)</i>						<0.01 (7)
Propiconazole (Tilt Top)	Jun 01	Jul 03	1928	944	3	<0.01 (6)
Fenpropimorph (Tilt Top)	Jun 01	Jul 03	1928	944	3	<0.01 (0)
- <i>fenpropimorphic acid</i>						<0.01 (1)
Dimethoate (Perfekthion 500 S)	Jul 01	Jul 03	1882	937	3	0.02 (2)
Maize 2002						
Glyphosate (Roundup Bio)	Oct 01	Apr 06	3802	1694	44	<0.13 (71 [*])
- <i>AMPA</i>						0.06 (137 [*])
<i>PHCP</i> ²⁾ (Lido 410 SC)	May 02	Jul 04	1764	738	6	0.06 (18)
Terbuthylazine (Lido 410 SC)	May 02	Apr 06	3320	1327	6	0.07 (96)
- <i>desethyl-terbuthylazine</i>		Apr 05				0.15 (269)
- <i>2- hydroxy-terbuthylazine</i>		Apr 05				³⁾ (26)
- <i>2-hydroxy-desethyl-terbuthylazine</i>		Apr 05				³⁾ (29)
- <i>desisopropyl-atrazine</i>		Apr 05				³⁾ (47)

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

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

³⁾ 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

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

The leaching risk of pesticides applied during 2000, 2001, 2002, 2003, 2004, 2005, 2006, 2007, and 2008 has been evaluated in Kjær *et al.* (2002, 2003, 2004, 2005c, 2007, 2008, and 2009), respectively.

Iodosulfuron-methyl-sodium was applied on 13 April 2007. Neither this nor its two degradation products (metsulfuron-methyl and triazinamin) have been found during a monitoring period of more than two years.

Chlormequat-chloride, also applied on 13 April 2007, was found in drainage water on 14 February 2008 at a concentration of 0.01 µg/l. Juhler *et al.* (2010) conducted a detailed analysis on the fate and transport of chlormequat-chloride at the site. This analysis was financially supported by Copenhagen Energy (Københavns Energi A/S).

Epoxiconazole applied in June 2007 has not been detected in any of the water samples.

Table 9 continued. Pesticides analysed at **Silstrup** with the product used shown in parentheses. Degradation products are in *italics*. Precipitation (prec.) and percolation (perc.) are accumulated from date of first application until end of monitoring. 1st month perc. refers to accumulated percolation within the first month after application. C_{mean} refers to average leachate concentration in the drainage water within the first drainage season after application (See Appendix 2 for calculation methods). The number of pesticide-positive samples is indicated in parentheses.

Crop and analysed pesticides	Application date	End of monitoring	Prec. (mm)	Perc. (mm)	1 st month Perc. (mm)	C _{mean} (µg/l)
Peas 2003						
Bentazone (Basagran 480)	May 03	Jul 06	2634	1055	44	0.26 (52)
- <i>AIBA</i>						<0.01 (0)
Pendimethalin (Stomp SC)	May 03	Apr 06	2634	1055	44	<0.01 (0)
Glyphosate (Roundup Bio)	Sep 03	Apr 06	2207	971	0	<0.01 (71 [*])
- <i>AMPA</i>						0.02 (137 [*])
Winter wheat 2004						
Prosulfocarb (Boxer EC)	Oct 03	Apr 06	2125	974	37	0.01 (6)
MCPA (Metaxon)	May 04	Jul 06	1797	710	4	<0.01 (0)
- <i>4-chlor,2-methylphenol</i>						<0.01 (0)
Azoxystrobin (Amistar)	Jun 04	Jul 06	1781	706	0	0.01 (6 [*])
- <i>CyPM</i>		Jul 07	2931	1202	0	0.09 (62 [*])
Pirimicarb (Pirimor G)	Jul 04	Jul 07	2818	1205	0	<0.01 (17 [*])
- <i>Pirimicarb-desmethyl</i>						<0.01 (1 [*])
- <i>Pirimicarb-desmethyl-formamido</i>						<0.02 (0)
Spring barley 2005						
Fluroxypyr (Starane 180 S)	May 05	Jul 07	2012	830	11	<0.02 (0)
Azoxystrobin (Amistar)	Jun 05	Jul 06	862	332	10	0.01 (6 [*])
- <i>CyPM</i>	Jun 05	Jul 07	2012	828	10	0.02 (62 [*])
Pirimicarb (Pirimor G)	Jul 05	Jul 07	1933	818	0	<0.01 (17 [*])
- <i>Pirimicarb-desmethyl</i>						<0.01 (1 [*])
- <i>Pirimicarb-desmethyl-formamido</i>						<0.01 (0 [*])
Winter rape 2006						
Propyzamide (Kerb 500 SC)	Nov 05	Apr 08	2345	1115	75	0.22 (32) ¹⁾
- <i>RH-24644</i>						0.01 (17) ¹⁾
- <i>RH-24580</i>						<0.01 (2) ¹⁾
- <i>RH-24655</i>						<0.01 (0) ¹⁾
Clopyralid (Matrigon)	Apr 06	Apr 08	2009	859	8	<0.01 (0)
Winter wheat 2007						
Pendimethalin (Stomp Pentagon)	Sep 06	Apr 08	1686	865	0	<0.04 (14)
Iodosulfuron-methyl-sodium (Hussar OD)	Apr 07	Apr 09	1940	875	3	<0.01 (0)
- <i>Metsulfuron-methyl</i>						<0.01 (0)
- <i>Triazinamin</i>						<0.01 (0)
Chlormequat-chloride (Cycocel 750)	Apr 07	Jul 08	1099	392	3	<0.01 (1)
Epoxiconazole (Opus)	Jun 07	Apr 09	1867	873	0	<0.01 (0)
Fodder beet 2008						
Triflusaluron-methyl (Safari)	May 08	Jul 09 [†]	1059	499	4	<0.01 (0)
- <i>IN-D8526</i>						<0.01 (0)
- <i>IN-E7710</i>						<0.01 (4)
- <i>IN-M7222</i>						<0.01 (1)
Metamitron (Goliath)	May 08	Jul 09 [†]	1059	499	4	0.01 (78 [*])
- <i>Metamitron-desamino</i>						0.01 (86 [*])
Ethofumesat	May 08	Jul 09 [†]	1059	499	4	<0.01(25 [*])
- <i>Fluazifop-P^{d)}</i> (Fusilade Max)	Jul 08	Jul 09 [†]	985	494	21	<0.01 (1)
- <i>TFMP^{d)}</i> (Fusilade Max)						0.22 (63)
Spring barley 2009						
Bentazone (Fighter 480)	May 09	Jul 09 [†]	95	0	1	<0.01 (52 [*])

^{*} Pesticide has been applied more than once, and the findings are not necessarily related to one specific application.

¹⁾ Drainage runoff commenced two weeks prior to the application of propyzamide, and the weighted concentrations refer to the period from the date of application until 1 July 2007.

^{d)} Degradation product of fluazifop-P-butyl. The parent compound degrades too rapidly to be detected by monitoring.

[†] Monitoring will continue for an additional year. The values for prec. and perc. are accumulated up to July 2009.

Regarding the pesticides applied to the fodder beet crop during spring and summer of 2008, these cannot be finally evaluated, but await an additional year of monitoring. Hitherto, there has been no leaching of triflurosulfuron-methyl, whereas one of its degradation products IN-E7710 (Table 9 and Figure 20 D) 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 twice, in May 2000 and May 2008. Ethofumesate, metamiltron and its degradation product metamiltron-desamino have all been found in drainage water (Table 9, Figure 20B and 20C) and groundwater (Appendix 5, Table A5.3). After the 2008 application, all concentrations measured were, however, less than 0.1 µg/l.

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 21B) nor groundwater (Figure 22B). When applying fluazifop-P-butyl in July 2008 and including its degradation product TFMP in the monitoring programme, a different picture emerged (Figure 21C and Figure 22C). At the onset of the drainage flow on 11 September 2008, a concentration of 0.52 µg/l TFMP was found. Concentrations remained above 0.1µg/l throughout the period of drainage runoff. At the last sampling from 18 March 2009 the TFMP concentration was 0.12 µg/l. 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 rootzone being relatively dry, and with percolation 1 m b.g.s. in July-August 2008 (Figure 16 and Figure 22A), this indicates pronounced macropore transport bypassing the tile drainage system.

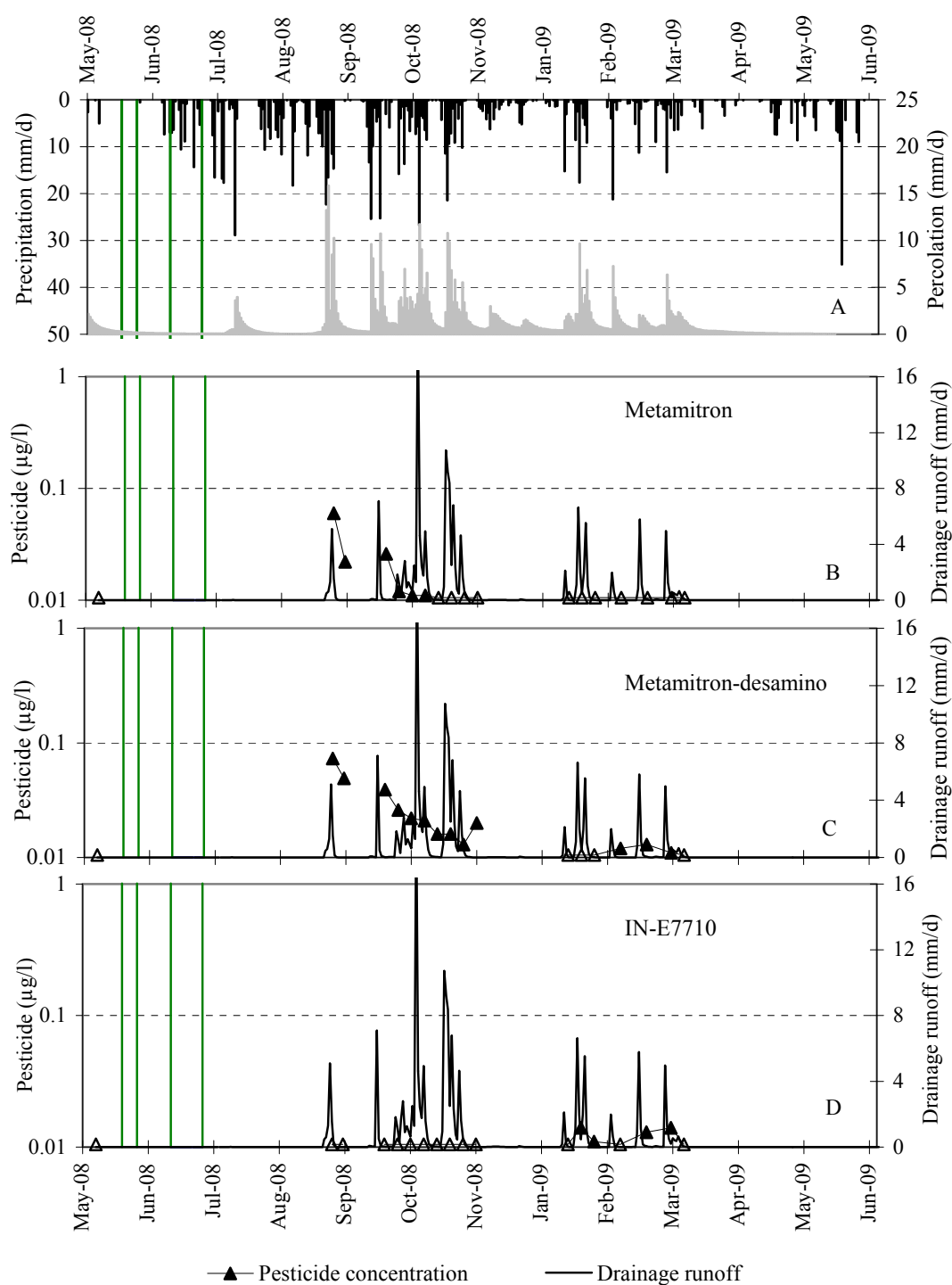


Figure 20. Precipitation and simulated percolation 1 m b.g.s. (A) together with the concentration of metamitron (B), metamitron-desamino (C) and IN-E7710 (D) in the drainage runoff at **Silstrup**. The green vertical lines indicate the dates of metamitron and triflurosulfuron-methyl applications. Open symbols indicate values below the detection limit of 0.01 µg/l.

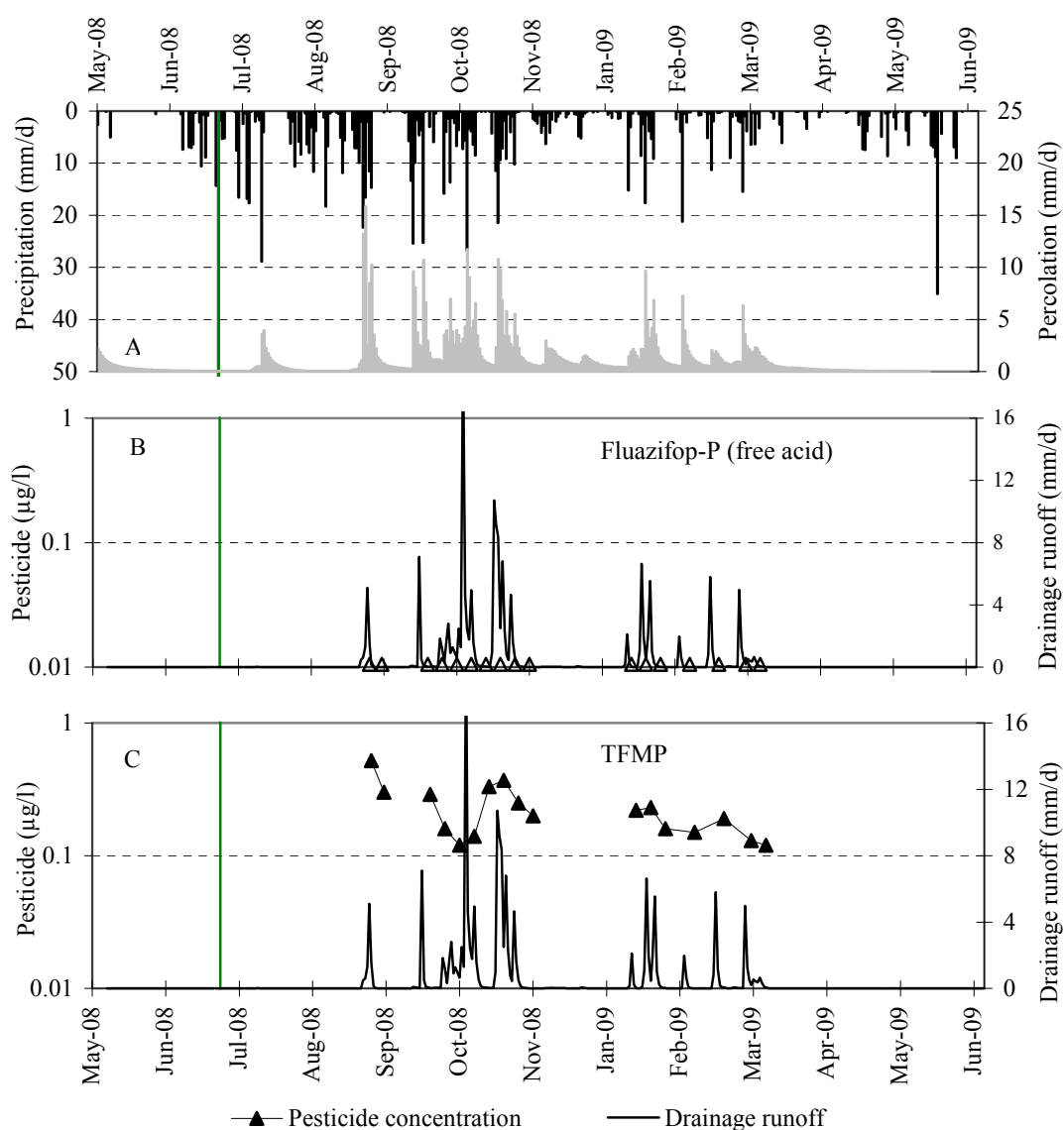


Figure 21. Precipitation and simulated percolation 1 m b.g.s. (A) together with the concentration of fluazifop-P (free acid) (B) and TFMP (C) in the drainage runoff at **Silstrup**. The green vertical line indicates the date of fluazifop-P-butyl application. Open symbols indicate values below the detection limit of 0.01 µg/l.

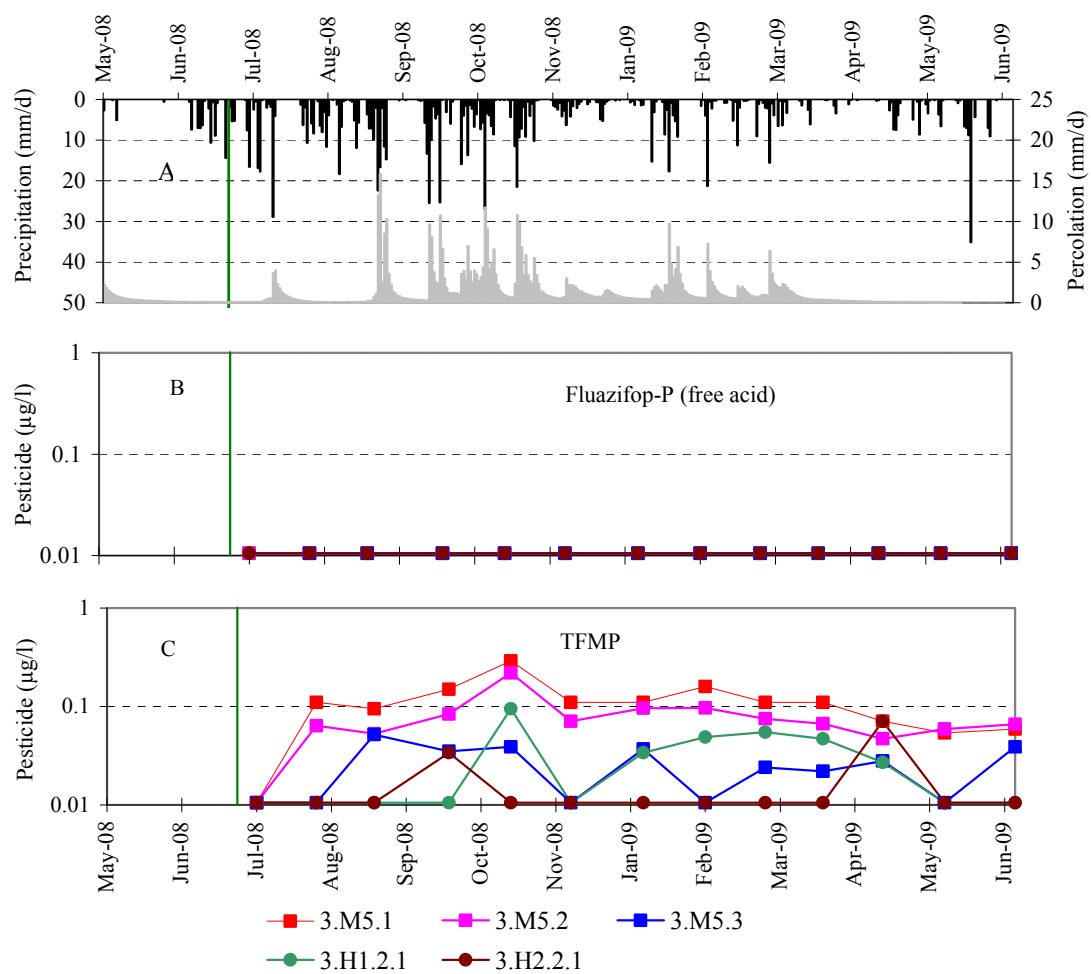


Figure 22. Precipitation and simulated percolation 1 m b.g.s. (A) together with the concentration of fluazifop-P (free acid) (B) and TFMP (C) in the groundwater monitoring screens at **Silstrup**. The green vertical line indicates the date of fluazifop-P-butyl application.

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 23). The site is highly heterogeneous with considerable variation in both topsoil and aquifer characteristics (Lindhardt *et al.*, 2001). Such heterogeneity is quite common for this geological formation, however. Based on three profiles excavated in the buffer zone bordering the field the soil was classified as Abruptic Argiudoll, Aquic Argiudoll and Fragiaquic Glossudalf (Soil Survey Staff, 1999). The topsoil is characterized as sandy loam with a clay content of 10–20%, and an organic carbon content of 1.7–7.3%. A C-horizon of low permeability also characterizes the site. The saturated hydraulic conductivity in the C-horizon is 10^{-8} m/s, which is about two orders of magnitude lower than 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 Kjær *et al.* (2002, 2003, 2004, 2005c, 2007, 2008, and 2009).

Having been sprayed with glyphosate on 14 September 2007, the field was ploughed on 2 October 2007 and the following day sown with winter wheat (cv. Frument). Due to the late sowing, the crop did not emerge until 17 October. On 30 October, when the crop had two leaves unfurled, it was sprayed with the herbicide picolinafen, and on 22 November with the fungicide tebuconazole, when it had three leaves unfurled. On 13 June 2008, at full flowering, the fungicide azoxystrobin was used. The winter wheat was harvested on 16 August, yielding 83.8 hkg/ha of grain (85% dry matter), whereas 40.7 hkg/ha straw was shredded at harvest and ploughed in on 12 March 2009. The grain yield was slightly above the average for the soil type and year (Plantedirektoratet, 2008).

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, bentazon and MCPA were used against weeds. Only bentazon 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% dry matter) and 39.9 hkg/ha of straw (100 dry matter), 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).

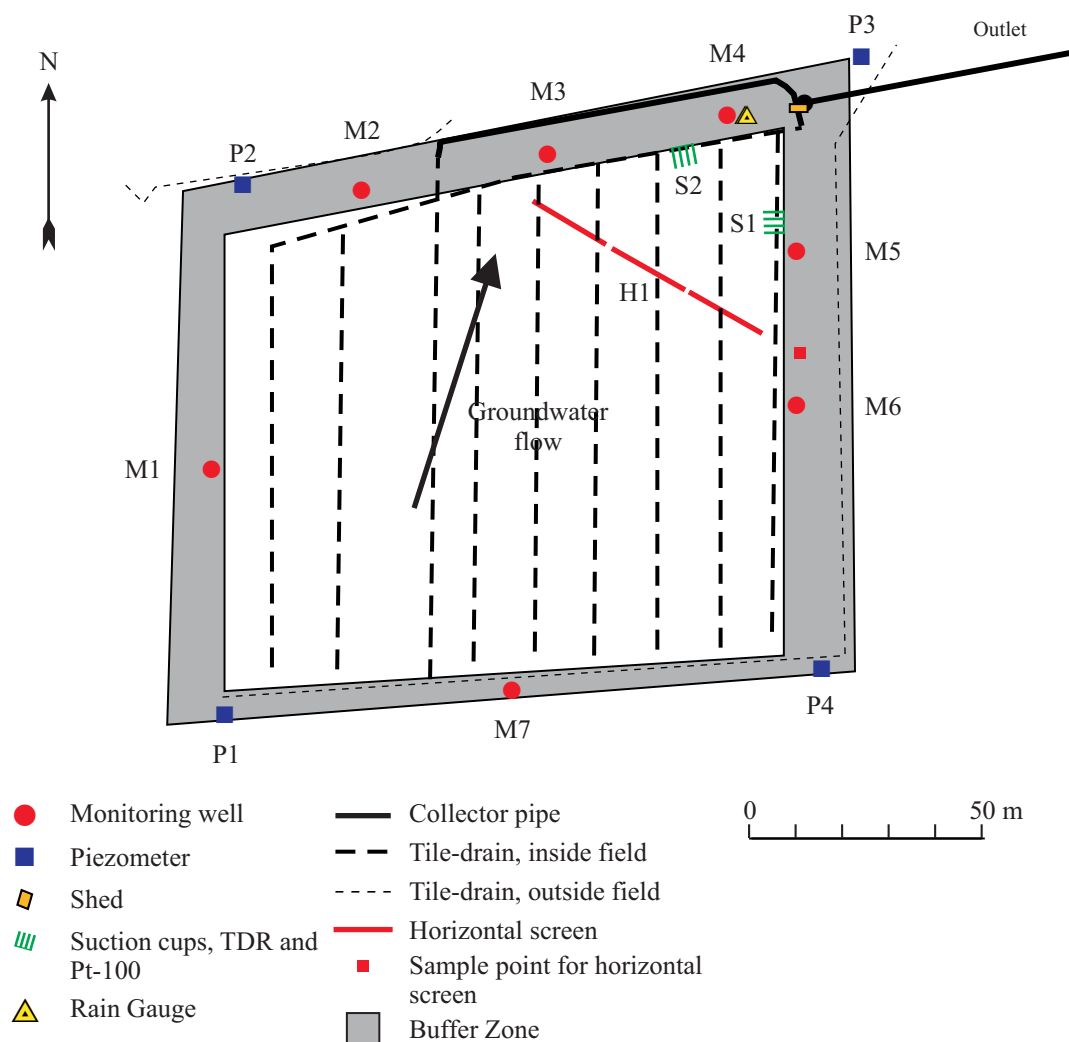


Figure 23. Overview of the **Estrup** site. The innermost white area indicates the cultivated land, while the grey area indicates the surrounding buffer zone. The positions of the various installations are indicated, as is the direction of groundwater flow (by an arrow).

