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The Danish Pesticide Leaching Assessment Programme

Monitoring results May 1999–June 2011

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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 Department of Agroecology (AGRO) at Aarhus University and the Department of Bioscience (BIOS) also at Aarhus University, under the direction of a management group comprising Jeanne Kjær (GEUS), Annette E. Rosenbom (GEUS), Walter Brüsch (GEUS), Lis Wollesen de Jonge (AGRO), Preben Olsen (AGRO), Ruth Grant (BIOS) and Steen Marcher (Danish Environmental Protection Agency).

This report presents the results for the period May 1999–June 2011. Results covering part of the period May 1999–June 2010 have been reported previously (Kjær *et al.*, 2002, Kjær *et al.*, 2003, Kjær *et al.*, 2004, Kjær *et al.*, 2005c, Kjær *et al.*, 2007, Kjær *et al.*, 2008, Kjær *et al.*, 2009, Rosenbom *et al.*, 2010b and Kjær et al., 2011). 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 2010.

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

- Pesticide and bromide leaching: Preben Olsen, Jeanne Kjær and Walter Brüsch.
- Soil water dynamics and water balances: Annette E. Rosenbom, Finn Plauborg and Carsten B. Nielsen.
- Pesticide analysis quality assurance: René K. Juhler.

Walter Brüsch and Jeanne Kjær
May 2013

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 43 pesticides and 47 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 from drains and suction cups) and detections in groundwater monitoring screens (1.5-4.5 meter below ground surface, hereafter m b.g.s.). This report presents the results for the entire monitoring period May 1999–June 2011. Results covering part of the period May 1999–June 2010 have been reported previously.

Highlights from the **monitoring period 2010-2011** where **11** pesticides were applied, show that:

- Metalaxyl-M was found in low concentrations in the unsaturated zone. However, two degradation products (CGA 62826 and CGA 108906) were leached from the root zone in average concentrations exceeding 0.1 µg/l. Leaching was most pronounced in the suctions cups, where both compounds were found 1 m b.g.s. at the end of the monitoring period, which indicate that leaching of especially CGA 108906 had not yet ceased. CGA 108906 was found in 95% of the analysed groundwater samples and in 27% of the analysed samples the concentration exceeded 0.1µg/l. The metabolites were present in the groundwater before Metalaxyl-M was applied. The background concentration of CGA 108906 makes it therefore difficult to determine whether the elevated concentrations observed in monitoring wells are due to the Metalaxyl-M applied in 2010 or partly to previous applications occurring at the "upstream" neighbouring fields. It should be noted that metalaxyl-M and CGA108906 concentrations in upstream screens increased after application of Metalaxyl-M on upstream fields.

- Fluazifop-P-buthyl was this year used in a new admissible dose 50% lower than in past applications. The new reduced dose resulted in negligible leaching of the break down product TFMP. Before the imposed regulation, fluazifop-P-buthyl was used at a much higher dose, and TMFP was leaching above 0.1 µg/l to both drains and groundwater monitoring wells.

- Aclonifen, cyafamid, triacloprid and tree metabolites all of which were tested for the first time the in PLAP programme, did not leach during the monitoring period. The leaching pattern of the remaining five pesticides (rimsulfuron bentazone, thriacloprid, tribenuronmethyl, iodosulfuronmethyl) all tested previously in PLAP programme was in line with the previous observations.

The results of the **entire monitoring period 1999-2011** covering **43** pesticides show that:

- Of the 43 pesticides applied, 11 pesticides and/or their degradation product(s) (clopyralid, chlormequat, desmedipham, fenpropimorph, florasulam, iodosulfuron-methyl-sodium, linuron, metsulfuron-methyl, thiamethoxam, tribenuron-methyl and triasulfuron) did not leach during the entire monitoring period.