5.1.3 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 2009 and to establish an annual water balance.

Compared to the setup in Kjær *et al.* (2009), a year of validation was added to the MACRO setup for the Estrup site. The setup was hereby calibrated for the monitoring period May 1999-June 2004 and validated for the monitoring period July 2004-June 2009. For this purpose, the following time series have been used: the observed groundwater table measured in the piezometers located in the buffer zone, measured drainage flow, and soil water content measured at two depths (25 and 40 cm b.g.s.) from the soil profile S1 (Figure 25). The TDR probes installed at the other depths yielded unreliable data with saturations far exceeding 100% and dynamics with increasing soil water content during the dryer 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). 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) and Rosenbom *et al.* (*In prep.*).

5.2 Results and discussion

5.2.1 Soil water dynamics and water balances

The model simulations were generally consistent with the observed data (which were limited compared to other PLAP sites, as noted above), indicating a good model description of the overall soil water dynamics in the unsaturated zone (Figure 24). 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 24B). 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 dynamics in these layers is difficult. However, the overall soil water saturation at 25 and 40 cm b.g.s. was captured (Figure 24D and 24E). Nothing special is noted for the groundwater table in the latest monitoring period (July 2008-June 2009). As in previous years (Kjær *et al.*, 2008), the simulated groundwater table often fluctuates slightly above the drain depth during periods of drainage flow.

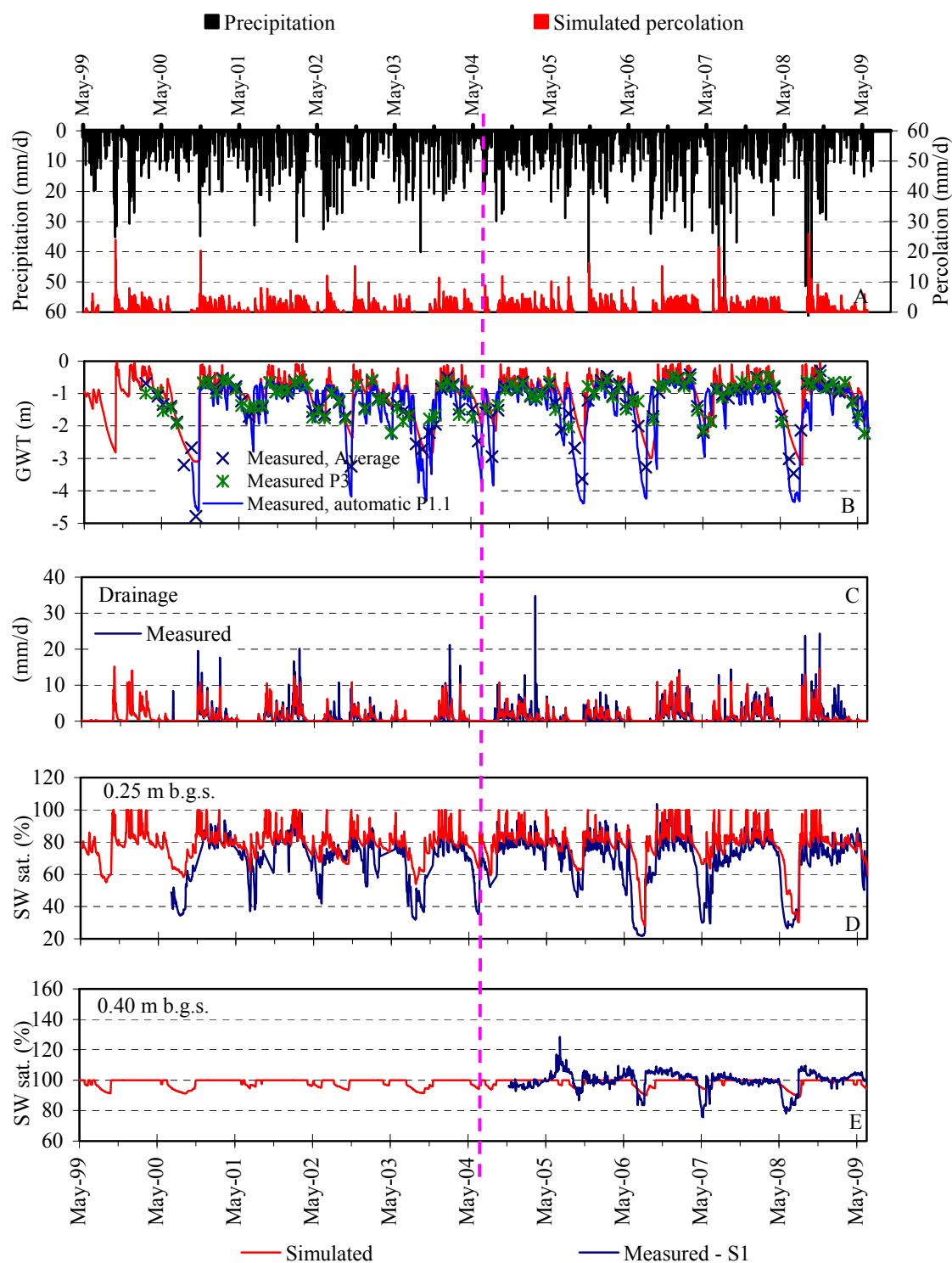


Figure 24. Soil water dynamics at **Estrup**: Measured precipitation and simulated percolation 0.6 m b.g.s. (A), simulated and measured groundwater level (B), simulated and measured drainage flow (C), and simulated and measured soil saturation (SW sat.) at two different soil depths (D and E). The measured data in B derive from piezometers located in the buffer zone. The measured data in D and E derive from TDR probes installed at S1 (Figure 23). The broken vertical line indicates the beginning of the validation period (July 2004-June 2009).

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

	Normal precipitation ²⁾	Precipitation	Actual evapotranspiration	Measured drainage	Simulated drainage	Groundwater recharge ³⁾
1.7.99–30.6.00 ¹⁾	968	1173	466	–	553	154 ⁴⁾
1.7.00–30.6.01	968	887	420	356	340	111
1.7.01–30.6.02	968	1290	516	505	555	270
1.7.02–30.6.03	968	939	466	329	346	144
1.7.03–30.6.04	968	928	499	298	312	131
1.7.04–30.6.05	968	1087	476	525	468	86
1.7.05–30.6.06	968	897	441	258	341	199
1.7.06–30.6.07	968	1365	515	547	618	303
1.7.07–30.6.08	968	1045	478	521	556	46
1.7.08–30.6.09	968	1065	480	523	362	62

¹⁾ Monitoring started in April 2000.

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

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

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

The simulated drainage (Figure 24C) matched the measured drainage flow quite well. The measured drainage flow from January to March was, however, underestimated by the MACRO model. In this period the temperature is periodically below zero degrees C, which could indicate periods with snow melt, which the model setup seems unable to capture. 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).

The resulting water balance for Estrup for the nine monitoring periods is shown in Table 10. Compared with the previous nine years, the latest hydraulic year July 2008-June 2009 was characterised by having the fifth highest precipitation, the fourth highest simulated actual evapotranspiration and the 3th highest measured drainage. Given that the model did not capture the snowmelt in the period January-Marts, large differences are observed between the measured and simulated drainage. Precipitation in this year was characterized by August-October being very wet and December-February and April being very dry (Appendix 4). Due to this precipitation pattern, the simulated percolation pattern of the year July 2008-June 2009 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 24A, 24B, and 24C).

5.2.2 Bromide leaching

Bromide has now been applied three times at Estrup. The bromide concentrations measured up to October 2005 (Figure 25 and Figure 26) relate to the bromide applied in spring 2000, as described further in Kjær *et al.* (2003). In March 2009, bromide measurements in the suction cups and monitoring wells M3 and M7 were suspended. Leaching of the bromide applied in November 2005 and April 2009 is evaluated in Rosenbom *et al.* (*In prep.*).

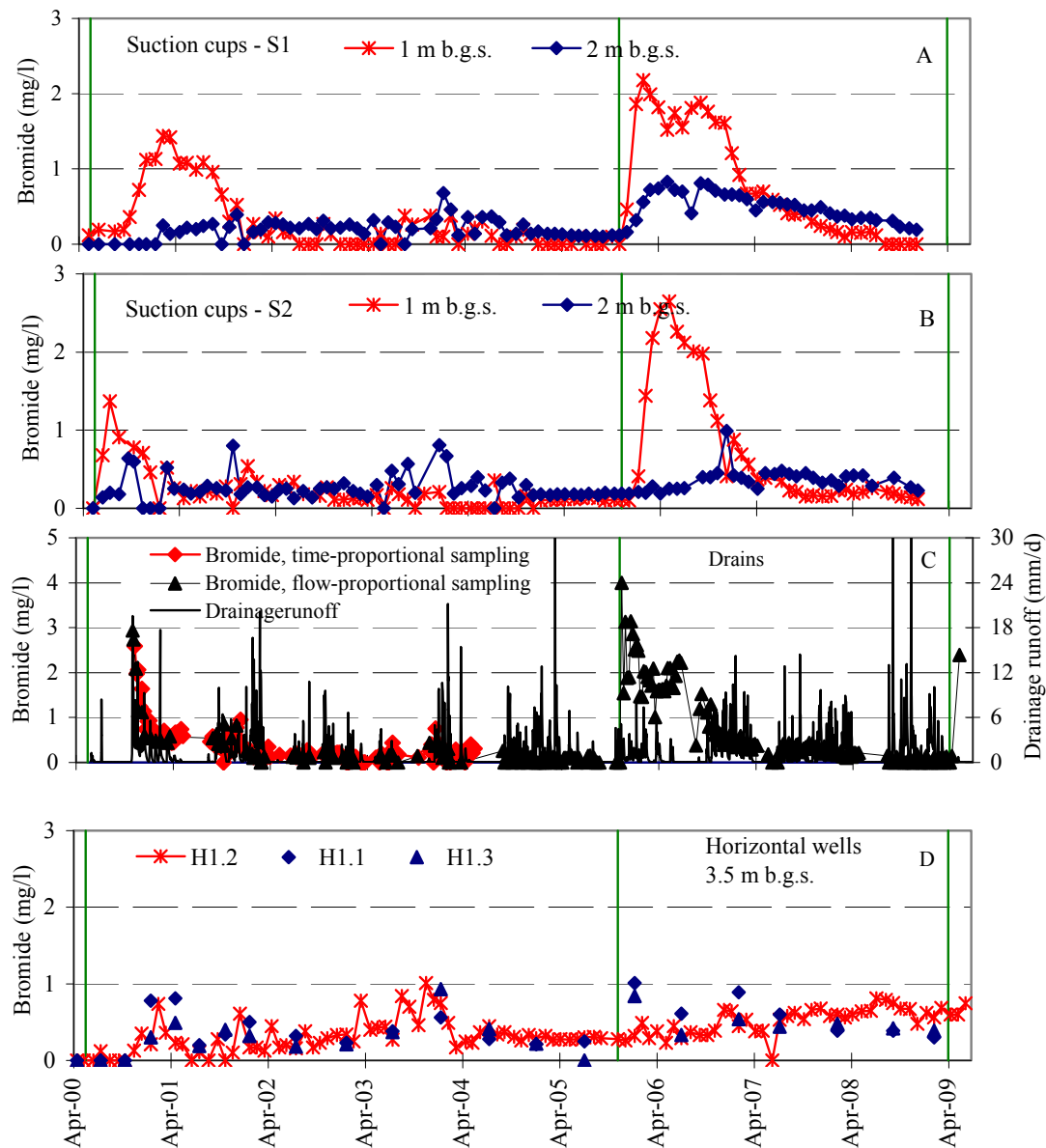


Figure 25. Bromide concentration at **Estrup**. A and B refer to suction cups located at S1 and S2, respectively. The bromide concentration is also shown for drainage runoff (C) and the horizontal monitoring well H1 (D). In September 2008, bromide measurements in the suction cups were suspended (Appendix 2). The green vertical lines indicate the dates of bromide applications.

5.2.3 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 (2007/2008 and 2008/2009) is shown together with precipitation and simulated precipitation in Figure 27. 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 2009 are not evaluated in this report and, hence, not included in Table 11.

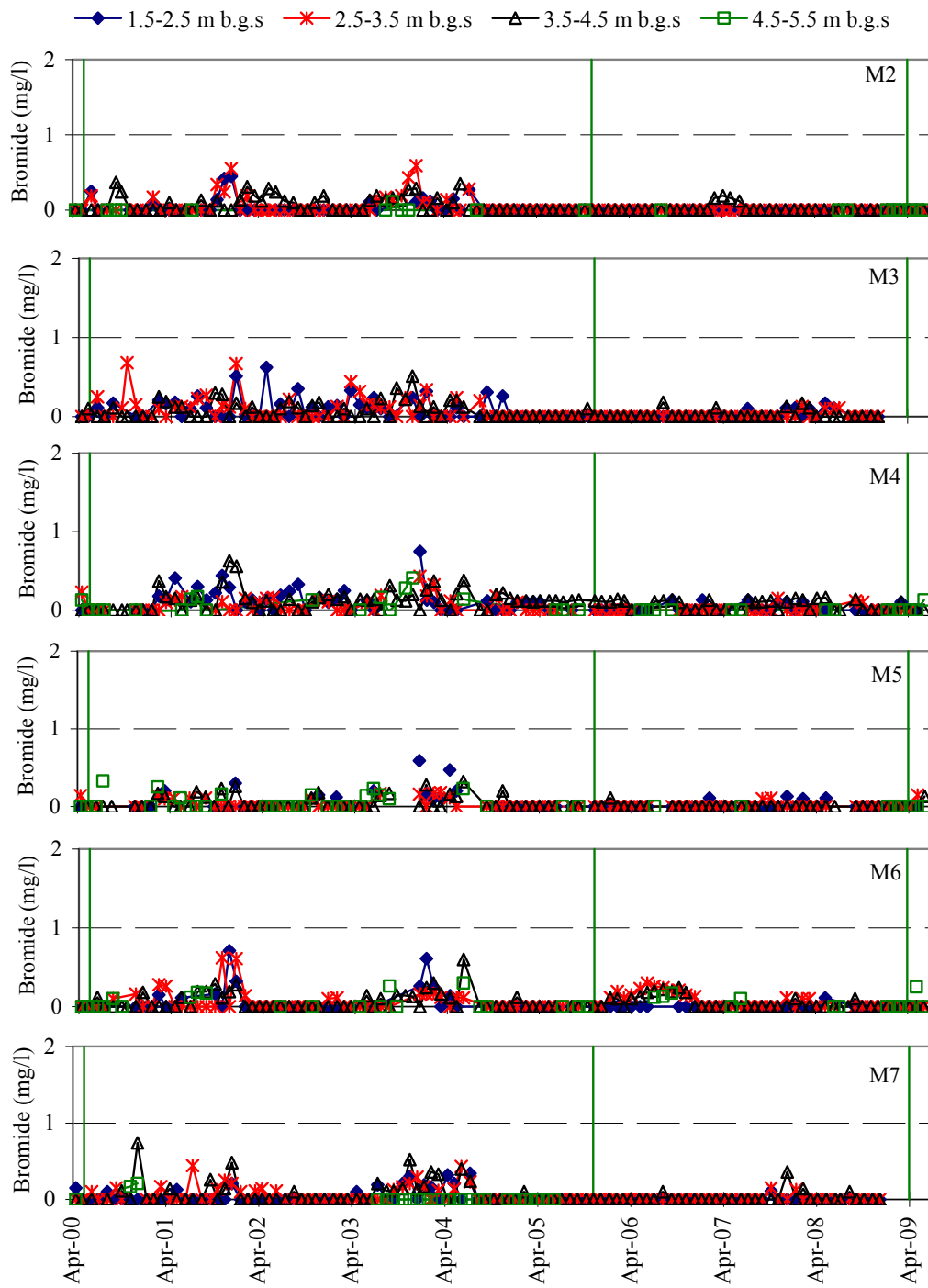


Figure 26. Bromide concentration at **Estrup**. The data derive from the vertical monitoring wells (M2–M7). Screen depth is indicated in m b.g.s. In September 2008, monitoring wells M3 and M7 were suspended (Appendix 2). The green vertical lines indicate the dates of bromide applications.

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

Crop and analysed pesticides	Application date	End of monitoring	Prec. (mm)	Perc. (mm)	1 st month Perc. (mm)	C_{mean} ($\mu\text{g/l}$)
Spring barley 2000						
Metsulfuron-methyl (Ally)	May 00	Apr 03	2990	1456	29	<0.01(1)
- <i>triazinamin</i>						<0.02(1)
Flamprop-M-isopropyl (Barnon Plus 3)	May 00	Apr 03	2914	1434	2	0.02(20)
- <i>flamprop (free acid)</i>						0.01(13)
Propiconazole (Tilt Top)	Jun 00	Apr 05	4938	2294	0	0.01(27 [*])
Fenpropimorph (Tilt Top)	Jun 00	Jul 02	2211	1048	0	<0.01(1)
- <i>fenpropimorphic acid</i>						<0.02(0)
Dimethoate (Perfekthion 500 S)	Jun 00	Jul 02	2211	1048	0	<0.01(0)
Pea 2001						
Glyphosate (Roundup Bio)	Oct 00	Jul 09 [†]	9294	4461	123	0.54(278 [*])
- <i>AMPA</i>						0.17(346 [*])
Bentazone (Basagran 480)	May 01	Jul 08	7629	3621	9	0.03 (139)
- <i>AIBA</i>						<0.01 (2)
Pendimethalin (Stomp SC)	May 01	Jul 03	2208	1096	9	<0.01(37 [*])
Pirimicarb (Pirimor G)	Jun 01	Jul 05	4251	1995	10	0.01(40 [*])
- <i>pirimicarb-desmethyl</i>						<0.02(0)
- <i>pirimicarb-desmethyl-formamido</i>						<0.02(26 [*])
Winter wheat 2002						
Ioxynil (Oxitril CM)	Nov 01	Jul 03	1580	860	52	0.04(20) ¹
Bromoxynil (Oxitril CM)	Nov 01	Jul 03	1580	860	52	0.01(3) ¹
Amidosulfuron (Gratil 75 WG)	Apr 02	Jul 04	2148	928	8	<0.01 (0)
MCPA (Metaxon)	May 02	Jul 04	2091	928	0	<0.01(12)
- <i>4-chlor,2-methylphenol</i>						<0.01(1)
Propiconazole (Tilt 250 EC)	May 02	Apr 05	2920	1336	39	0.02 (27 [*])
Pirimicarb (Pirimor G)	Jun 02	Jul 05	2982	1403	58	0.01(40 [*])
- <i>pirimicarb-desmethyl</i>						<0.02(0)
- <i>pirimicarb-desmethyl-formamido</i>		Apr 06				<0.02(26 [*])

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

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

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

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

The leaching risk of pesticides applied during 2000, 2001, 2002, 2003, 2004, 2005, 2007, and 2008 has been evaluated in Kjær *et al.* (2002, 2003, 2004, 2005c, 2007, 2008 and, 2009), respectively.

Since the applications of terbuthylazine in 2005 and glyphosate in 2005 and 2007, both compounds together with their degradation products have been included in the monitoring, the results of which are summarised in Table 11. For a detailed description of the leaching pattern including primary data and climate condition characterising the monitoring periods, reference is made to Kjær *et al.* (2007).

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

Crop and analysed pesticides	Application date	End of monitoring	Prec. (mm)	Perc. (mm)	1 st month perc. (mm)	C_{mean} ($\mu\text{g/l}$)
Fodder beet 2003						
Glyphosate (Roundup Bio)	Sep 02	Jul 09 [†]	7099	3384	0	0.43 (278 [*])
- AMPA						0.19 (346 [*])
Ethofumesate (Betanal Optima)	May 03	Apr 06	2901	1371	50	0.11(35)
Metamitron (Goltix WG)	May 03	Apr 06	2901	1371	50	1.1(42)
- <i>metamitron-desamino</i>						0.21(49)
Pirimicarb (Pirimor G)	Jul 03	Jul 05	2071	939	0	<0.01(40 [*])
- <i>pirimicarb-desmethyl</i>		Jul 05				<0.01(0)
- <i>pirimicarb-desmethyl-formamido</i>		Apr 06				0.12 (26 [*])
Spring barley 2004						
Fluroxypyr (Starane 180)	May 04	Jul 06	2073	1030	0	<0.02 (2)
Azoxystrobin (Amistar)	Jun 04	Jul 08	4452	2209	38	0.12 (65 [*])
- CyPM						0.23 (132 [*])
Maize 2005						
Terbuthylazine (Inter-Terbuthylazin)	May 05	Apr 09	4247	2042	32	0.48 (112)
- <i>desethyl-terbuthylazine</i>		Jul 09	4406	2051	32	0.31 (152)
- <i>2-hydroxy-terbuthylazine</i>		Jul 08	3338	1628	32	0.11 (87)
- <i>desisopropyl-atrazine</i>		Apr 09	4247	2042	32	0.02 (98)
- <i>2-hydroxy-desethyl-terbuthylazine</i>		Jul 08	3338	1628	32	0.24 (86)
Bentazone (Laddok TE)	Jun 05	Jul 08	3338	1628	10	0.18 (139)
- AIBA						<0.01 (2)
Glyphosate (Roundup Bio)	Nov 05	Jul 09 [†]	4001	1944	68	4.04 ((278 [*]) ¹⁾)
- AMPA						0.42 (346 [*]) ¹⁾
Spring barley 2006						
Florasulam (Primus)	Jun 06	Jul 08	2442	1163	0	<0.01 (0)
- <i>florasulam-desmethyl</i>						<0.03 (0)
Azoxystrobin (Amistar)	Jun 06	Jul 08	2414	1170	0	0.03 (65 [*])
- CyPM						0.13 (132 [*])
Winter wheat 2007						
Mesosulfuron-methyl (Atlantis WG)	Oct 06	Jul 08	2059	1095	63	<0.01 (13) ¹⁾
- <i>mesosulfuron</i>						<0.02 (0)
Chlormequat-chloride (Cycocel 750)	Apr 07	Jul 08	1337	603	0	<0.01 (1)
Epoxiconazole (Opus)	May 07	Jul 08	1199	600	45	0.01 (13)
Glyphosate (Roundup Bio)	Sep 07	Jul 09 [†]	1816	877	64	0.14 ((278 [*]) ¹⁾)
- AMPA						0.10 (346 [*]) ¹⁾
Winter wheat 2008						
Picolinafen (Pico 750 WG)	Oct 07	Jul 09 [†]	1680	805	52	0.03 (17) ¹⁾
- CL153815						0.24 (31) ¹⁾
Tebuconazol (Folicur EC 250)	Nov 07	Jul 09 [†]	1632	768	77	0.43 (41) ¹⁾

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

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

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

¹⁾ 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.