- The monitoring data indicate pronounced leaching of 15 of the applied pesticides and/or their degradation products. The following compounds leached through the soil entering drains and suction cups (placed 1 m b.g.s.) in average concentrations exceeding 0.1 µg/l:

    - *azoxystrobin* and its degradation product *CyPM*
    - *bentazone*
    - *CL153815* (degradation product of picolinafen)
    - *pirimicarb-desmethyl-formamido* (degradation product of pirimicarb)
    - *propyzamide*
    - *tebuconazole*
    - *glyphosate* and its degradation product *AMPA*
    - **CGA 108906 and CGA 62826** (degradation products of metalaxyl-M)
    - **PPU** (degradation products of rimsulfuron)
    - **bifenox-acid** (degradation product of bifenox)
    - **ethofumesate**
    - **TFMP** (degradation product of fluazifop-P-butyl)
    - *metamitron* and its degradation product **desamino-metamitron**
    - **desamino-diketo-metribuzin** and **diketo-metribuzin** (degradation products of metribuzin)
    - **terbuthylazine** and its degradation products: **desethyl-terbuthylazine**, *2-hydroxy-desethyl-terbuthylazine* and *hydroxy-terbuthylazine.*

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

- Glyphosate has been frequently applied on one loamy soil, and detections in groundwater monitoring wells have gradually increased over time. On two occasions heavy rain events and snowmelt induced leaching to the groundwater monitoring wells in concentrations exceeding 0.1 µg/l more than two years after the application.

- It was reported last year that Bifenox-acid (degradation product of Bifenox) leached through the root zone on loamy soil and enter both the drainage water system and groundwater monitoring wells in very high concentrations. In groundwater bifenox-acid was found frequently in concentration exceeding 0.1 µg/l. The degradation product nitrofen was found in drain water in concentrations being rather low however. Today Bifenox is not used in Denmark.

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

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 2011 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 2010.

Dansk sammendrag

I 1998 vedtog Folketinget at iværksætte projektet ”Varslingssystem for udvaskning af Pesticider til grundvandet” (VAP). VAP er et omfattende moniteringsprogram, der undersøger udvaskning af pesticider anvendt i landbrug under reelle markforhold. Programmet har til formål at undersøge, om godkendte pesticider eller deres nedbrydningsprodukter – ved regelret brug og dosering – udvaskes til grundvandet i koncentrationer over grænseværdien for herigennem at udvide det videnskabelige grundlag for danske myndigheders (Miljøstyrelsen) procedurer for regulering af godkendte sprøjtemidler. Udvaskningsrisikoen for 43 pesticider og 47 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 moniteringsresultater henholdsvis repræsenterende fund i en meters dybde (indhentet via dræn og sugeceller) og fund i grundvandsmoniteringsfiltre (1.5-4.5 meter under terræn, herefter m u.t.).

Denne rapport opsummerer resultaterne for den samlede moniteringsperiode fra maj 1999 til juni 2011, mens resultater fra de foregående år, fra maj 1999 til juni 2010, er afrapporteret i de tidligere rapporter.

”Highlights” fra den seneste **moniteringsperiode 2010-2011**, hvor **11** pesticider blev udbragt, viser følgende:

- Metalaxyl-M blev det første år, ca. 9 måneder efter udbringningen på de to sandjorde, fundet i små koncentrationer i den umættede zone, mens to nedbrydningsprodukter (CGA 62826 og CGA 108906) blev udvasket fra rodzonen og fundet i sugeceller i høje koncentrationer, der gennemsnitlig i en meters dybde overskred 0,1 µg/l. Da begge stoffer blev fundet i sugeceller placeret 1 meter under terræn, kan dette betyde, at udvaskningen ikke har toppet endnu. CGA 108906 blev fundet i ca. 95% af de analyserede grundvandsprøver. I 27% af prøverne var koncentrationerne større end 0,1 µg/l. Det er væsentligt at bemærke, at nedbrydningsprodukterne og moderstoffet var til stede i grundvandet opstrøms markerne før sprøjtningen med metalaxyl-M. Dette gør det vanskeligt at skelne mellem indflydelsen fra sprøjtningen af VAP-markerne og det bidrag, der er kommet fra sidste og tidligere sprøjtninger på nabomarkerne. Det kan bemærkes, at koncentrationen af metalaxyl-M og CGA 108906 i opstrøms boringer i flere tilfælde stiger efter anvendelsen på VAP markerne, og efter stoffet har været anvendt opstrøms.

- Fluazifop-P-buthyl er blevet testet med de anvendelsesbegrænsninger, der nu er indført for at beskytte grundvandet. Udvaskningen af nedbrydningsproduktet TMFP i denne moniteringsperiode var ganske lille, hvilket er i modsætning til den tidligere anvendelse, hvor der blev observeret udvaskning, der overskred 0,1 µg/l ved anvendelse af en højere dosis, der ikke længere er godkendt.