Terbuthylazine was applied during the growing of maize in May 2005. Terbuthylazine and all of its four measured degradation products leached to the drainage system (Kjær *et al.*, 2009; Figure 28). Three years after application both terbuthylazine and desethyl-terbuthylazine were found in several drainage water samples, concentrations in all instances being less than 0.1 $\mu\text{g/l}$ (Table 11), whereas desisopropyl-atrazine was detected once. Neither terbuthylazine nor its degradation product were detected in groundwater samples, expect for one detection of desisopropyl-atrazine on 15 January 2009 at a concentration of 0.011 $\mu\text{g/l}$ (Table A5.4 in Appendix 5).

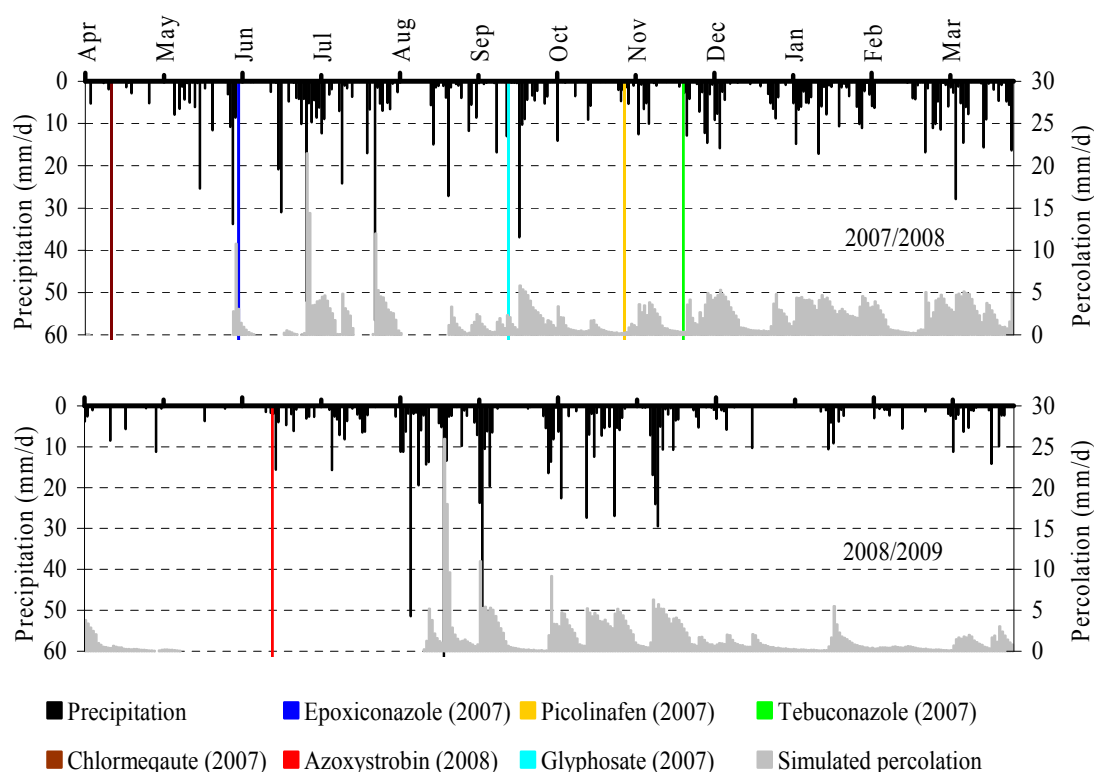


Figure 27. Application of pesticides included in the monitoring programme and precipitation (primary axis) together with simulated percolation 0.6 m b.g.s. (secondary axis) at **Estrup** in 2007/2008 (upper) and 2008/2009 (lower).

The herbicide glyphosate has now been applied at Estrup in 2000, 2002, 2005, and 2007 (Figure 30). Following all applications, both glyphosate and AMPA could be found in the drainage water. Out of 379 drainage water samples analysed for glyphosate and AMPA in the period 31 October 2000-13 May 2009, the concentrations of glyphosate and AMPA exceeded 0.1 µg/l in 89 and 98 samples, respectively. In the same period, 677 groundwater samples were analyzed for glyphosate and 681 for AMPA. During that periode AMPA never exceeded 0.1 µg/l, whereas glyphosate did so in two samples both taken on 7 July 2005 but from two different wells, concentrations being 0.67 and 0.59 µg/l (Table A5.4 in Appendix 5). In the period 2008/2009, glyphosate and AMPA have been detected in nine ($C_{\text{glyphosat}} = 0.011\text{-}0.075$ µg/l) and two ($C_{\text{AMPA}} = 0.013$ and 0.046 µg/l) groundwater samples (detection limit 0.01 µg/l), respectively. Five of the nine glyphosate detections were from groundwater samples collected at the beginning of September 2008 after the wettest August at all sites since monitoring started (250 mm, Appendix 4). With a very low recovery (~40%) in samples spiked with glyphosate and AMPA in the external QA (See paragraph 7.2.2.) for the period 2007/2008 and 2008/2009, the true concentration of glyphosate and AMPA in these periods is likely to be underestimated. The concentrations detected in drainage water samples taken after the glyphosate application in September 2007 were also remarkably lower than those taken after the other three applications (Figure 30), which may also be related to the low recovery.

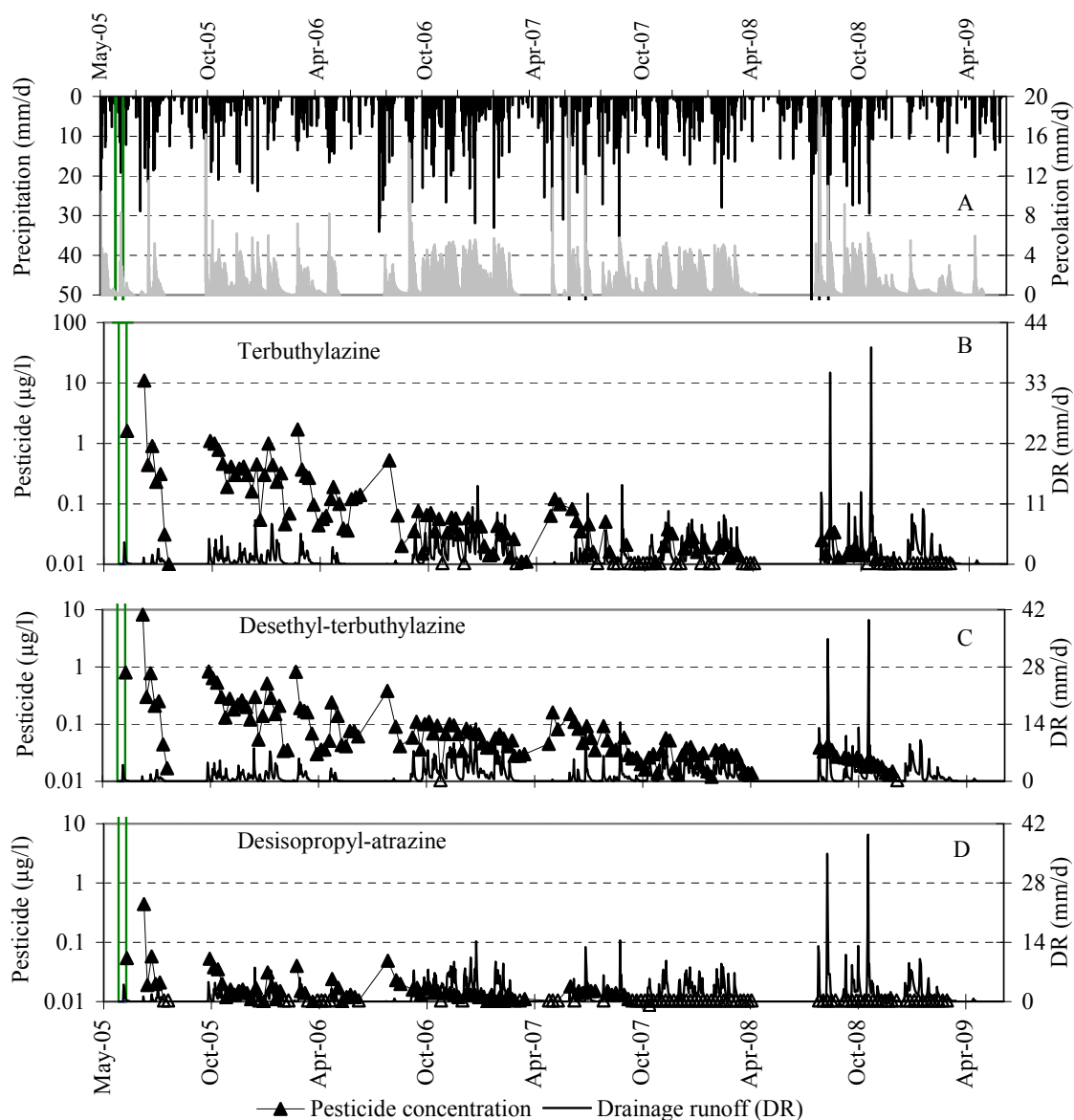


Figure 28. Precipitation and simulated percolation (A) together with concentration of terbutylazine (B), desethyl-terbutylazine (C), 2-hydroxyl-terbutylazine (D), desisopropyl-atrazine (E) and 2-hydroxy-desethyl-terbutylazine (F) in the drainage runoff (DR on the secondary axis) at Estrup. The green vertical lines indicate the dates of applications. Open symbols indicate values below the detection limit of 0.01 µg/l.

Florasulam, applied on 6 June 2006, and its degradation product florasulam-desmethyl have not been detected in any of the water samples analyzed (Table 11).

Azoxystrobin has now been applied three times at Estrup: 22 June 2004, 29 June 2006, and 13 June 2008. Concentrations in drainage water of the substance and its degradation product CyPM are shown in Figure 31. Azoxystrobin and CyPM leached to the depth of the drainage system following all three applications at the onset of drainage due to infiltration of excess rain. At all three applications, the surface had dessication cracks. The maximum measured concentration of azoxystrobin was 1.4 µg/l on 24 August 2006 and 2.1 µg/l of CyPM on 11 September 2008. As illustrated in Figure 31, CyPM seemed to be more persistent than azoxystrobin.

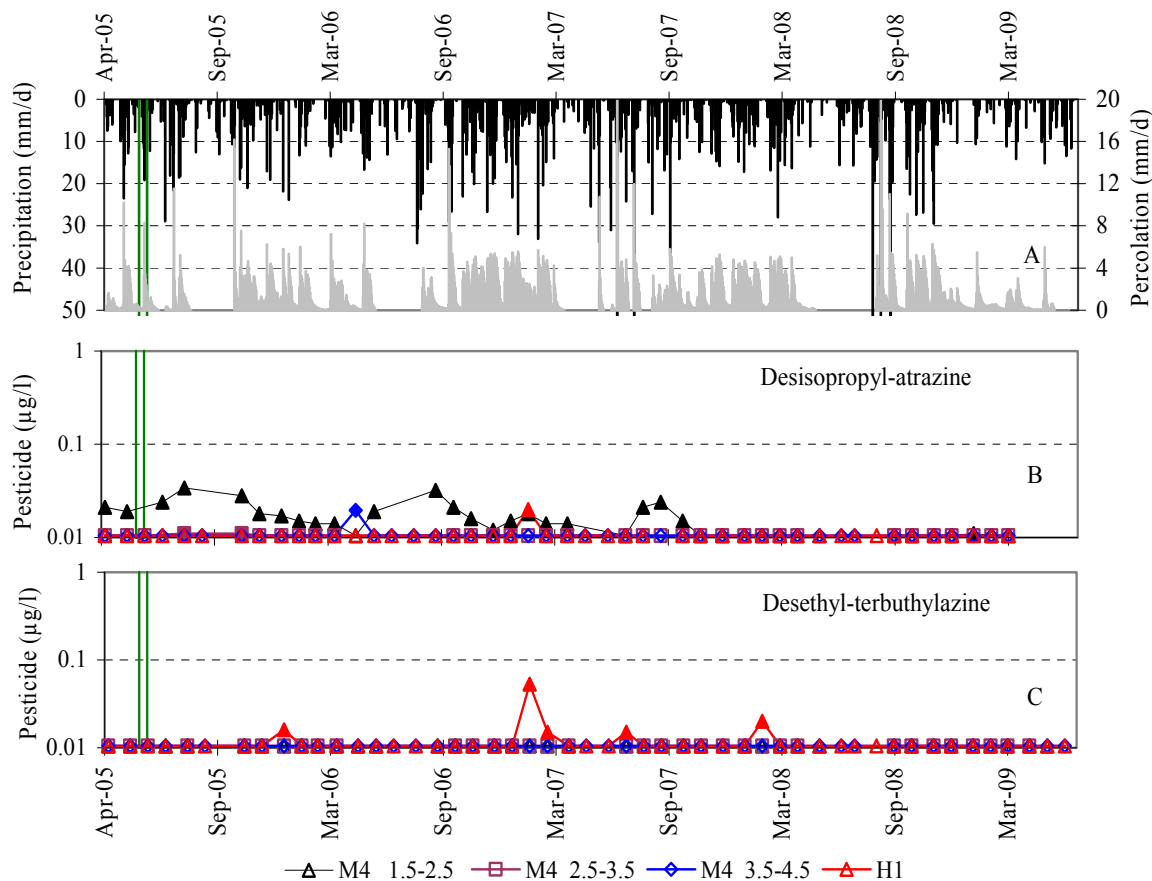


Figure 29. Precipitation and simulated percolation (A) together with concentration of desisopropyl-atrazine (B) and desethyl-terbuthylazine (C) in groundwater monitoring screens at **Estrup** in 2005/2009. The green vertical lines indicate the dates of applications, and numbers in parentheses the screen depth.

While leaching of azoxystrobin ceased one year after application, leaching of CyPM could continue for an additional year. Azoxystrobin has not been detected in samples collected from the groundwater monitoring screens, whereas CyPM has been found in seven samples, concentrations always below 0.1 µg/l (Table A5.4 in Appendix 5).

Chlormequat-chloride was applied once in April 2007 and detected once in the drainage water at a concentration of 0.017 µg/l. 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).

On two occasions epoxiconazole concentrations (applied on 31 May 2007) exceeded 0.1 µg/l, namely 0.39 and 0.19 µg/l on 28 June 2007 and 5 July 2007, respectively. The average first-year concentration was 0.01 µg/l (Table 11). Epoxiconazole was last detected on 13 March 2008.

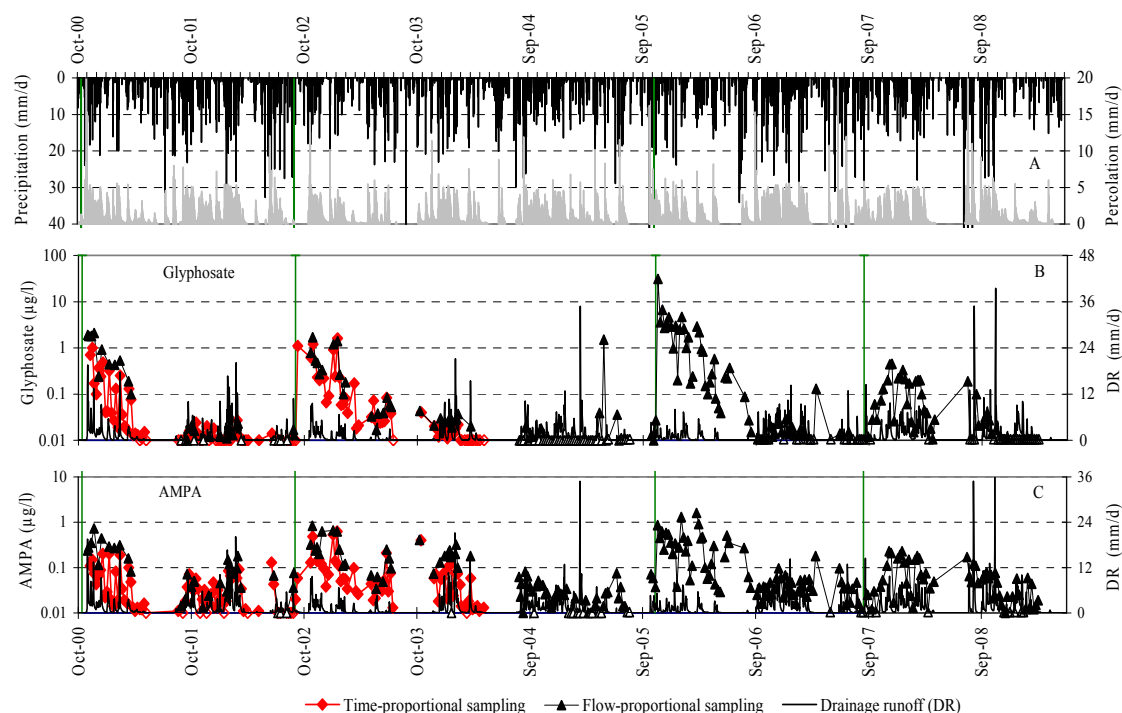


Figure 30. Precipitation and simulated percolation (A) together with the concentration of glyphosate (B) and AMPA (C) in the drainage runoff (DR, on the secondary axis) at **Estrup**. Data represent a nine-year period including four applications of glyphosate as indicated by the green vertical lines. Open symbols indicate values below the detection limit of 0.01 µg/l.

Picolinafen was applied on 30 October 2007. Concentrations of picolinafen never exceeded 0.1 µg/l in drainage water (Figure 32B). However, its degradation product CL153815 did so in several instances (Figure 32C), reaching a maximum of 0.5 µg/l on 6 December 2007. By comparing Figure 32B and Figure 32C, CL153815 can clearly be seen to be more persistent than picolinafen. Nearly a year after application of picolinafen (9 September 2008), CL153815 could be found in the drainage water at a concentration of 0.078 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).

Tebuconazole, applied on 22 October 2007, was seen in drainage water leachate on several occasions and reached a maximum concentration of 2.0 µg/l on 20 November 2008, over a year after application. Out of 60 drainage water samples analysed, 17 contained concentrations of tebuconazole above 0.1 µg/l (Figure 32D). Tebuconazole was, however, never detected in the groundwater (Table A5.4 in Appendix 5).

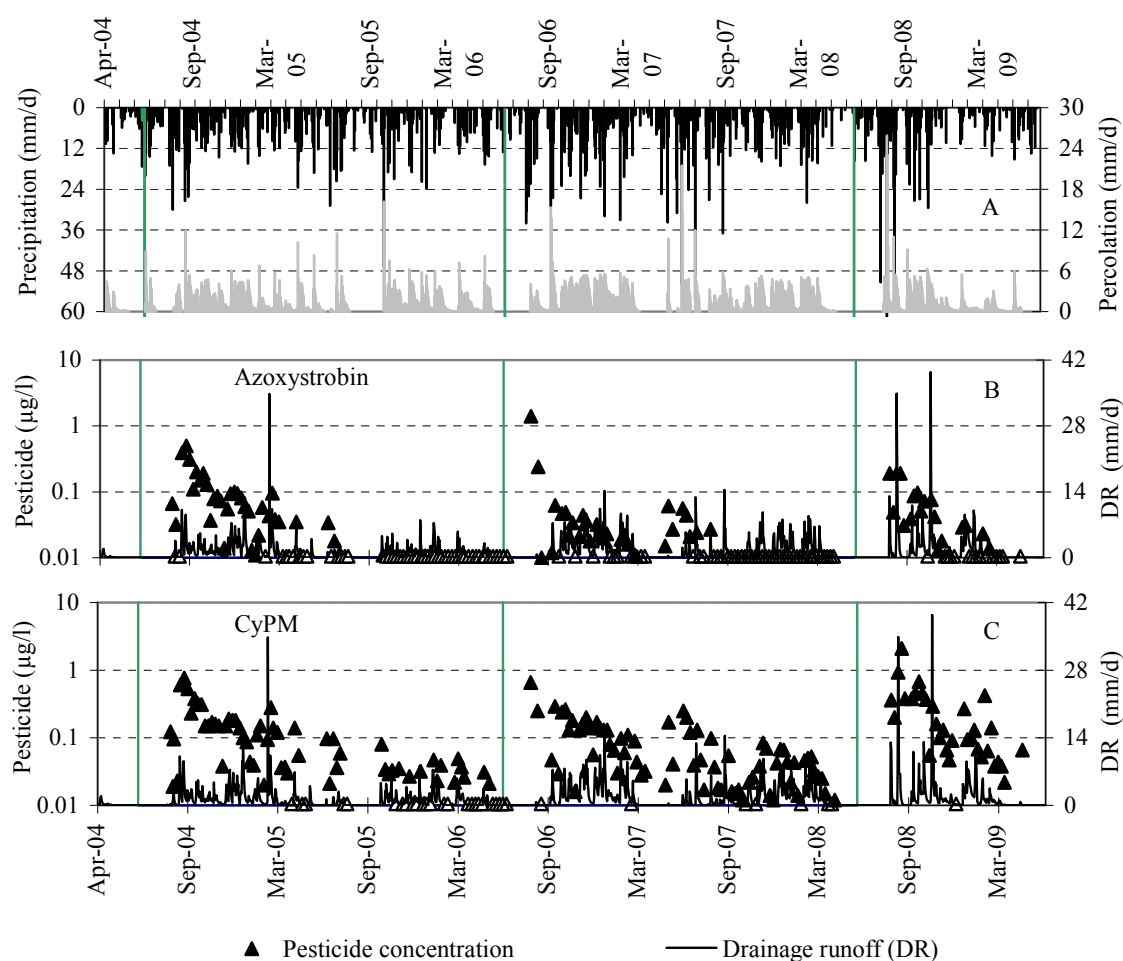


Figure 31. Precipitation and simulated percolation (A) together with concentration of azoxystrobin (B) and CyPM (C) in the drainage runoff (DR on the secondary axis) at **Estrup** in 2004/2009. The green vertical lines indicate the date of applications. Open symbols indicate values below the detection limit of 0.01 µg/l.

Pesticide leaching at Estrup is mostly confined to the depth of the drainage system. Apart from AMPA, CyPM, bentazone, desethylterbuthylazin, desisopropylatrazin, and glyphosate having been detected in 7, 14, 8, 7, 27, and 35 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).

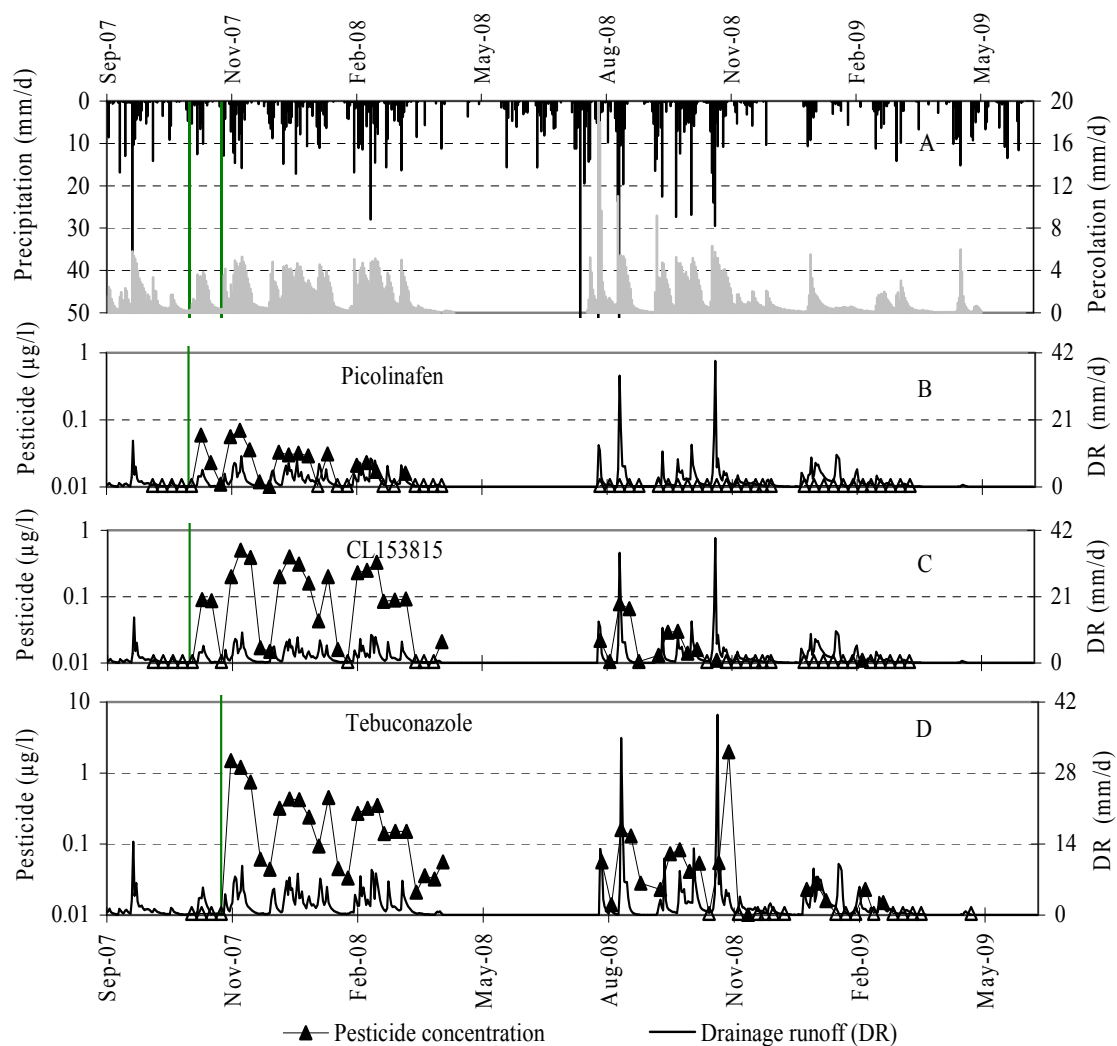


Figure 32. Precipitation and simulated percolation (A) together with concentration of epoxiconazole (B), picolinafen (C), CL153815 (D), and tebuconazole (E) in the drainage runoff (DR on the secondary axis) at **Estrup** in 2004/2009. The green vertical lines indicate the dates of applications. Open symbols indicate values below the detection limit of 0.01 µg/l.

6 Pesticide leaching at Faardrup

6.1 Materials and methods

6.1.1 Site description and monitoring design

Faardrup is located in southern Zealand (Figure 1). The test field covers a cultivated area of 2.3 ha (150 x 160 m). The terrain slopes gently to the west by 1–3° (Figure 33). Based on three profiles in the buffer zone bordering the field, the soil was classified as Haplic Vermudoll, Oxyaquic Hapludoll and Oxyaquic Argiudoll (Soil Survey Staff, 1999). The topsoil is characterized as sandy loam with 14–15% clay and 1.4% organic carbon. Within the upper 1.5 m numerous desiccation cracks coated with clay are present. The test field contains glacial deposits dominated by sandy till to a depth of about 1.5 m overlying a clayey till. The geological description shows that small channels or basins filled with meltwater clay and sand occur both interbedded in the till and as a large structure crossing the test field (Lindhardt *et al.*, 2001). The calcareous matrix and the reduced matrix begin at 1.5 m and 4.2 m b.g.s., respectively.

The dominant direction of groundwater flow is towards the west in the upper part of the aquifer (Figure 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 34 og Figure 37), 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).

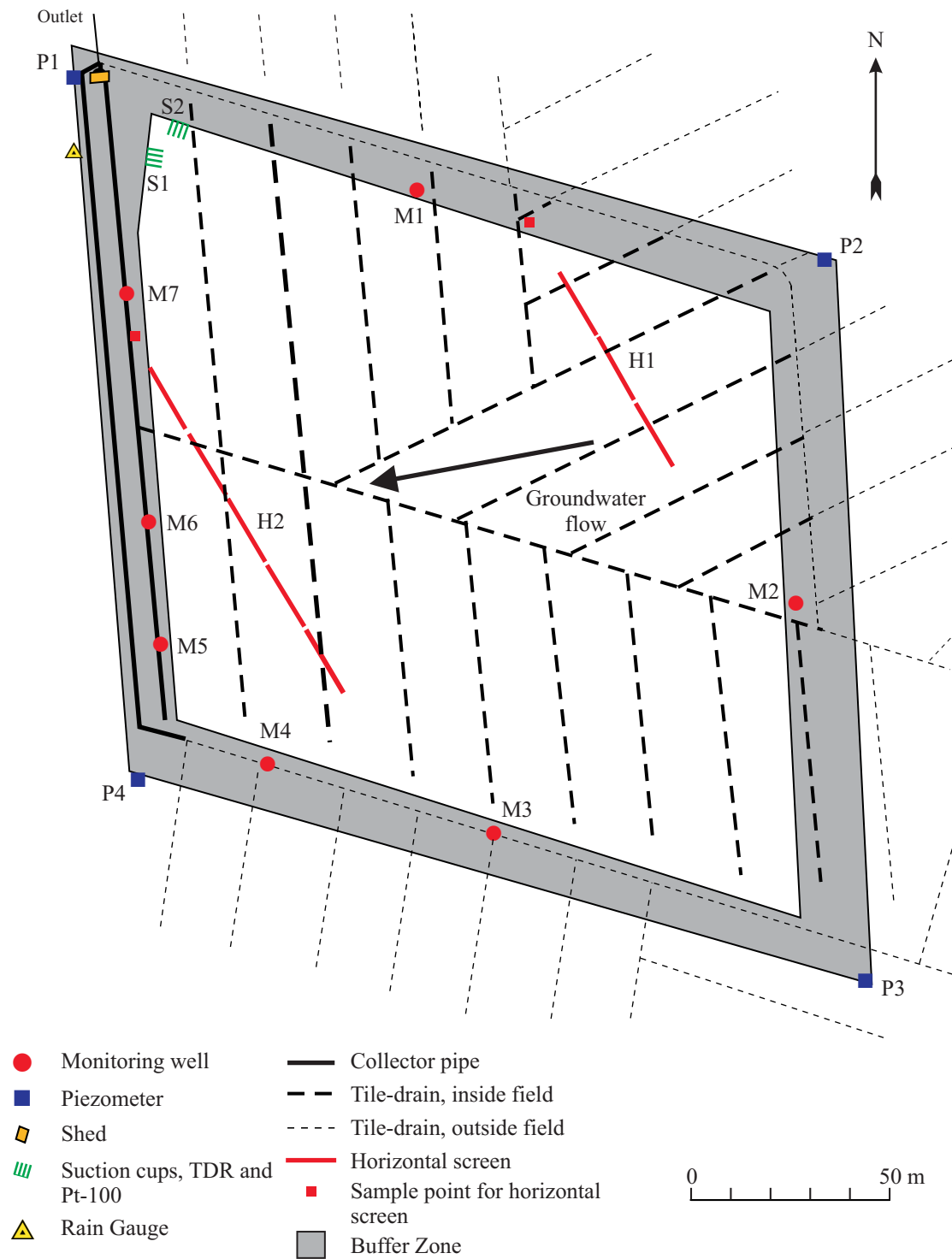


Figure 33. Overview of the **Faardrup** site. The innermost white area indicates the cultivated land, while the grey area indicates the surrounding buffer zone. The positions of the various installations are indicated, as is the direction of groundwater flow (by an arrow).

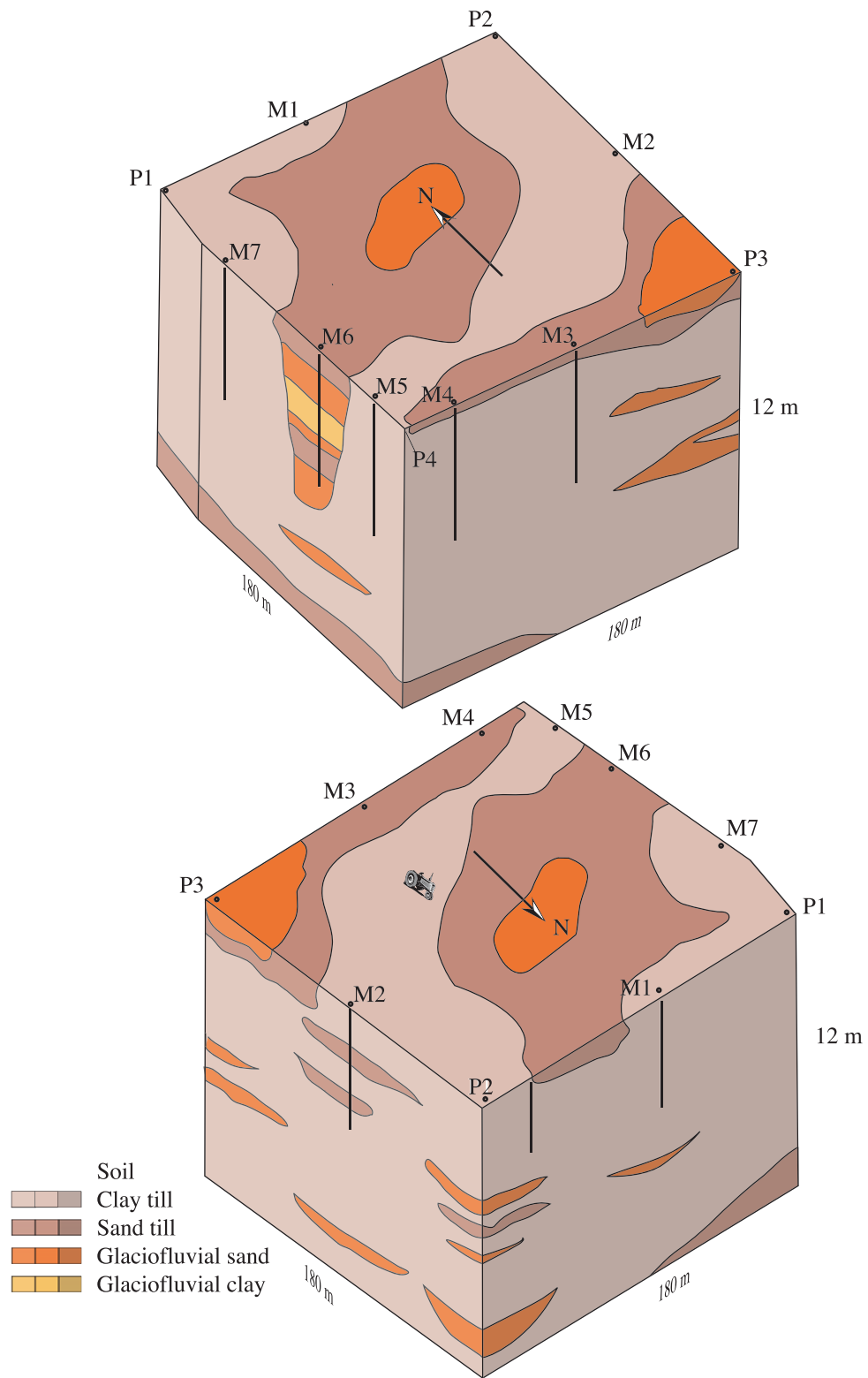


Figure 34. Geological description of **Faardrup** (Lindhardt *et al.*, 2001).

6.1.2 Agricultural management

Management practice during the two recent growing seasons is briefly summarized below and detailed in Appendix 3 (Table A3.5). For information about management practice during the previous monitoring periods, see Kjær *et al.* (2002, 2003, 2004, 2005c, 2007, 2008, and 2009).

Ploughing and sowing of a winter wheat crop (cv. Ambition) took place on 18 September 2007. Ten days later the wheat emerged. Pendimethalin was used against weeds on 9 October when the wheat had two leaves unfurled. The fungicide tebuconazol was applied on 20 November. On 20 August 2008 grain yield amounted to 89.6 hkg/ha (85% dry matter), the average for the soil type for this year (Plantedirektoratet, 2008). Straw yield was 65.2 hkg/ha (100% dry matter).

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 metamitron. On 30 April, when the first pair of beet leaves were visible, but not yet unfurled (pea-size), weeds were sprayed with triflurosulfuron-methyl, metamitron, 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 triflurosulfuron-methyl, metamitron, 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 23 October 2009.

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 2009 and to establish an annual water balance.

Compared to the setup in Kjær *et al.* (2009), 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 2009. For this purpose, the following time series were used: observed groundwater table measured in the piezometers located in the buffer zone, water content measured at three depths (25, 60 and 110 cm b.g.s.) from the two profiles S1 and S2 (Figure 35) and measured drainage flow. Data acquisition and model setup are described in Barlebo *et al.* (2007) and Rosenbom *et al.* (*In prep.*).

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

	Normal precipitation ¹⁾	Precipitation ²⁾	Actual evapotranspiration	Measured drainage	Simulated drainage	Groundwater recharge ³⁾
1.7.99–30.6.00	626	715	572	192	152	-50
1.7.00–30.6.01	626	639	383	50	34	206
1.7.01–30.6.02	626	810	515	197	201	98
1.7.02–30.6.03	626	636	480	49	72	107
1.7.03–30.6.04	626	685	505	36	18	144
1.7.04–30.6.05	626	671	469	131	55	72
1.7.05–30.6.06	626	557	372	28	15	157
1.7.06–30.6.07	626	790	515	202	212	72
1.7.07–30.6.08	626	645	521	111	65	13
1.7.08–30.6.09	626	713	459	46	20	207

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

²⁾ For July 1999-June 2002, July 2003-June 2004, in January and February of both 2005 and 2006, and July 2006-June 2007, measured at the DIAS Flakkebjerg meteorological station located 3 km from the test site (see detailed text above).

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

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

6.2 Results and discussion

6.2.1 Soil water dynamics and water balances

The level and dynamics of the soil water saturation in all three horizons in the hydraulic year July 2008-June 2009 were generally well described by the model (Figure 35D, 35E, and 35F). However, for the summer period 2009 the model underestimated the drop in the measured groundwater table (Figure 35B).

The resulting water balance for Faardrup for the ten monitoring periods is shown in Table 12. Compared with the previous nine years, the latest hydraulic year July 2008-June 2009 was characterised by having the fourth highest precipitation, the third lowest simulated actual evapotranspiration, and the third lowest measured and simulated drainage. Precipitation in this year was characterized by September, January, February and April being very dry and August, October, and June being very wet (Appendix 4). Due to this precipitation pattern, the duration of the simulated percolation period of the year July 2008-June 2009 was represented by continuous percolation throughout the period October-June (Figure 35A). 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 35B and 35C). The difference in measured and simulated yearly amount of drainage could be caused by an underestimation of the simulated drainage flow in February given snowmelt, which the model, here as at Estrup, was not able to capture.

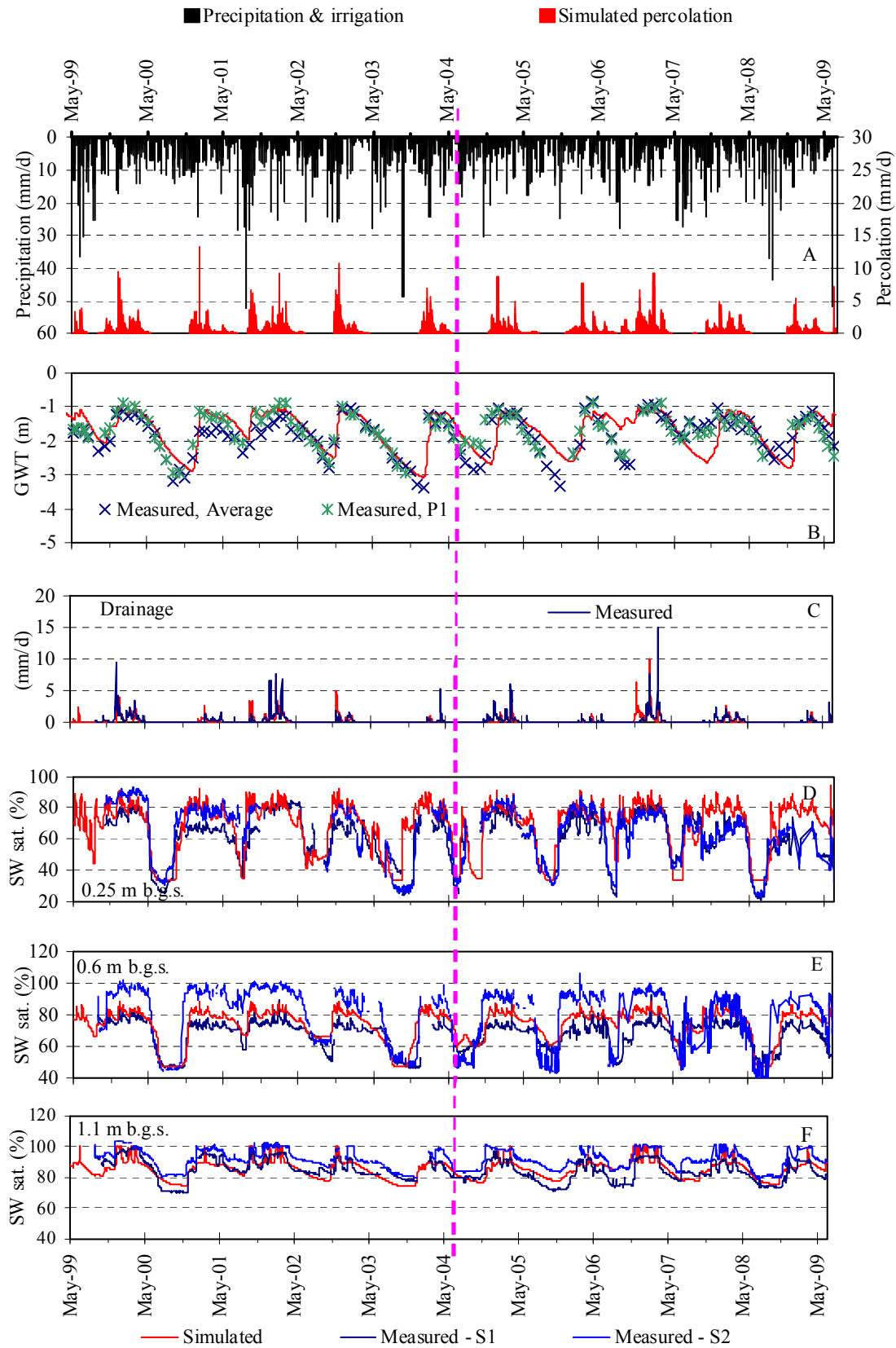


Figure 35. Soil water dynamics at **Faardrup**: Measured precipitation and simulated percolation 1 m b.g.s. (A), simulated and measured groundwater level GWT (B), simulated and measured drainage flow (C) and simulated and measured soil water saturation (SW sat.) at three different soil depths (D, E, 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 33). The broken vertical line indicates the beginning of the validation period (July 2004-June 2009).

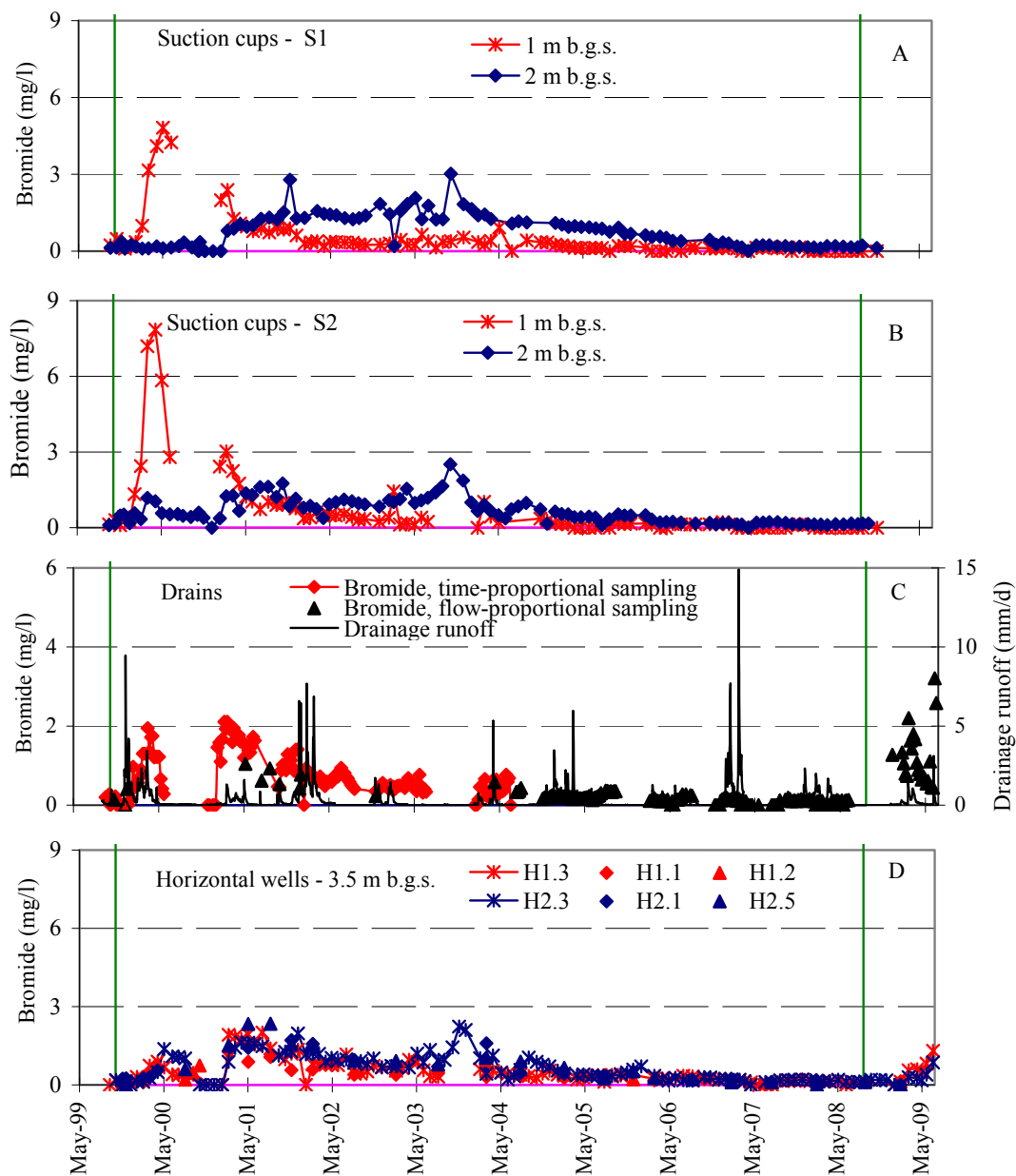


Figure 36. Bromide concentrations at **Faardrup**. A and B refer to suction cups located at S1 and S2. The bromide concentration is also shown for drainage runoff (C) and the horizontal monitoring wells (D). In September 2008, bromide measurements in the suction cups were suspended. The green vertical lines indicate the date of bromide applications.