- Aclonifen, cyazofamid, thiacloprid og 3 af disses metabolitter blev testet for første gang i Varslingssystemet, og ingen af disse stoffer blev udvasket i moniteringsperioden. Udvaskningen af 5 andre pesticider, der alle tidligere er testet i VAP (rimsulfuron, bentazone, thiacloprid, tribenuron-methyl, iodosulfuron-methyl), var på niveau med tidligere målinger, hvilket bekræfter at grænseværdien overholdes ved den godkendte anvendelse.

Resultater for **hele moniteringsperioden 1999-2011**, som omfatter **43** pesticider viser følgende:

- Af de 43 pesticider, der er blevet udbragt, blev 11 pesticider eller nedbrydningsprodukter heraf (clopyralid, chlormequat, desmedipham, fenpropimorph, florasulam, iodosulfuron-methyl-natrium, linuron, metsulfuron-methyl, thiamethoxam, tribenuronmethyl og triasulfuron) ikke fundet udvasket i løbet af den samlede moniteringsperiode.

- 15 af de udbragte stoffer eller nedbrydningsprodukter heraf, gav anledning til en større udvaskning fra rodzonen. Følgende stoffer blev udvasket til dræn og sugeceller, beliggende i ca. 1 meters dybde i gennemsnitskoncentrationer på årsniveau over 0,1 µg/l:

    - *azoxystrobin* og dets nedbrydningsprodukt *CyPM*
    - *bentazon*
    - *CL153815* (nedbrydningsprodukt af picolinafen)
    - *pirimicarb-desmethyl-formamido* (nedbrydningsprodukt af pirimicarb)
    - *propyzamid*
    - *tebuconazol*
    - *glyphosat* og dets nedbrydningsprodukt *AMPA*
    - **CGA 108906 og CGA 62826** (nedbrydningsprodukt af metalaxyl-M)
    - **PPU** (nedbrydningsprodukt af rimsulfuron)
    - **bifenox-syre** (nedbrydningsprodukt af bifenox)
    - **ethofumesat**
    - **TFMP** (nedbrydningsprodukt af fluazifop-P-butyl),
    - *metamitron* og dets nedbrydningsprodukt d**esamino-metamitron**
    - **desamino-diketo-metribuzin** og **diketo-metribuzin** (nedbrydningsprodukter af metribuzin)
    - **terbuthylazin** og dets nedbrydningsprodukter **desethyl-terbuthylazin**, *2-hydroxy-desethyl-terbuthylazin og 2-hydroxy-terbuthylazin.*

For de pesticider eller nedbrydningsprodukter der er *fremhævet med kursiv* var udvaskningen primært begrænset til 1 m u.t., hvor de blev fundet hyppigt i dræn og sugeceller. Selvom hovedparten af stofferne blev fundet i koncentrationer over 0,1 µg/l i grundvandsfiltrene, var antallet af overskridelser få (mindre end 5 pr. mark). Pesticider **markeret med fed** blev dog udvasket til grundvandsfiltrene i en større grad. På nær PPU blev samtlige stoffer relativt hyppigt fundet i koncentrationer over 0,1 µg/l i grundvandsfiltrene, hvor koncentrationer over 0,1 µg/l blev fundet mere end seks måneder efter udbringning.

Om end der kun var enkelte prøver som indeholdt mere end 0,1 µg/l PPU, blev der igennem en toårig periode fundet PPU i grundvandet i koncentrationer tæt på de 0,1 µg/l på en af de to testede marker, hvilket bekræfter den høje persistens af PPU i jord og grundvand. Gentagne udbringninger af rimsulfuron (PPU) kan potentielt forurene det allerøverste grundvand. Rimsulfuron er ikke længere tilladt at anvende i Danmark.

Glyphosat er blevet udbragt flere gange på en af de lerede forsøgslokaliteter. På denne mark er der igennem de seneste år konstateret et stigende antal fund af glyphosat i grundvandsfiltrene. To gange har markante nedbørshændelser samt snesmeltning forårsaget enkeltstående udvaskning af glyphosat til grundvandfiltrene i koncentrationer over 0,1 µg/l mere end to år efter udbringning.