6.2.2 Bromide leaching

The bromide concentration shown in Figure 36 and Figure 37 relates primarily to the bromide applied in May 2000, as described further in Kjær *et al.* (2003), and further evaluated in Rosenbom *et al.* (*In prep.*). 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 37).

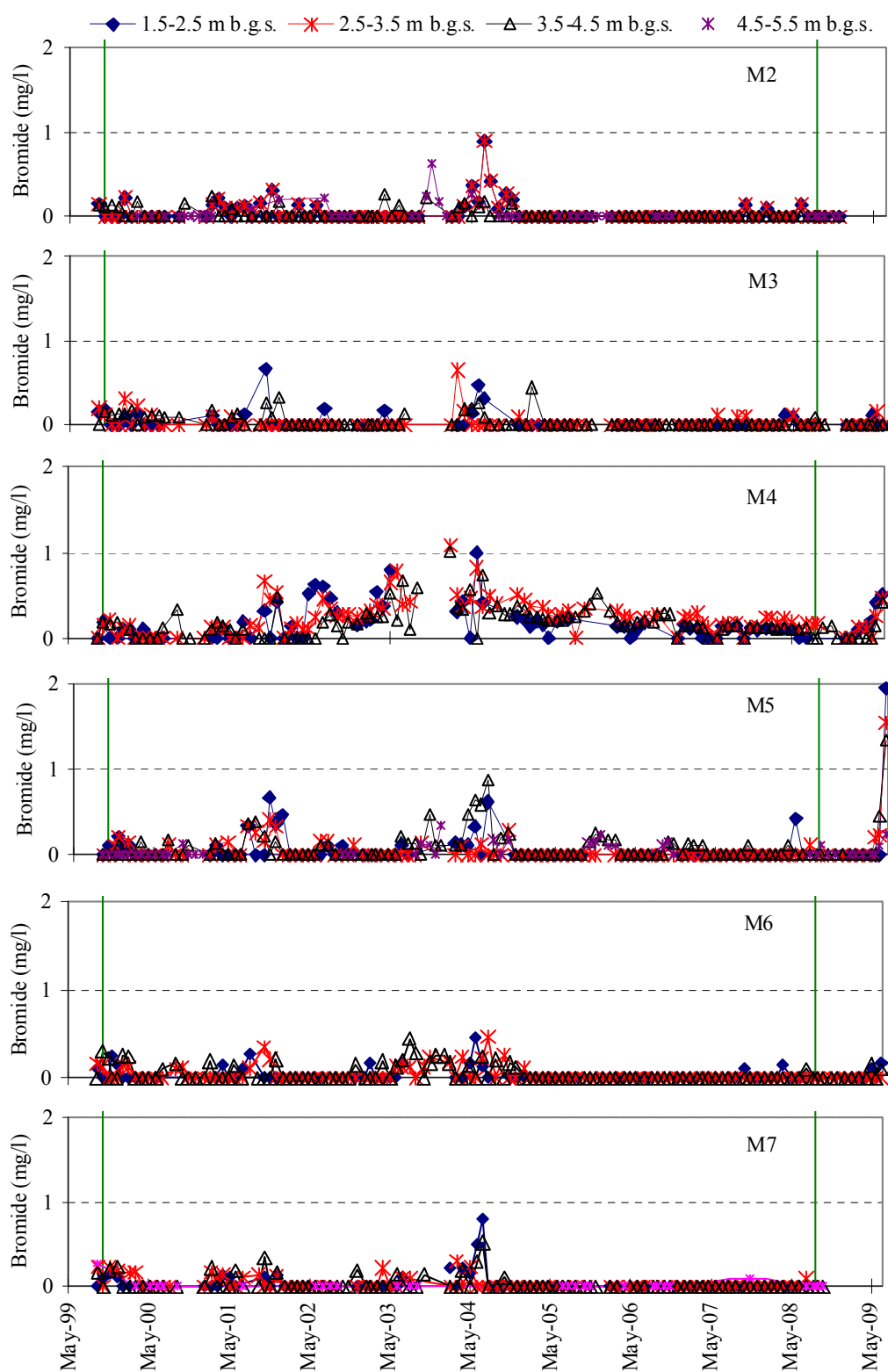


Figure 37. Bromide concentrations at **Faardrup**. The data derive from the vertical monitoring wells (M2–M7). Screen depth is indicated in m b.g.s. In September 2008, monitoring wells M2 and M7 were suspended (Appendix 2). The green vertical line indicates the date of bromide applications.

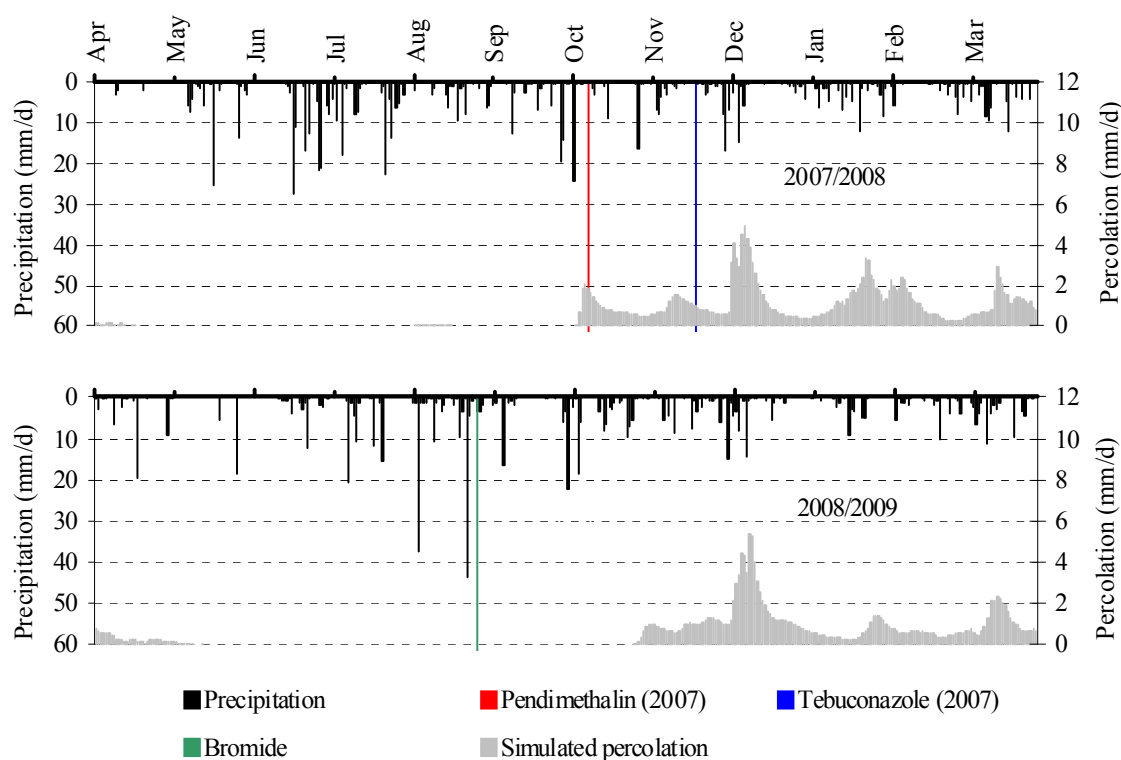


Figure 38. Application of pesticides included in the monitoring programme and precipitation (primary axis) together with simulated percolation (secondary axis) at **Faardrup** in 2007/2008 (upper) 2008/2009 (lower).

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 38. 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. 1st month perc. refers to accumulated percolation within the first month after application. C_{mean} refers to average leachate concentration in the drainage water the first drainage season after application (See Appendix 2 for calculation methods). The number of pesticide-positive samples is indicated in parentheses.

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

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

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

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

The leaching risk of pesticides applied during 2000, 2001, 2002, 2004, 2005, 2006, 2007, and 2008 has been evaluated in Kjær *et al.* (2002, 2003, 2004, 2005c, 2007, 2008, and 2009).

The degradation products of terbutylazine (applied in 2005) and its degradation products were included in the monitoring period until 2008, and the results of these applications are reported in Kjær *et al.* (2009).

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

Crop and analysed pesticides	Application Date	End of monitoring	Prec. (mm)	Perc. (mm)	1 st month perc. (mm)	C _{mean} (µg/l)
Winter rape 2003						
Clomazone (Command CS)	Aug 02	Apr 05	1761	509	4	<0.02(1)
- <i>propanamide-clomazone (FMC65317)</i>						<0.02(1)
Winter wheat 2004						
Prosulfocarb (Boxer EC)	Oct 03	Apr 06	1542	454	0	<0.01 (0)
MCPA (Metaxon)	Jun 04	Jul 06	1307	331	0	<0.01 (2*)
- <i>4-chlor-2-methylphenol</i>						<0.01(1*)
Azoxystrobin (Amistar)	Jun 04	Jul 07	2098	636	0	<0.01 (0)
- <i>CyPM</i>						<0.01 (4)
Maize 2005						
Terbuthylazine (Inter-Terbutylazin)	May 05	Jul 08	2078	666	4	0.67 (93)
- <i>desethyl-terbuthylazine</i>	May 05	Jul 08	2078	666		0.59 (156)
- <i>2-hydroxy-terbuthylazine</i>	May 05	Jul 08	2078	666		0.04 (56)
- <i>desisopropyl-atrazine</i>	May 05	Jul 08	2078	666		0.03 (85)
- <i>2-hydroxy-desethyl-terbuthylazine</i>	May 05	Jul 07	1428	465	4	0.07 (16)
Bentazone (Laddok TE)	May 05	Jul 07	1408	464	6	2.82 (28)
- <i>AIBA</i>						<0.01 (1)
Spring barley 2006						
Fluroxypyr (Starane 180 S)	May 06	Jul 08	1496	524	17	<0.02 (2)
Epoxiconazole (Opus)	Jun 06	Jul 08	1441	507	3	<0.01 (0)
Winter Rape 2007						
Thiamethoxam (Cruiser RAPS)	Aug 06	Jul 08	1304	505	27	<0.01 (0)
- <i>CGA 322704</i>						<0.02 (0)
Propyzamide (Kerb 500 SC)	Feb 07	Apr 09	1476	375	46	0.138 (5) ¹⁾
- <i>RH-24644</i>						<0.01 (4) ¹⁾
- <i>RH-24580</i>						<0.01 (0) ¹⁾
- <i>RH-24655</i>						<0.01 (1) ¹⁾
Winter wheat 2008						
Pendimethalin (Stomp)	Oct 07	Jul 09 [†]	1098	377	24	<0.01 (2*)
Tebuconazole (Folicur EC 250)	Nov 07	Jul 09 [†]	1042	340	56	<0.01 (5)
Sugar beet 2009						
Triflusaluron-methyl (Safari)	Apr 09	Jul 09 [†]	145	28	2	<0.01(0)
- <i>IN-D8526</i>						<0.01(0)
- <i>IN-E7710</i>						<0.01(0)
- <i>IN-M7222</i>						<0.01(0)

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

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

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

¹⁾ Drainage runoff commenced prior to the application of propyzamide and the weighted concentrations refer to the period from the date of application (Feb 07) until 1 July 2007.

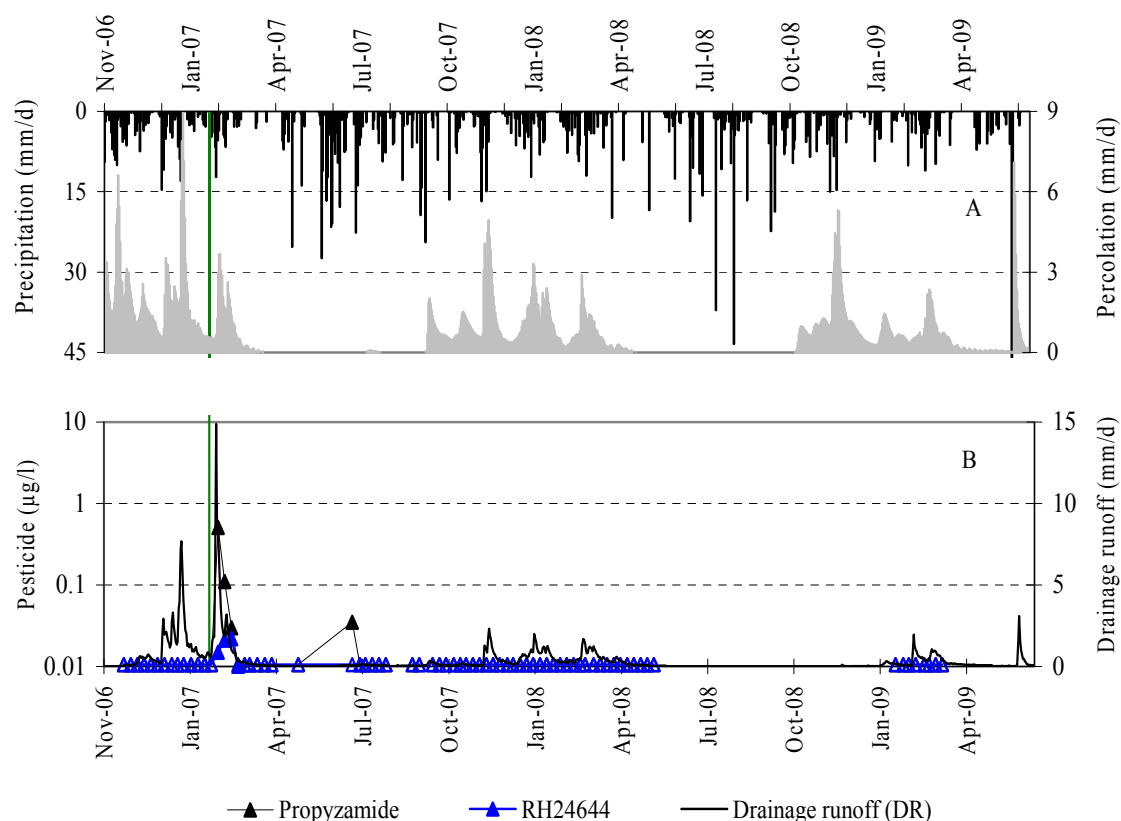


Figure 39. Precipitation and simulated percolation (A) together with concentration of propyzamide and RH24644 (B) in the drainage runoff (DR on secondary axis) at **Faardrup** in 2006 to 2009. The green vertical lines indicate the date of applications. Open symbols indicate values below the detection limit of 0.01 µg/l.

Fluroxypyr and epoxiconazole were applied in May and June 2006. Both pesticides have been monitored until July 2008. Only fluroxypyr has been found, but in low concentrations and only in two samples (Table 13).

Propyzamide and one of its degradation products RH24644 leached to the drainage system (Figure 39, Table 13, Table A5.5 in Appendix 5). Due to four very high concentrations of propyzamide, the calculated average concentration amounted to 0.138 µg/l. It should be noted that drainage runoff commenced more than two and a half months prior to the application of propyzamide and the weighted concentrations refer to a period of 4.5 months (17 February-1 July 2007). Figure 39 shows that propyzamide and the degradation product RH24644 were only found in high concentrations in the first flow event following the application, and that none of them have been detected since July 2007. The degradation product RH24655 has been found in drainage water once: 0.017 µg/l on 19 September 2007. Propyzamide was detected once in one of the horizontal screens 3.5 m b.g.s. at a concentration of 0.033 µg/l (data not shown).

Tebuconazole and pendimethalin were applied in 2007 and these pesticides have until now been detected in five and two samples, respectively (Figure 40). 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 below the upper meter. The final evaluation of the leaching risk of these three pesticides applied in 2008 and 2009 will be conducted two years after application.

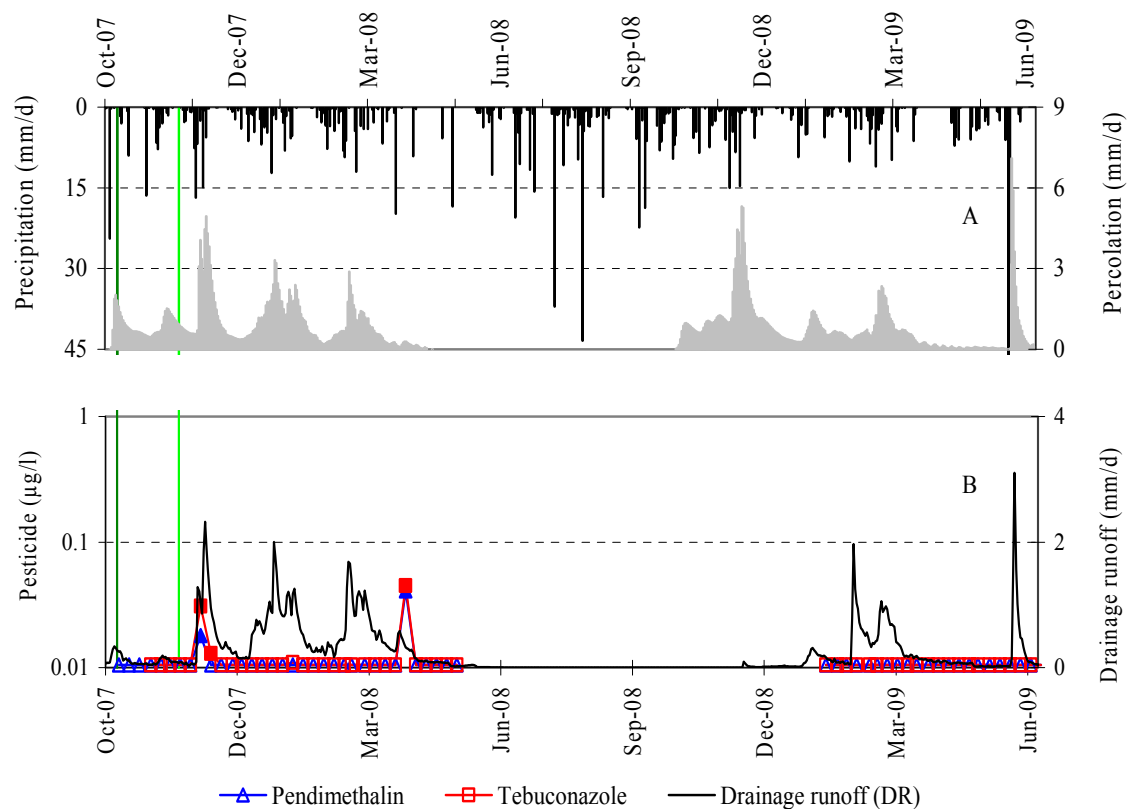


Figure 40. Precipitation and simulated percolation (A) together with concentration of pendimethalin and tebuconazole (B) in the drainage runoff (DR on secondary axis) at **Faardrup** in 2007 to 2009. The green vertical lines indicate the date of applications. Open symbols indicates values below the detection limit of 0.01 µg/l.

7 Pesticide analysis quality assurance

Reliable results and scientifically valid methods of analysis are essential for the integrity of the present monitoring programme. Consequently, the field monitoring work has been supported by intensive quality assurance entailing continuous evaluation of the analyses employed. Two types of sample are used in the quality control – samples with known pesticide composition and concentration are used for *internal monitoring* of the laboratory method, while *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 2008-June 2009 are presented below, while those for the preceding monitoring periods are given in Kjær *et al.* (2002, 2003, 2004, 2005c, 2007, 2008, and 2009).

7.1 Materials and methods

Apart from chlormequat, which was analysed at GEUS, 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 an upstream 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)	#	High-level control (µg/l)	Low-level control (µg/l)
CL153815	1.000	1	0.117	0.050
CYPM Azoxystrobin (freeacid)	1.000	1	0.117	0.050
Epoxyconazole	1.000	1	0.117	0.050
Ethofumesate	1.000	1	0.117	0.050
IN-M7222	1.000	1	0.117	0.050
IN-70941	1.000	1	0.117	0.050
Metamitron	1.000	1	0.117	0.050
Metsulfuron-methyl	1.000	1	0.117	0.050
Pendimethalin	1.000	1	0.117	0.050
Tebuconazole	1.000	1	0.117	0.050
TFFPM	1.000	1	0.117	0.050
AMPA	1.000	2	0.117	0.050
Glyphosate	1.000	2	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-terbutylazine and desisopropyl-atrazine. When all compounds are considered, a particularly high S_b/S_w ratio is apparent for CL153815, and relatively high values have also been observed in previous reports. Such relatively high values 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. Thus, low values of S_w rather than critical values of S_b caused the high ratios, as reflected by the low S_t . However, with the compound CL153815 and others it is apparent that the between-day (S_b) contribution is high. As reflected by the data in Table 15, the three compounds with the highest observed between-day contribution were florasulam-desmethyl, CL153815, and triazinamin.

The total standard deviations (S_t) of the various analyses of pesticides and degradation products lie within the range 0.003-0.225 $\mu\text{g/l}$, the highest value being observed for triazinamin (only data with $n \geq 3$ are included in the analysis). In general, the data suggest that the analytical procedure used for the quantification of CL153815 and triazinamin may benefit from a critical review. The overall mean S_t was 0.03 $\mu\text{g/l}$, which is a factor 2 to 3 higher than previous years.

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. Only data for $n \geq 3$ are included.

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. ($\mu\text{g/l}$)
<i>2-hydroxy-terbuthylazine</i> *	yes		0.010	0.008	0.013	0.79	27	0.050
<i>AMPA</i> *		yes	0.004	0.002	0.004	0.45	35	0.030
Azoxystrobin			0.005	0.007	0.009	1.29	51	0.053
<i>CL153815</i> *			0.004	0.092	0.093	23.07	42	0.129
Clopyralid	yes	yes	0.017	0.005	0.018	0.28	9	0.050
<i>Desethyl-terbuthylazine</i>	yes		0.002	0.005	0.006	2.66	44	0.053
<i>Desisopropyl-atrazine</i> *	yes		0.004	0.010	0.011	2.43	34	0.053
Epoxiconazole			0.003	0.006	0.007	2.34	58	0.050
Florasulam		yes	0.065	0.006	0.065	0.09	27	0.050
<i>Florasulam-desmethyl</i> *			0.009	0.077	0.078	8.70	37	0.117
Glyphosate		yes	0.003	0.002	0.003	0.58	36	0.030
<i>PPU</i> *	yes		0.004	0.013	0.014	3.18	24	0.053
<i>PPU-desamino</i> *			0.003	0.010	0.010	3.83	24	0.053
Iodosulfuron-methyl-sodium			0.004	0.020	0.021	5.80	24	0.050
Mesosulfuron			0.011	0.056	0.057	5.30	40	0.100
<i>Mesosulfuron-methyl</i> *			0.007	0.051	0.051	7.13	37	0.050
<i>Metribuzin-desamino-diketo</i> *			0.007	0.021	0.023	3.05	5	0.050
<i>Metribuzin-diketo</i> *	yes		0.004	0.006	0.007	1.30	12	0.050
Metsulfuron-methyl			0.007	0.023	0.024	3.25	24	0.050
Pendimethalin			0.003	0.007	0.008	2.64	37	0.050
Picolinafen			0.037	0.048	0.060	1.30	43	0.114
Propyzamid			0.003	0.007	0.008	2.27	37	0.053
Tebuconazole			0.002	0.006	0.006	2.36	69	0.050
Terbuthylazine	yes		0.002	0.003	0.004	1.74	38	0.051
Triazinamin			0.037	0.222	0.225	6.01	20	0.110
<i>Triazinamin-methyl</i> *	yes		0.005	0.009	0.010	1.88	5	0.054
Triflurosulfuron-methyl			0.002	0.019	0.019	9.01	6	0.050

*Degradation product.