Sidste års rapport nævnte at bifenox-syre (nedbrydningsprodukt af bifenox) på lerjorde blev udvasket fra rodzonen til både dræn og grundvandsfiltre, hvor stoffet blev fundet hyppigt i koncentrationer større end 0,1 µg/l. I den sidste periode er nedbrydningsproduktet, nitrofen fundet i drænvand, men kun i relativt små koncentrationer under 0,1µg/l. Bifenox må ikke længere anvendes i Danmark.

- Andre 17 stoffer gav anledning til udvaskning. Selv om flere af disse stoffer i 1 meters dybde ofte blev fundet i koncentrationer over 0,1 µg/l, var der ikke tale om, at udvaskningen som årsmiddel oversteg 0,1 µg/l i dræn i en meters dybde. Stofferne blev sjældent fundet i grundvandsfiltre og ikke i koncentration over 0,1 µg/l.

Bromid er anvendt som sporstof for at beskrive vandtransporten. Bromid- og pesticidkoncentrationer bliver analyseret månedligt i prøver udtaget i den umættede og mættede zone, og ugentligt i prøver af drænvand. I denne rapport præsenteres moniteringsresultaterne for de fem områder for perioden fra maj 1999 til juni 2011 primært med fokus på pesticider udbragt i 2010.

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 50% of all screens monitored and in 60% of the screens placed in the upper groundwater (Thorling, L. (red), 2011).

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

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

1.1 Objective

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

The objective of the PLAP is to improve the scientific foundation for decision-making in the Danish registration and approval procedures for pesticides, enabling field studies to be included in risk assessment of selected pesticides. The specific aim is to analyse whether pesticides applied in accordance with current regulations leach at levels exceeding the maximum allowable concentration of 0.1 µg/l.

1.2 Structure of the PLAP

The pesticides included in the PLAP were selected by the Danish Environmental Protection Agency on the basis of expert judgement. At present, 42 pesticides and 41 degradation products are included in the PLAP. All the compounds analysed are listed in Appendix 1.