7.2.2 External QA

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. In the programme, upstream samples are collected and analysed to evaluate the suitability of these samples as blanks in the spiking procedure of the external QA part of the PLAP programme. In a single upstream sample trace of TFPM was reported (level 0.03 $\mu\text{g/l}$). No pesticides or pesticide degradation products were detected in the other 98 blank samples collected in the period.

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.

	Tylstrup		Jyndevad		Silstrup		Estrup		Faardrup		Average	$n_{\text{low}}/n_{\text{high}}$
	Low	High	Low	High	Low	High	Low	High	Low	High		
<i>AMPA</i> *							72	73			73	2/2
<i>CL153815</i> *							73	72			73	3/3
<i>CyPM</i> *	138	105			72	80	110	119			112	7/7
Epoxiconazole			110	108	113	119					112	4/5
Ethofumesate					87	90			64	77	84	4/4
Glyphosate							48	31			40	3/3
<i>PPU</i> *	72	66	153	92							91	5/6
<i>IN-M7222</i> *					114	113			108	128	115	4/4
Metamitron					66	65			54	55	63	4/4
Metsulfuron-methyl					135	132					134	2/2
Pendimethalin	72	73							74	77	75	6/6
Tebuconazole	96	95	105	95			90	79	97	93	94	11/12
<i>TFMP</i> *					127	131					129	3/3

*Degradation product

Whereas the recovery of the most spiked compounds in the samples is generally good, the broad range of average recoveries from 19 to 134% indicates that for some compounds low recovery may cause concern. The very low recovery of glyphosate (~40%) calls for concern and indicates that the procedures in the sample processing and/or analytical procedure may need to be improved. As the internal control data for glyphosate demonstrate acceptable quality parameters (Table 15), the source of the low recovery in the external control may be related to matrix effects on the quantification of this particular compound - a problem that has been reported previously for certain derivatisation-based analytical assays in groundwater. A low recovery of glyphosate was also observed in the previous report. This coincides with a shift in analytical procedure from GC-MS to LC-MS-based residue analysis. Previously, the annual average recoveries ranged from 71-93% during 2001-2006 and 69% in 2007. Two consecutive periods with relatively low recovery calls for concern, and an effort to improve the analysis has been initiated in cooperation between PLAP and the laboratory. Further, it should be emphasised that the data set is very limited. At the upper end of the recovery scale, metsulfuron-methyl (134%) and TFMP (129%) demonstrate high recovery, but based on experience from other programmes and projects, these levels do not cause concern.

All the compounds included in the spiking procedure (Table 14) were detected in the laboratory. Additionally, two compounds that were not included in the spiking were reported by the analytical laboratory: metamitron-desamino in samples from Silstrup and PPU-desamino from Tylstrup and Jyndevad. Both compounds may be formed from compounds present in the spiking solution, i.e. PPU-desamino from PPU and metamitron-desamino from metamitron. In general, since the levels were low and in the range of the detection limit (observed values were <0.05 µg/l for PPU-desamino and <0.02 µg/l for metamitron-desamino), these findings are not causing concern for the overall quality of the programme.

During the 2008/2009 monitoring period a total of 9 pesticides and 12 degradation products were detected in samples from the experimental fields, and the external and internal QA data relating to these particular pesticides/degradation products are of special interest. These data (when available) are therefore illustrated in Appendix 6.

7.3 Summary and concluding remarks

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

- Reproducibility of the pesticide analyses was good, total standard deviation being in the range 0.003-0.093 µg/l, except for triazinamin displaying a large S_t caused in particular by S_b .
- Recovery was generally good (average recovery ranging between 63–134%) in externally spiked samples. Low recovery of glyphosate was, however, observed in all samples. A process evaluating the analytical method applied by the laboratory has been initiated in the PLAP-programme.
- Contamination of samples during collection, storage and analysis is not likely to occur. In only one sample of a total of 99 blank samples a trace of TFPM 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 Kjær *et al.*, 2002, 2003, 2004, 2005c, 2007, 2008, and 2009). 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 leaching exceeding an yearly 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. The number of applied pesticides (or their degradation products) exhibiting pronounced leaching from the upper meter is thirteen and detected in the groundwater monitoring screens in concentrations exceeding 0.1 µg/l is nine.

- Azoxystrobin, and in particular its degradation product CyPM, leached 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 (Table 19 and 20). 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. Yearly average concentrations 1 m b.g.s. of pesticides and/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 2009 are not included in the table.

	Tylstrup (Sandy soil)	Jyndevad (Sandy soil)	Silstrup (Loamy soil)	Estrup (Loamy soil)	Faardrup (Loamy soil)
Azoxystrobin (F)	*				
Bentazone (H)	*	*	*		
Ethofumesate (H)					
Fluazifop-P-butyl (H)			*		
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)	*				*
Propiconazole (F)					
Prosulfocarb (H)					
Pyridate (H)					
Triflusaluron-methyl (H)			*		
Clopyralid (H)					
Chlormequat (GR)					
Desmedipham (H)					
Fenpropimorph (F)					
Florasulam (H)					
Iodosulfuron-methyl-sodium (H)					
Linuron (H)					
Metsulfuron-methyl (H)					
Phenmedipham (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/or 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 2009 are not included.

	Tylstrup	Jyndeavad	Silstrup	Estrup	Faardrup
Azoxystrobin	0	0	6(0.034)	83(1.4)	0
- <i>CyPM</i>	0	0	51(0.34)	162(2.1)	4(0.059)
Bentazone	1(0.012)	30(1.6)	31(6.4)	127(20)	17(43)
- <i>AIBA</i>	0	2(0.034)	0	1 (0.06)	1(0.057)
Ethofumesate			20(0.227)	35(3.362)	15(12)
- <i>Fluazifop-P</i> ²⁾	0	0	0		11(3.8)
- <i>TFMP</i> ²⁾			17(0.52)		
Glyphosate		0	67(4.7)	244(31)	5(0.093)
- <i>AMPA</i>		1(0.014)	122(0.35)	340(1.6)	15(0.11)
Metamitron			49(0.551)	42(26.369)	12(1.7)
- <i>metamitron-desamino</i>			58(0.67)	49(5.549)	16(2.5)
Metribuzin	2(0.024)	0			
- <i>metribuzin-desamino-diketo</i>	81(2.1)	0			
- <i>metribuzin-diketo</i>	225(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-formamido</i>	0	0	0	26(0.379)	3(0.039)
Propyzamide	0		23(1.6)		4(0.51)
- <i>RH-24644</i>	0		15(0.051)		4(0.022)
- <i>RH-24580</i>	0		2(0.016)		0
- <i>RH-24655</i>	0		0		1(0.017)
- <i>PPU</i> ³⁾	96(0.15)	147(0.29)			
- <i>PPU-desamino</i> ³⁾	30(0.042)	89(0.13)			
Terbuthylazine	0	0	60(1.55)	111(11)	41(10)
- <i>desethyl-terbuthylazine</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 -terbuthylazine</i>	5(0.016)		28(0.11)*	86(6.3)	8(1)
- <i>2-hydroxy-terbuthylazine</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>propanamide-clomazone</i>	0				1(0.3)
Dimethoate	0	0	1(1.417)	0	0
Epoxiconazole	0	0	0	13(0.39)	0
ETU ¹⁾	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	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)
- <i>MHPC</i>			0		2(0.19)
Propiconazole	0	0	6(0.033)	25(0.862)	0
Prosulfocarb			5(0.18)		0
Pyridate		0			
- <i>PHCP</i>		0	4(2.69)		
Triflurosulfuron-methyl			0		
- <i>IN-E7710</i>			4(0.014)		

¹⁾Degradation product of mancozeb. ²⁾Degradation product of fluazifop-P-butyl.

³⁾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/or their degradation products in water samples from the groundwater monitoring screens 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 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 2009 are not included in the table.

	Tylstrup (Sandy soil)	Jyndeved (Sandy soil)	Silstrup (Loamy soil)	Estrup (Loamy soil)	Faardrup (Loamy soil)
Azoxystrobin (F)	*				
Bentazone (H)	*	*	*		
Ethofumesate (H)					
Fluazifop-P-butyl (H)			*		
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)	*				*
Propiconazole (F)					
Prosulfocarb (H)					
Pyridate (H)					
Triflusaluron-methyl (H)			*		
Clopyralid (H)					
Chlormequat (GR)					
Desmedipham (H)					
Fenpropimorph (F)					
Florasulam (H)					
Iodosulfuron-methyl-sodium (H)					
Linuron (H)					
Metsulfuron-methyl (H)					
Phenmedipham (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 (µg/l) in parentheses. Degradation products are indicated in *italics*. Pesticides applied in spring 2009 are not included.

	Tylstrup	Jynde vad	Silstrup	Estrup	Faardrup
Azoxystrobin	0	0	0	0	0
- <i>CyPM</i>	0	0	12(0.051)	7(0.085)	0
Bentazone	0	0	21(0.44)	12(0.015)	10(0.6)
- <i>AIBA</i>	0	0	0	1(0.026)	0
Ethofumesate			5(0.038)	0	31(1.4)
- <i>Fluazifop-P</i> ²⁾	0	0	1(0.072)		6(0.17)
- <i>TFMP</i> ²⁾			46(0.29)		
Glyphosate		0	4(0.03)	34(0.67)	3(0.017)
- <i>AMPA</i>		2(0.022)	15(0.08)	6(0.057)	2(0.029)
Metamitron			29(0.168)	0	24(0.63)
- <i>metamitron-desamino</i>			28(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-formamido</i>	0	0	0	0	2(0.076)
Propyzamide	0		9(0.14)		1(0.033)
- <i>RH-24644</i>	0		2(0.032)		0
- <i>RH-24580</i>	0		0		0
- <i>RH-24655</i>	0		0		0
- <i>PPU</i> ³⁾	1(0.045)	229(0.11)			
- <i>PPU-desamino</i> ³⁾	0	61(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 -terbuthylazine</i>	1(0.026)		1(0.016)*	0	7(0.092)
- <i>2-hydroxy-terbuthylazine</i>	0		0*	0	34(0.069)
Tebuconazole	1(0.011)	1(0.014)		0	1(0.01)
Amidosulfuron		0		0	
Bromoxynil	0	0		0	0
Clomazone	0				0
- <i>propanamide-clomazone</i>	0				0
Desmedipham			1(0.033)		0
Dimethoate	0	0	1(0.085)	0	0
- <i>ETU</i> ¹⁾	2(0.024)				
Epoxiconazole	0	1(0.011)	0	0	0
Fenpropimorph	0	1(0.029)	0	0	0
- <i>fenpropimorph-acid</i>	0	0	1(0.072)	0	0
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	1(0.019)	0
- <i>4-chlor-2-methylphenol</i>		0	0	0	0
Mesosulfuron-methyl		0		0	
Pendimethalin	0	0	0		0
- <i>MHPC</i>			0		1(0.053)
Phenmedipham			0		2(0.025)
Propiconazole	0	0	0	2(0.022)	1(0.035)
Prosulfocarb			1(0.027)		0
Pyridate		0			
- <i>PHCP</i>		0	14(0.309)		
Triflurosulfuron-methyl			0		
- <i>IN-E7710</i>			0		

¹⁾Degradation product of mancozeb. ²⁾Degradation product of fluazifop-P-butyl.

³⁾Degradation product of rimsulfuron.

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

- Bentazone leached 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 four 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 0.1 µg/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).
- In the loamy soil of Estrup, ethofumesate, metamitron, and its degradation product metamitron-desamino leached through the upper meter 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 (see Kjær *et al.*, 2002 and Kjær *et al.*, 2004 for details).
- 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 at concentrations in some cases exceeding 0.1 µg/l (Figure 22, Table 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 21). The leaching pattern of TFMP indicates pronounced preferential flow also in periods with a relatively dry vadose zone.
- Glyphosate and its degradation product AMPA were found to leach through the upper meter to the drainage system at high average concentrations within the first season after application 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. The concentrations of both glyphosate and AMPA tend to decrease in periods with continuous drainage flow and then increase, if detected, at the initiation of a new drain event. This tendency is, however, most pronounced and of longer duration for AMPA, which has been detected as late as three years after application. 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 just following the wettest August (2008) in the history of this monitoring programme (including two rain events of 51 mm/day on 7 August and 68 mm/day on 20 August, respectively) and an additional rain event of 52 mm/day on 4 September (2008), evidence of the latter is also documented. Otherwise, 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, and only at Estrup has the concentration exceeded 0.1 µg/l in two samples taken from the groundwater monitoring screens (Table 19 and 20). For the detection at Estrup in the period 2007/2008 and 2008/2009, external quality assurance has shown that the true concentration of glyphosate and AMPA in these periods may be underestimated by up to 69% (Table 15). 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 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 1 m b.g.s. in high average concentrations from the loamy soil of Estrup into the drainage water, average concentrations exceeding 0.1 µg/l (Table 17). Both degradation products have been detected in deeper monitoring screens at Faardrup (Table 19 and 20). 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).

- Propyzamide leached 1 m b.g.s. at the loamy Silstrup and Faardrup sites, entering the drainage water 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).
- No rimsulfuron was detected in the water samples from Tylstrup and Jyndevad. At Jyndevad, PPU was detected in the vadose zone at a depth of 1 m for as long as three years in annual average concentrations exceeding 0.1 µg/l. At Tylstrup, PPU was detected at a depth of 1 m and 2 m in concentrations or just below and just exceeding 0.1 µg/l, respectively (Table 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. 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.*, 2010).
- Terbutylazine as well as its degradation products leached 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 terbutylazine and desethyl-terbutylazine 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-terbutylazine 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-terbutylazine was also seen at the two sandy sites Jyndevad and Tylstrup, where desethyl-terbutylazine was detected in low concentrations (<0.1 µg/l) in the soil water sampled 1 m b.g.s. While desethyl-terbutylazine 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 terbutylazine was also seen at two of the three loamy sites (Estrup and Faardrup), the leaching pattern being similar to that of desethyl-terbutylazine. 2-hydroxy-desethyl-terbutylazine and 2-hydroxy-terbutylazine leached at both Faardrup and Estrup and at the latter site the average

drainage concentration exceeded 0.1 µg/l. Leaching of these two 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, Jynde vad, Estrup and Faardrup. Only on the loamy soil of Estrup did it leach through the upper meter and into the drainage water in average concentrations exceeding 0.1 µg/l (Table 17 and 18). 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 samples from the groundwater monitoring screens (Table 19 and 20).

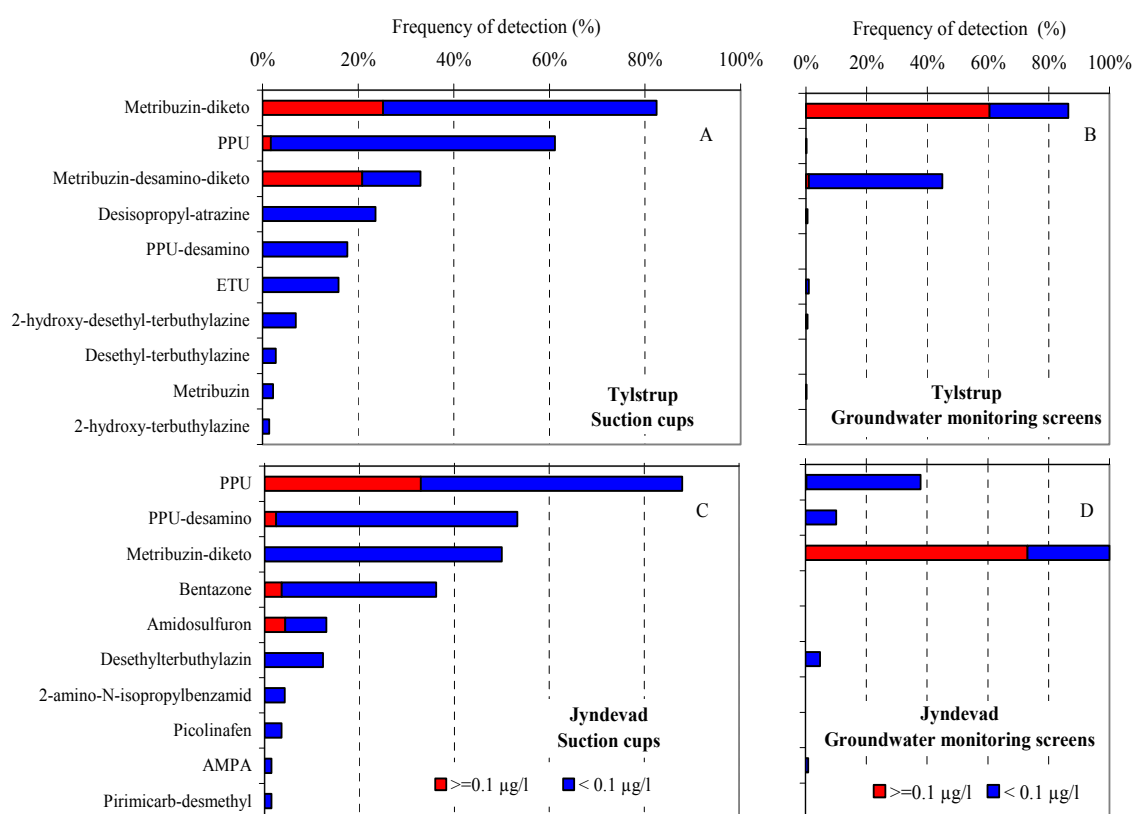


Figure 41. Frequency of detection in samples from the suction cups (left) and groundwater monitoring screens located deeper than the suction cups (right) at the sandy soil sites: **Tylstrup** (A, B) and **Jynde vad** (C, D). Frequency is estimated for the entire monitoring period and the length of time 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 ten most frequently detected pesticides. Pesticides monitored for less than two years are indicated by an asterisk and pesticides monitored for less than one year are not included.

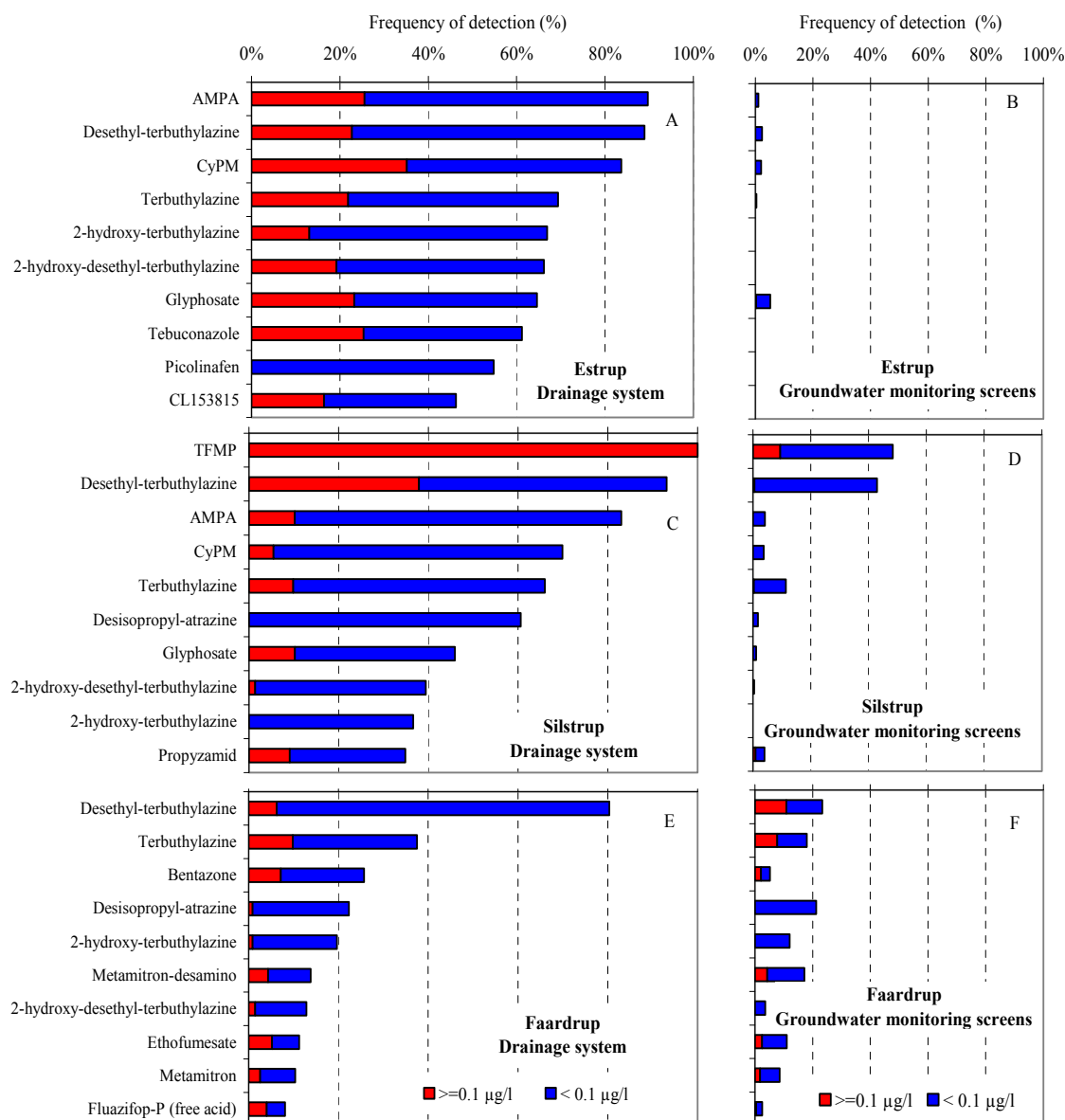


Figure 42. Frequency of detection in samples from the drainage system (left) and groundwater monitoring screens located deeper than the drainage system (right) at the loamy soil sites: **Silstrup** (A, B), **Estrup** (C, D), and **Faardrup** (E, F). Frequency is estimated for the entire monitoring period and the time that the different pesticides have been included in the programme and the number of analysed samples thus varies considerably among the different pesticides. The figure only includes the ten most frequently detected pesticides. Pesticides monitored for less than two years are indicated by an asterisk and pesticides monitored for less than one year are not included.

The monitoring data also indicate leaching 1 m b.g.s. of a further 16 pesticides (or their degradation products), but often in low concentrations. Although the concentrations detected 1 m b.g.s. exceeded $0.1 \mu\text{g/l}$ 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.

Twelve of the 41 pesticides applied – about 29% – did not leach at all from 1 m b.g.s. during the monitoring period (Table 17). Three of the 12 were, however, detected in the groundwater monitoring screens (Table 19). The group of 12 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 41 and 42, showing the frequency of detection in samples collected 1 m b.g.s. (suction cups on sandy soils and drainage systems on loamy soils) and the deeper located groundwater monitoring screens.

On the sandy soils the number of leached pesticides as well as the frequency of detection was much lower than on loamy soils (Figure 41 and 42), 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 amount of pesticide reaching the monitoring screens situated beneath the drainage system was limited and varied considerably within the three sites (Figure 42). 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 34 and 27 samples containing glyphosate and desisopropylatrazin, respectively, pesticides have only sporadically been detected in the screens beneath the drainage system (Appendix 5). The differences are, however, largely attributable to the hydrological conditions. Compared to the Silstrup

and Faardrup sites, the C horizon (situated beneath the drainage depth) at the Estrup site is less permeable with less preferential flow through macropores (se Kjær *et al.* 2005c for details). The movement of water and solute may therefore be slower at Estrup, allowing for dispersion, dilution, sorption and degradation and thereby reducing the risk of transport to deeper soil layers.

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-hydroxybenzonitrile
Bifenox	methyl 5-(2,4-dichlorophenoxy)-2-nitrobenzoate
- <i>Bifenox-syre</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>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-P²⁾</i>	(R)-2-(4-((5-(trifluoromethyl)-2-pyridinyl)oxy)phenoxy)-propanoic acid
- <i>TFMP²⁾</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>ETU¹⁾</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>PHCP³⁾</i>	3-phenyl-4-hydroxy-6-chloropyridazine
Picolinafen	4'-fluoro-6-(α,α,α -trifluoro-m-tolylloxy)pyridine-2-carboxanilide
- <i>CL153815</i>	6-(3-trifluoromethylphenoxy)-2-pyridine carboxylic acid
Pirimicarb	2-(dimethylamino)-5,6-dimethyl-4-pyrimidinyl dimethylcarbamate

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

Parameter	Systematic chemical nomenclature
- <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-oxazoline
- <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-pyridyl)-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-4ylidene-N-nitroamine
- <i>CGA 322704</i>	[C(E)]-N-[(2-chloro-5-thiazolyl)methyl]-N'-methyl-N'-nitroguanidine
Tribenuron-methyl	methyl 2-[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)methylamino]carbonyl]amino]sulfonyl]benzoate
Triflurosulfuron-methyl	methyl 2-[4-dimethylamino-6-(2,2,2-trifluoroethoxy)-1,3,5-triazin-2-yl]carbamoylsulfamoyl]-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

¹⁾Degradation product of mancozeb. ²⁾Degradation product of fluzifop-P-butyl.³⁾Degradation product of pyridate.

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.

This optimization was based on the outcome of the monitoring of inorganic parameters, which has been included in PLAP from the very beginning in 1999. The number of parameters and the intensity by which and where they have been monitored, vary over time. In 2009, a quality procedure for all the measured inorganic parameters and DOC (dissolved organic carbon) was initiated and the development in some of the parameters has been used to optimize the future monitoring programme. A comprehensive description of the inorganic monitoring data will be given in the future reports. In Figure A2.1-A2.5, the development in the nitrate concentrations is given for some of the wells that no longer are monitored and included in PLAP.

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 the hydrological year 2008/2009 are given in bold. Well M10 at Silstrup was included in the programme on 5 February 2009.

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

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.

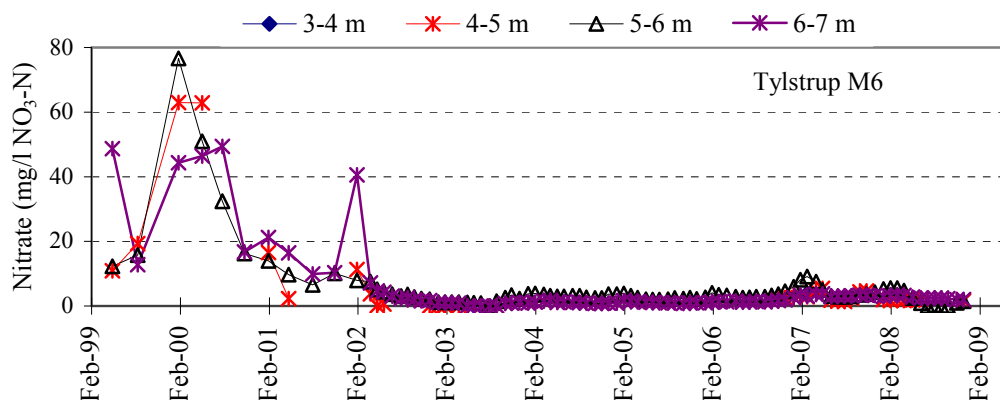


Figure A2.1. Nitrate-N concentrations in the vertical monitoring well M6 at Tylstrup. Screen depth is indicated in m b. g.s. High concentrations of nitrate measured just after installation reflect the former agricultural management as well as the effect of installation of the monitoring well. Decreasing concentrations of nitrate indicate that the water is replaced by water from the buffer zone covered by grass. The low concentrations of nitrate in all four screens from about February 2002 show how effectively the grass in the buffer zone receiving limited N-fertilization reduces the nitrate concentration in the water percolating through the soil. The water in the vertical well M6 does not reflect the water quality of the cultivated site at Tylstrup and was excluded from the monitoring programme from 10 September, 2008.

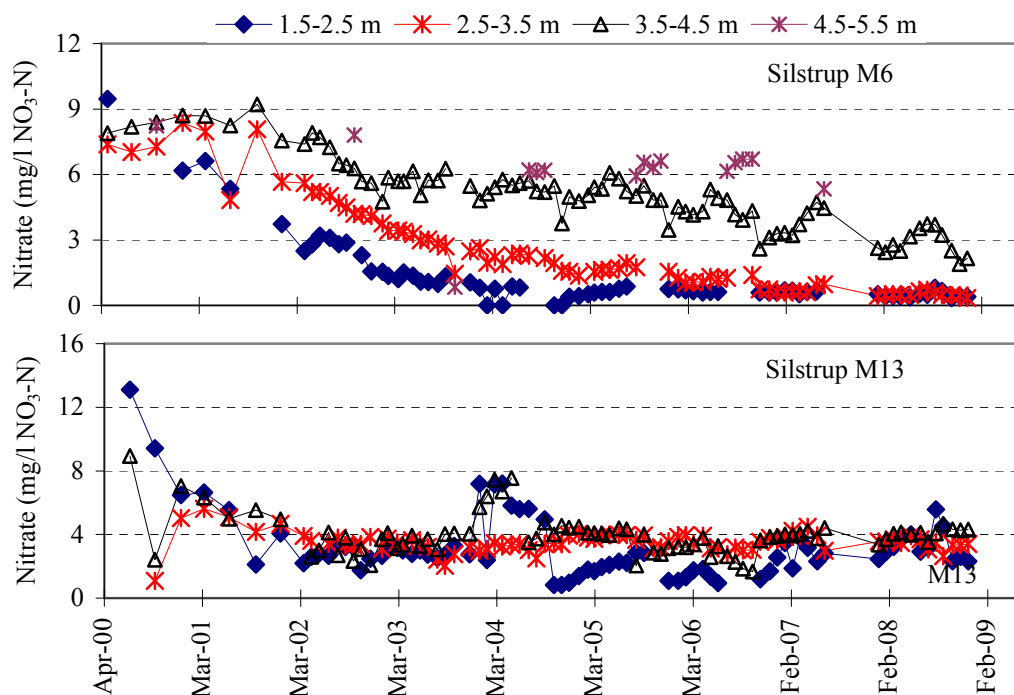


Figure A2.2. Nitrate-N concentrations in the vertical monitoring wells M6 and M13 at **Silstrup**. Screen depth is indicated in m b.g.s. The high concentrations of nitrate in M6 measured just after installation reflects the former agricultural management. Decreasing concentrations of nitrate in the screens indicate that the water is replaced by water from the buffer zone covered by grass. At M6 decreasing concentrations of nitrate were first detected in the screen at 1.5-2.5 m and later in the screen at 2.5-3.5 m. Also the concentrations of nitrate in water collected from the screen at 3.5-4.5 m b.g.s. show slowly decreasing concentrations of nitrate, which are explained by the gradual replacement of agriculturally sourced water with local water from the buffer zone. The replacement of water from the grass-covered buffer zone is later and only weakly noticeable for the water collected at 4.5-5.5 m b.g.s. As the vertical well M6 does not reflect the water quality of the cultivated site at Silstrup it was excluded from subsequent monitoring. The low and rather constant concentrations of nitrate at M13 are not characteristic for downward leaching water from a cultivated field and the well was excluded from the monitoring programme. Both well M6 and M13 were excluded from the monitoring programme from 3 September, 2008.

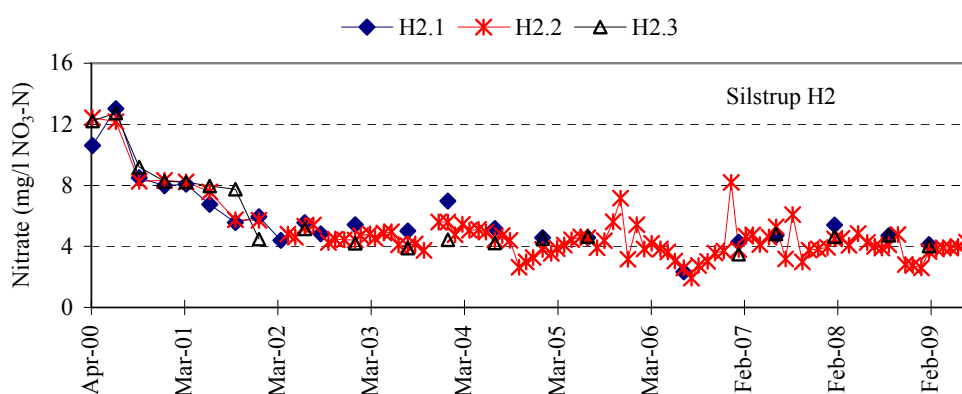


Figure A2.3. Nitrate-N concentrations in water collected from the outlet tubes H2.1, H2.2, and H2.3 from the horizontal monitoring well H2 at a depth of 3.5 m at **Silstrup**. The concentration of nitrate decreases in water collected within the first two years of monitoring and subsequently remains low and rather constant. According to Lindhardt et al. (2001) part of the H2 horizontal well follows a “pavement”, probably made up of clay till rich in stones and boulders. The H2 horizontal well will be excluded from the future monitoring programme due to the development in nitrate over time and the uncertainty related to the geological setting.

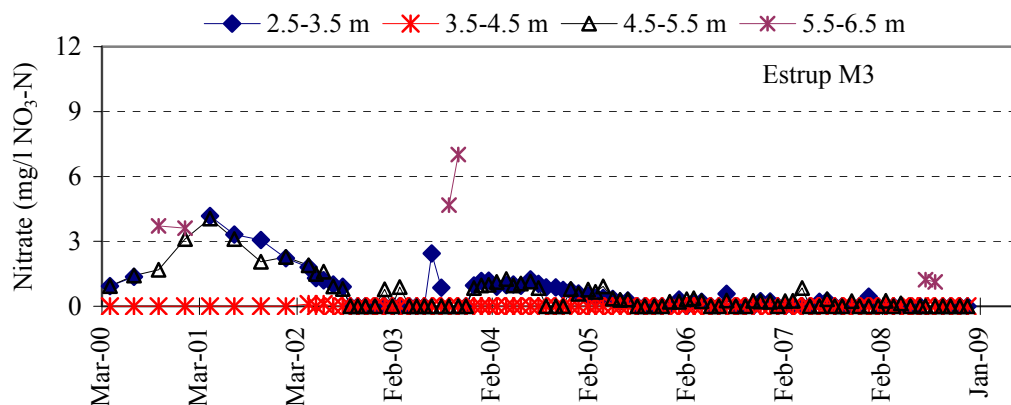


Figure A2.4. Nitrate-N concentrations in the vertical monitoring well M3 at **Estrup**. Screen depth is indicated in m b.g.s. A few water samples from the screen 2.5-3.5 m b.g.s. have measurable concentrations of nitrate. Water samples collected deeper down are generally free of nitrate and may be collected from the reduced zone. The water in the vertical well M3 was excluded from the monitoring programme from 11 September 2008.

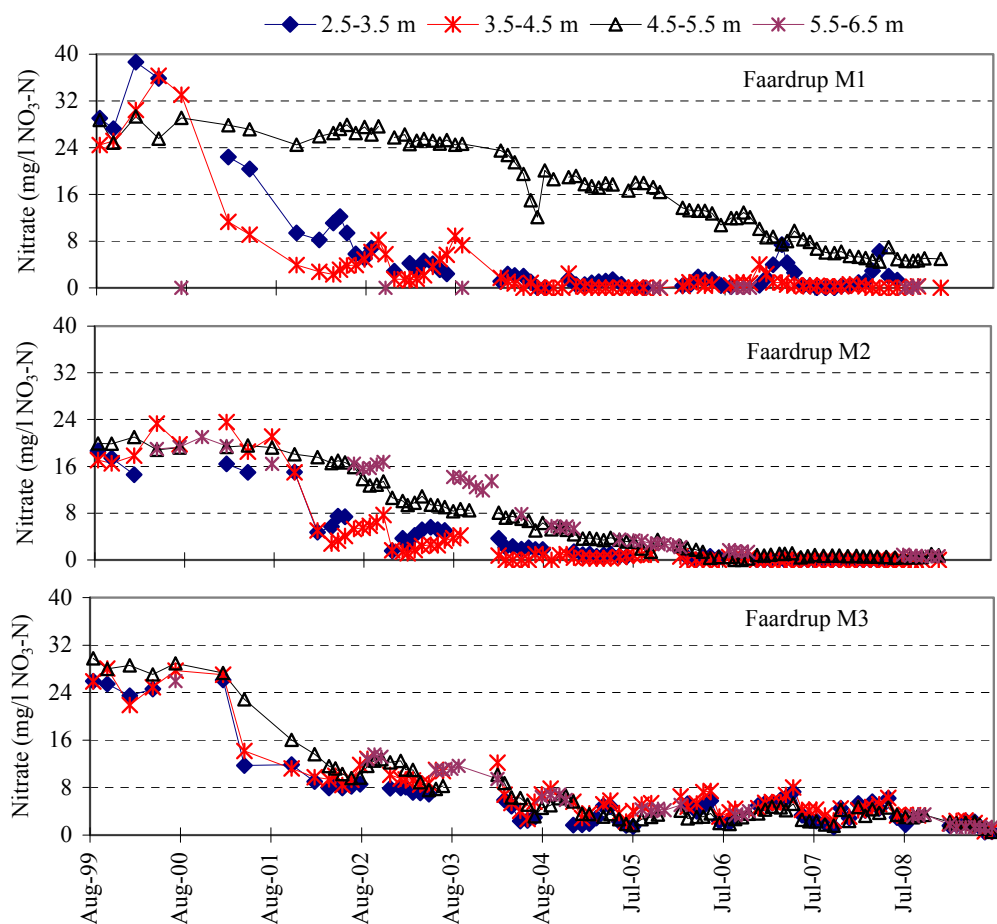


Figure A2.5. Nitrate-N concentrations in the vertical monitoring wells M1, M2, and M3 at **Faardrup**. Screen depth is indicated in m b.g.s. Measurements of water samples collected from all three wells show a decrease in concentration of nitrate over time in all screens. The decreasing concentrations of nitrate in M1 and M2 are first seen in the upper screen and subsequently in deeper screens after the replacement of “agricultural” water with water from the grass-covered buffer zone. At the M3 well the decrease in nitrate and the replacement of water from the buffer zone are measured almost simultaneously in all four screens. Well M2 and M3 have been included in the pesticide monitoring programme. Both wells are now excluded from the programme from 3 September 2008 and 6 May 2009, respectively.

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_i = Weekly accumulated drainage runoff (mm/week).

C_i = Pesticide concentration collected by means of the flow-proportional sampler (µg/l).

Until July 2004 where both time and flow-proportional sampling was applied the numbers were:

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

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

where:

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

V_i = Weekly accumulated drainage runoff (mm/week).

V_{fi} = Drainage runoff accumulated during a “flow event” (mm/storm event).

C_{fi} = Pesticide concentration in the “event samples” collected by means of the flow-proportional sampler (µg/l).

C_{ti} = 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.

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.

Table A3.1 Management practice at **Tylstrup** during the 2006 to 2009 growing seasons. The active ingredients of the various pesticides are indicated in parentheses.

Date	Management practice
21.04.06	Ploughed - 22 cm depth
21.04.06	Rolled with a concrete roller
23.04.06	Spring barley sown - cv Cabaret
06.06.06	Herbicide - 4.25 tablets/ha Express ST (tribenuron-methyl)
03.07.06	Fungicide - 1.0 l/ha Opus (epoxiconazole)
19.06.05	Irrigation - 29 mm
24.08.06	Spring barley harvested (seed yield 55.6 hkg/ha 85% DM)
24.08.06	Straw shredded - 33.2 hkg/ha 100% DM
25.08.06	Rotary cultivated - depth 5.0 cm (straw incorporation)
26.08.06	Ploughed - 23 cm depth
26.08.06	Winter rape sown (cv. Lioness)
26.08.06	Herbicide - 0.33 l/ha Command CS (clomazone)
06.09.06	Seedbed preparation – 7 cm depth
06.09.06	Winter rape resown (cv. Castille)
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

Table A3.2 Management practice at **Jynde vad** during the 2006 to 2009 growing seasons. The active ingredients of the various pesticides are indicated in parentheses.

Date	Management practice
29.03.06	Rotary cultivated - 5 cm depth
30.03.06	Ploughed - 20 cm depth
04.04.06	Rolled with a concrete roller
11.04.06	Spring barley sown - cv. Simba
26.05.06	Herbicide - 0.1 l/ha Primus (florasulam)
06.06.06	Irrigation - 27 mm
08.06.06	Herbicide - 1.0 l/ha Opus (epoxiconazole)
12.06.06	Irrigation - 30 mm
26.06.06	Irrigation - 27 mm
02.07.06	Irrigation - 30 mm
07.07.06	Irrigation - 30 mm
07.08.06	Spring barley harvested (seed yield 60.5 kgh/ha 85% DM, straw yield 26.8 hkg/ha 100% DM)
20.09.06	Ploughed - 22 cm depth
20.09.06	Rolled with a concrete roller
21.09.06	Triticale sown - cv. Dinaro
10.10.06	Herbicide - 250 g/ha Atlantis WG (mesosulfuron-methyl/iodosulfuron)
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 kgh/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 (boscalid + epoxiconazole)
27.05.09	Irrigation - 30 mm
05.06.09	Irrigation - 27 mm
29.06.09	Irrigation - 27 mm

Table A3.3 Management practice at **Silstrup** during the 2006 to 2009 growing seasons. The active ingredients of the various pesticides are indicated in parentheses.

Date	Management practice
20.09.06	Ploughed - 22 cm depth
22.09.06	Winter wheat sown - cv. Skalmeye
22.09.06	Herbicide - 5.0 l/ha Stomp Pentagon (pendimethalin)
13.04.07	Herbicide - 100 ml/ha Husar 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 (triflusalufuron-methyl) + 0.5 l/ha Goliath (metamitron) + 1.5 l/ha Betanal (phenmedipham)
30.05.08	Herbicide - 30 g/ha Safari (triflusalufuron-methyl) + 0.5 l/ha Goliath (metamitron) + 1.5 l/ha Betanal (phenmedipham) + 0.07 l/ha Trammat 500 SC (ethofumesat)
17.06.08	Herbicide - 30 g/ha Safari (triflusalufuron-methyl) + 0.5 l/ha Goliath (metamitron) + 1.5 l/ha Betanal (phenmedipham) + 0.07 l/ha Trammat 500 SC (ethofumesat)
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 (triflusalufuron-methyl) + 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)

Table A3.4 Management practice at **Estrup** during the 2006 to 2009 growing seasons. The active ingredients of the various pesticides are indicated in parentheses.

Date	Management practice
12.04.06	Ploughed – depth 18 cm - packed with a ring roller
07.04.06	Spring barley sown – cv. Simba
01.05.06	Rolled with a cambridge roller
17.05.06	Herbicide – 0.25 l/ha Starane 180 (fluroxypyr, not analyzed)
02.06.06	Herbicide – 0.25 l/ha Starane 180 (fluroxypyr, not analyzed)
06.06.06	Herbicide – 0.10 l/ha Primus (florasulam)
29.06.06	Fungicide - 1.0 l/ha Amistar (azoxystrobin)
17.08.06	Spring barley harvested (seed yield 59.2 hkg/ha; 85% DM)
11.09.06	Straw removed (straw yield 26.79 hkg/ha, 100% DM)
13.09.06	Ploughed - 18 cm depth (packed with a ring roller)
14.09.06	Rotary cultivated - 4 cm depth
14.09.06	Winter wheat sown – cv. Smuggler
11.10.06	Herbicide - 250 g/ha Atlantis WG (mesosulfuron/iodosulfuron)
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 (bentazon/MCPA)
04.06.09	Fungicide - 1.0 l/ha Amistar (azoxystrobin)

Table A3.5 Management practice at **Faardrup** during the 2006 to 2009 growing seasons. The active ingredients of the various pesticides are indicated in parentheses.

Date	Management practice
28.04.06	Spring barley sown - cv. Scandium
26.05.06	Herbicide - 0.8 l/ha Starane 180 S (fluroxypyr)
29.06.06	Fungicide - 1.0 l/ha Opus (epoxiconazole)
11.08.06	Spring barley harvested (seed yield 67.3 hkg; 85% DM. Straw yield 51.1 hkg/ha 100% DM)
17.08.06	Ploughed - 22 cm depth
17.08.06	Winter rape sown – cv. Labrador
18.08.06	Herbicide - 0.33 l/ha Command CS (clomazone – not analysed)
19.02.07	Herbicide - 1.0 l/ha Kerb 500 SC (propyzamide)
30.03.07	Herbicide – 0.8 l/ha Matrigon (clopyralid)
03.07.07	Windrowed, stubble height 20 cm
19.07.07	Winter rape harvested (seed yield 30.0 hkg/ha, 91% DM)
19.07.07	Straw shredded. 68.5 hkg/ha, 100% DM
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 (triflurosulfuron-methyl) + 1.5 l/ha Betanal (phenmedipham) + 1.0 l/ha Goliath (metamitron) + 0.07 l/ha Ethosan (ethofumesate)
11.05.09	Herbicide - 10 g/ha Safari (triflurosulfuron-methyl) + 1.5 l/ha Betanal (phenmedipham) + 1.0 l/ha Goliath (metamitron) + 0.07 l/ha Ethosan (ethofumesate)
14.05.09	Herbicide - 1.0 l/ha Focus Ultra (cycloxydim)
17.06.09	Herbicide - 1.0 l/ha Focus Ultra (cycloxydim)

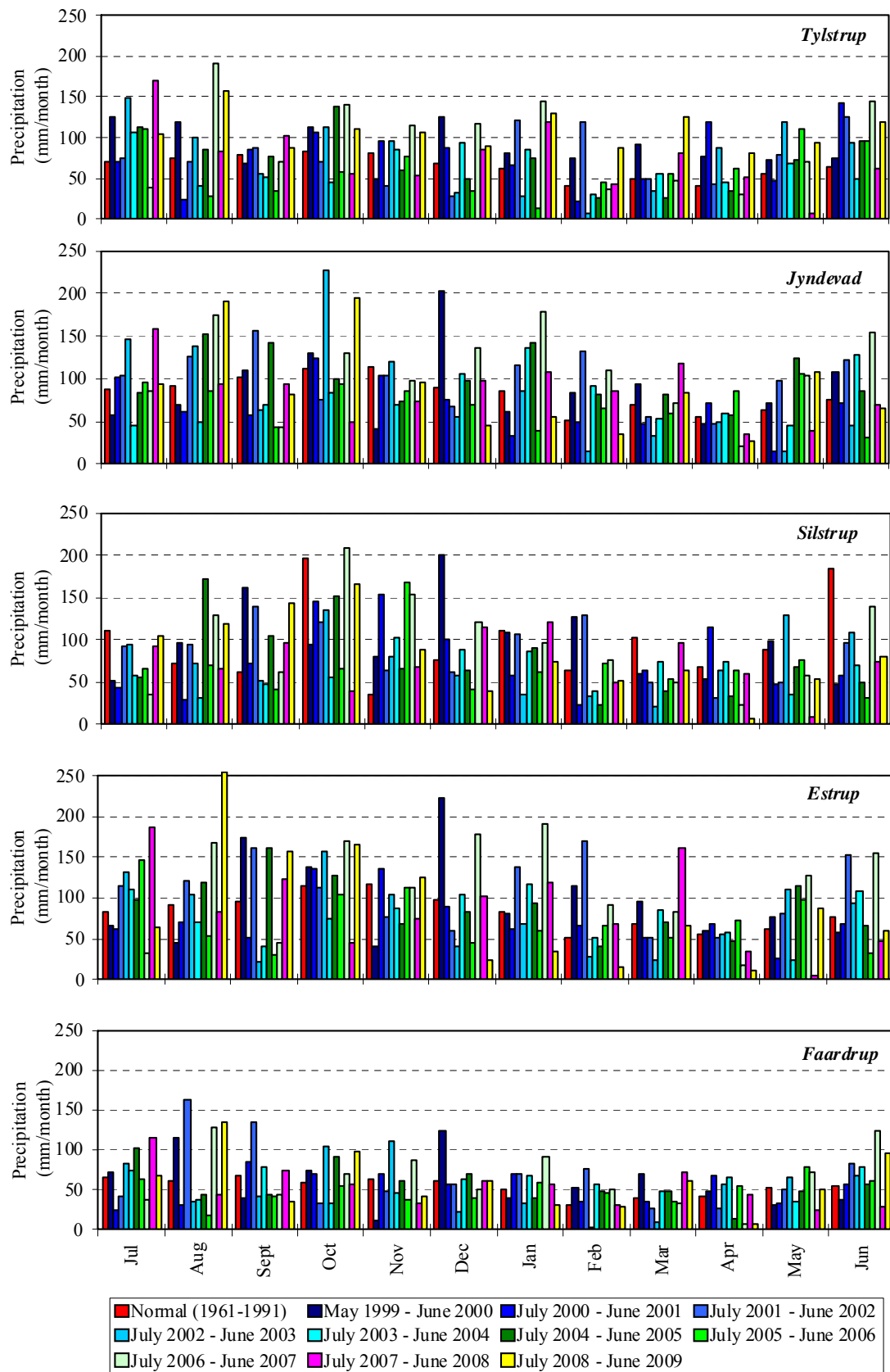


Figure A4.1. Monthly precipitation at all localities for the monitoring period July 2000 – June 2009. Normal values (1961 – 1990) are included for comparison.

Table A5.1 Number of samples where pesticides were either not detected (n.d.), detected in concentrations below 0.1 µg/l (det<0.1 µg/l) or detected in concentrations above 0.1 µg/l (det≥0.1µg/l) at **Tylstrup**. Numbers are accumulated for the entire monitoring period, and pesticides monitored for less than one year are not included.

	Vertical screens			Suction cups		
	n.d.	det.<0.1 µg/l	det.≥0.1 µg/l	n.d.	det.<0.1 µg/l	det.≥0.1 µg/l
AIBA	191			72		
2-hydroxy-desethyl-terbuthylazine	190	1		67	5	
2-hydroxy-terbuthylazine	191			71	1	
Azoxystrobin	130			50		
Bentazone	244			91	1	
Bromoxynil	192			72		
CGA 322704	175			64		
Clomazone	224			82		
Clopyralid*	6			63		
CyPM	130			50		
Desethylterbuthylazine	191			70	2	
Desisopropylatrazine	190	1		55	17	
Dimethoate	176			65		
Epoxiconazole	199			74		
ETU	198	2		37	7	
Fenpropimorph	307			89		
Fenpropimorph-acid	276			73		
Flamprop (free acid)	176			65		
Flamprop-M-isopropyl	176			65		
Fluazifop-P (free acid)	178			65		
Fluroxypyr	194			70		
FMC65317	208			74		
PPU	475	1		68	104	3
PPU-desamino	476			144	31	
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	66	169	63
Pendimethalin	424			140		
Pirimicarb	295			82		
Pirimicarb-desmethyl	295			81		
Pirimicarb-desmethyl-formamido	167			52		
Propiconazol	307			89		
Propyzamid	221			82		
RH24580	221			82		
RH24644	221			82		
RH24655	157			58		
Rimsulfuron	178			65		
Tebuconazole	175	1		68		
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).

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	296			53	27	3
Bifenox	19			6		
Bifenox-acid				2		
Bromoxynil	218			61		
CL153815*				28		
Chlormequat	14			28		
CyPM	233			65		
Desethylterbutylazine	472	24		128	18	
Desmethyl-amidosulfuron	88			23		
Dimethoate	169			48		
Epoxiconazole	278	1		78		
Fenpropimorph	246	1		76	1	
Fenpropimorph-acid	259			79		
Flamprop (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	376	227	2	20	92	55
PPU-desamino	545	61		78	85	4
Ioxynil	218			61		
MCPA	189			52		
Mesosulfuron*				39		
Mesosulfuron-methyl	240			66		
Metribuzin	26			6		
Metribuzin-desamino	26			4		
Metribuzin-desamino-diketo	6	7	13	6		
Metribuzin-diketo		7	19	3	3	
Nitrofen	19			6		
Pendimethalin	257			71		
PHCP	184			59		
Picolinafen				27	1	
Pirimicarb	251			69		
Pirimicarb-desmethyl	251			68	1	
Pirimicarb-desmethyl-formamido	251			69		
Propiconazole	230			73		
Pyridate	116			39		
Rimsulfuron	168			48		
Tebuconazole	145	1		40		
Terbutylazin	239			75		
TFMP	3					
Triazinamin-methyl	247			77		

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

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≥0.1 µg/l) at **Silstrup**. Numbers are accumulated for the entire monitoring periode, and pesticides monitored for less than one year are not included.

	Drainage			Horizontal screens			Vertical screens			Suction cups		
	n.d.	det <0.1 µg/l	det ≥0.1 µg/l	n.d.	det <0.1 µg/l	det ≥0.1 µg/l	n.d.	det <0.1 µg/l	det ≥0.1 µg/l	n.d.	det <0.1 µg/l	det ≥0.1 µg/l
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	44	6		73			134					
Bentazone	58	26	5	102	5	1	184	12	3			
Clopyralid	44			63			118					
Chlormequat	20	1		36			66					
CyPM	22	47	4	107	3		200	9				
Desethylterbuthylazin	8	64	44	101	32		113	127	2			
Desisopropylatrazin	28	43		84			148	4				
Desmedipham	101			107	1		240			58		
Dimethoat	81		1	73	1		147			27		
EHPC	68			62			118			20		
Epoxiconazole	36			62			117					
Ethofumesat	104	14	1	144	2		305	3		54	3	2
Fenpropimorph	82			74			148			27		
Fenpropimorph-acid	81	1		74			147			27		
Flamprop (free acid)	73	7		74			148			26		
Flamprop-M-isopropyl	70	11	1	73	1		148			27		
Fluazifop-P (free acid)	91			115	1		249			56		
Fluroxypyr	50			74			142					
Glyphosat	79	52	15	128			232	4		8		
IN-D8526	18			38			68					
IN-E7710	14	4		38			68					
IN-M7222	18			37	1		68					
Iodosulfuron-methyl-sodium	37			62			117					
MCPA	51			66			123					
Metamitron	88	27	4	136	10		289	17	2	40	9	9
Metamitron-desamino	80	36	3	140	3	3	286	21	1	40	15	4
Metsulfuron methyl	37			62			117					
MHPC	100			106			234			55		
Pendimethalin	90	14		121			223					
PHCP	62		4	66	2		109	8	4			
Phenmedipham	101			108			240			59		
Pirimicarb	160	14		209			433	3		59		
Pirimicarb-desmethyl	173	1		209			436			59		
Pirimicarb-desmethyl- formamido	141			159			308			20		
Propiconazol	76	6		74			148			27		
Propyzamide	43	17	6	75	2	1	143	5	1			
Prosulfocarb	69	4	1	78	1		147					
RH24580	64	2		78			149					
RH24644	51	15		77	1		148	1				
RH24655	66			78			149					
Terbuthylazin	31	51	9	107	5		173	30	1			
TFMP	17		17	24	10		25	27	9			
Triazinamin	32			62			116					
Triazinamin-methyl	82			74			148			27		
Triflursulfuron-methyl	18			38			68					

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≥0.1 µg/l) at **Estrup**. Numbers are accumulated for the entire monitoring periode, and pesticides monitored for less than one year are not included.

	Drainage			Horizontal screens			Vertical screens			Suction cups		
	n.d.	det <0.1 µg/l	det ≥0.1 µg/l	n.d.	det <0.1 µg/l	det ≥0.1 µg/l	n.d.	det <0.1 µg/l	det ≥0.1 µg/l	n.d.	Det <0.1 µg/l	det ≥0.1 µg/l
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	39	242	98	143			508	6		23		
Azoxystrobin	112	69	14	80			283					
Bentazone	168	112	11	95	11		367	1		3	2	2
Bifenox	2		1	3			9					
Bifenox-acid	1			3			12					
Bromoxynil	135	1	2	41			125			3		
CL153815	30	20	11	27			85					
Clopyralid	1											
Chlormequat	44	1		18			56					
CyPM	33	97	65	77	3		279	4				
Desethylterbuthylazine	18	108	37	59	7		232					
Desisopropylatrazine	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 (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	135	155	89	140	1		479	31	2	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	3			3			9					
Pendimethalin	162	42	30	83			297	1		7		
Picolinafen	44	17		27			85					
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	19	24	17	26			88					
Terbuthylazine	49	76	35	63			222	1				
Triazinamin	125			52			195	1		22		
Triazinamin-methyl	1											

Table A5.5 Number of samples where pesticides were either not detected (n.d), detected in concentrations below 0.1 µg/l (det<0.1 µg/l) or detected in concentrations above 0.1 µg/l (det≥0.1µg/l) at **Faardrup**. Numbers are accumulated for the entire monitoring periode, and pesticides monitored for less than one year are not included.

	Drainage			Horizontal screens			Vertical screens			Suction cups		
	n.d.	det <0.1 µg/l	det ≥0.1 µg/l	n.d.	det <0.1 µg/l	det ≥0.1 µg/l	n.d.	det <0.1 µg/l	det ≥0.1 µg/l	n.d.	det <0.1 µg/l	det ≥0.1 µg/l
AIBA	68	1		61			132					
2-hydroxy-desethyl- terbuthylazine	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	52	12	5	58	2	1	125	4	3			
Bromoxynil	101			81			225			73		
CGA 322704	68			58			126					
Clomazone	84		1	69			166					
CyPM	103	4		92			194					
Desethylterbuthylazine	22	82	7	68	21		149	14	31			
Desisopropylatrazine	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	100	7	6	74			151	24	7	27	2	
Fenpropimorph	70			58	1		156			54		
Fenpropimorph-acid	70			59			156			54		
Flamprop (free acid)	76	1		58			148					
Flamprop-M-isopropyl	70	1		56			142					
Fluazifop-P (free acid)	91	4	4	66			159	5	1	26	3	
Fluazifop-P-buthyl	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	13			8			17					
IN-E7710	13			8			17					
IN-M7222	13			8			17					
Ioxynil	99	1		81			224	1		73		
MCPA	142	1	1	109			255					
Metamitron	101	9	3	74			158	19	5	29		
Metamitron-desamino	97	11	5	74			134	36	12	29		
MHPC	97	1	1	66			163	1		29		
Pendimethalin	53	2		47			108					
Phenmedipham	99			66			163	2		29		
Pirimicarb	113	7		90			243	2		52		
Pirimicarb-desmethyl	94	6		66			162	3		29		
Pirimicarb-desmethyl- formamido	97	3		66			163	2		29		
Propiconazol	147			116			303	1		54		
Propyzamid	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	48	4		45			103	1				
Terbuthylazine	70	30	11	83	5	1	149	24	21			
TFMP				1			2					
Thiamethoxam	68			58			126					
Triazinamin-methyl	77			57			147					

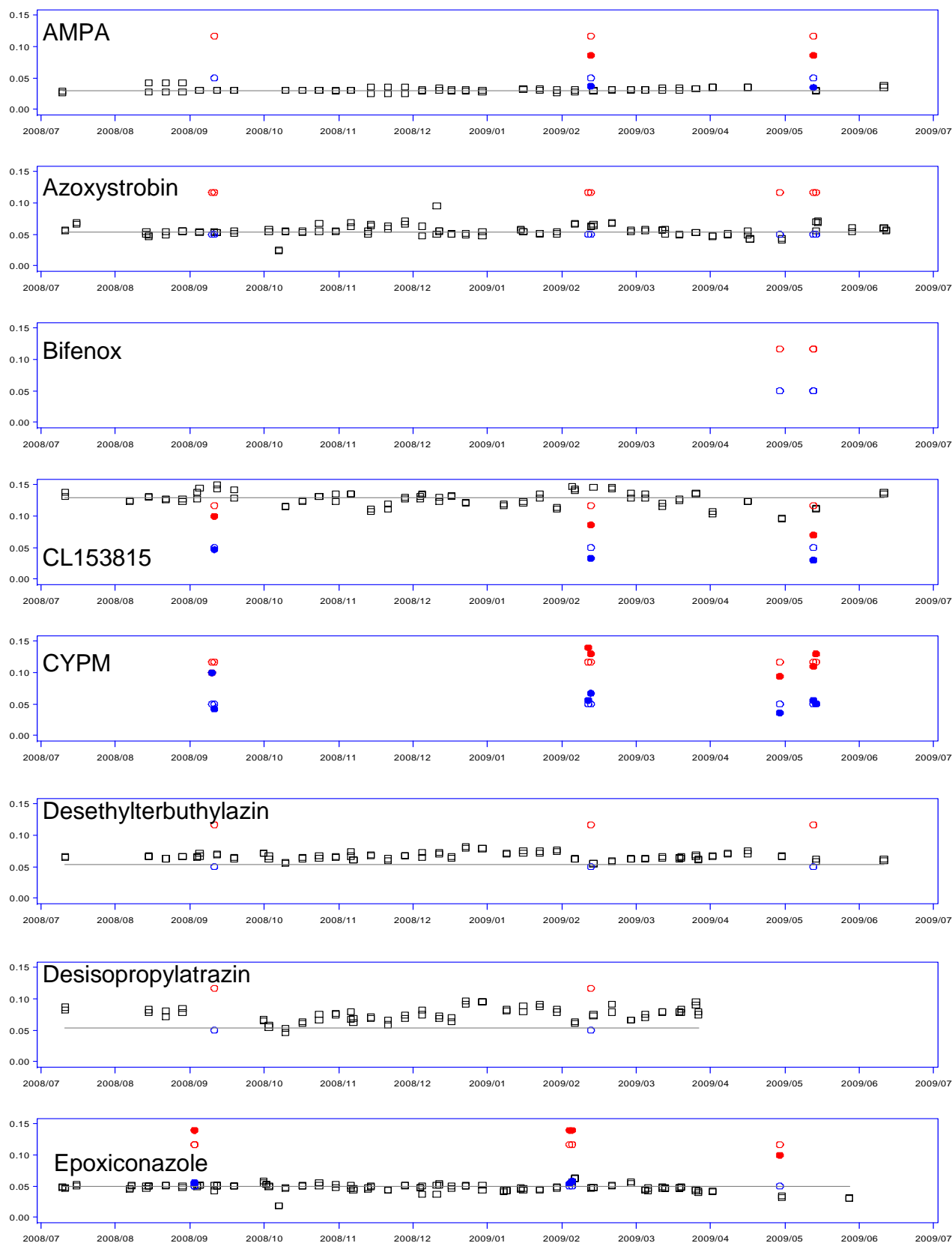


Figure A6.1 Quality control data for pesticide analysis by laboratory 1. Internal laboratory control samples are indicated by square symbols and the nominal level is indicated by the solid grey line (■ IQ measured, — IQ nominal concentration). External control samples are indicated by circles. Open circles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

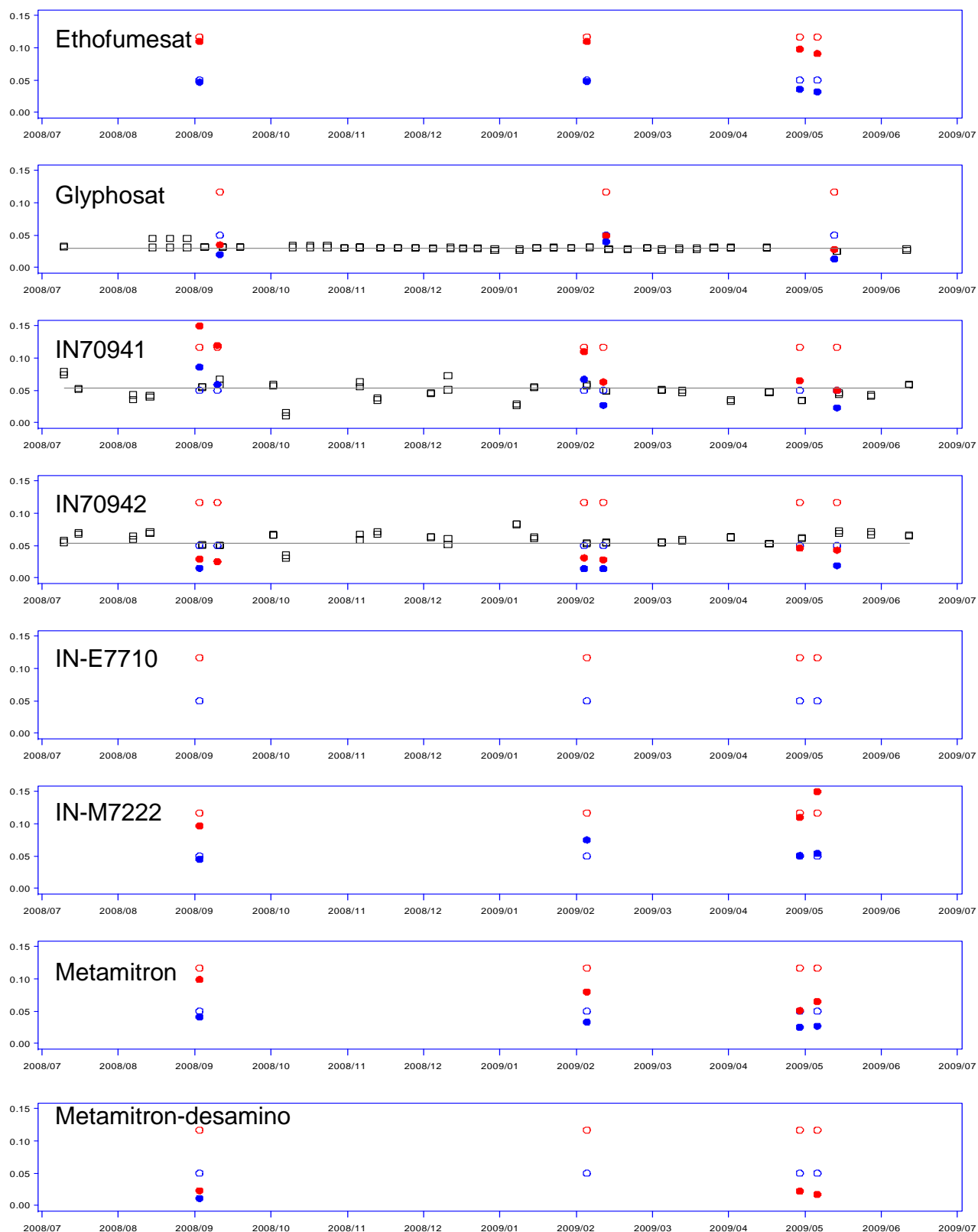


Figure A6.1 continued. Quality control data for pesticide analysis by laboratory 1. Internal laboratory control samples are indicated by square symbols and the nominal level is indicated by the solid grey line (■ IQ measured, — IQ nominal concentration). External control samples are indicated by circles.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

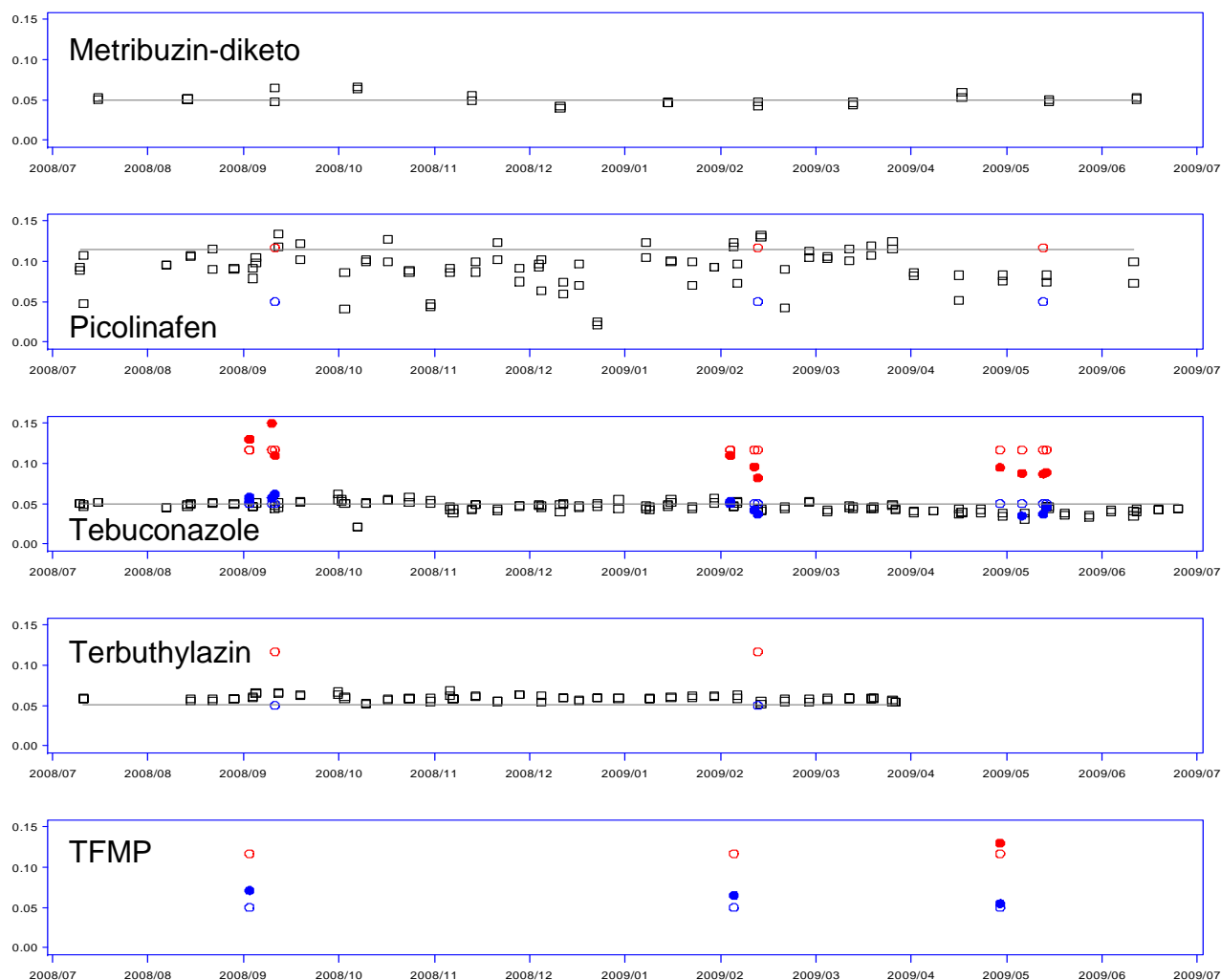


Figure A6.1 continued. Quality control data for pesticide analysis by laboratory 1. Internal laboratory control samples are indicated by square symbols and the nominal level is indicated by the solid grey line (■ IQ measured, — IQ nominal concentration). External control samples are indicated by circles.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