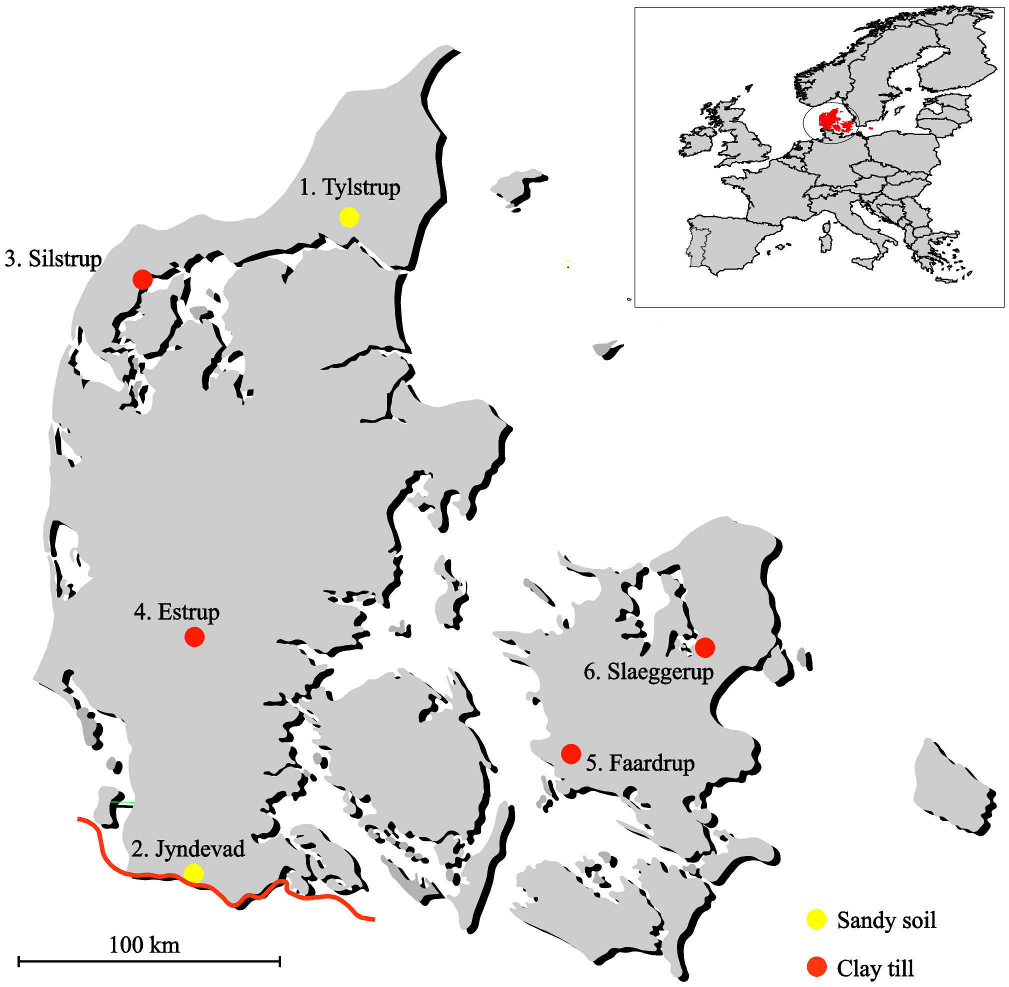


Figure 1. Location of the PLAP sites **Tylstrup**, **Jyndevad**, **Silstrup**, **Estrup** and **Faardrup**. Monitoring at Slaeggerup was terminated on 1 July 2003.

Soil type and climatic conditions are considered to be some of the most important parameters controlling pesticide leaching. The PLAP initially encompassed six test sites representative of the dominant soil types and the climatic conditions in Denmark (Figure 1). Monitoring at the Slaeggerup site was terminated on 1 July 2003, and results from that site are not included in the present report. For the monitoring results from this site see Kjær *et al.* (2003). The groundwater table at all the sites is shallow, thereby enabling pesticide leaching to groundwater to be rapidly detected (Table 1). Cultivation of the PLAP sites is in line with conventional agricultural practice in the vicinity. The pesticides are applied 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)	$2.0\cdot10^{-5}$	$1.3\cdot10^{-4}$	$3.4\cdot10^{-6}$	$8.0\cdot10^{-8}$	$7.2\cdot10^{-6}$
Topsoil characteristics					
– DK classification	JB2	JB1	JB7	JB5/6	JB5/6
– Classification	Loamy sand	Sand	Sandy clay loam/ sandy loam	Sandy loam	Sandy loam
– Clay content (%)	6	5	18–26	10–20	14–15
– Silt content (%)	13	4	27	20–27	25
– Sand content (%)	78	88	8	50–65	57
– pH	4–4.5	5.6–6.2	6.7–7	6.5–7.8	6.4–6.6
– TOC (%)	2.0	1.8	2.2	1.7–7.3	1.4

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

[2] *Large variation within the field.*

[3] *Maximum fracture depth refers to the maximum fracture depth found in excavations and wells.*

Site characterization and monitoring design are described in detail in Lindhardt *et al.* (2001). The present report presents the results of the monitoring period May 1999–June 2011. The main focus of this report is on the leaching risk of pesticides applied during 2010. For a detailed description of the earlier part of the monitoring period (May 1999–June 2009), see previous publications on http://pesticidvarsling.dk/publ_result-/index.html.

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 2011. The five site models have been calibrated for the monitoring period May 1999–June 2004 and validated for the monitoring period July 2004–June 2011.

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

2 Pesticide leaching at Tylstrup

2.1 Materials and methods

2.1.1 Site description and monitoring design

Tylstrup is located in northern Jutland (Figure 1). The test field covers a cultivated area of 1.1 ha (70 x 166 m) and is practically flat, with windbreaks bordering the eastern and western sides. Based on two soil profiles dug in the buffer zone around the test field the soil was classified as a Humic Psammentic Dystrudept (Soil Survey Staff, 1999). The topsoil is characterised as loamy sand with 6% clay and 2.0% total organic carbon (Table 1). The aquifer material consists of an approx. 20 m deep layer of marine sand sediment deposited in the Yoldia Sea. The southern part is rather homogeneous, consisting entirely of fine-grained sand, whereas the northern part is more heterogeneous due to the intrusion of several silt and clay lenses (Lindhardt *et al.,* 2001). The overall direction of groundwater flow is towards the west (Figure 2). During the monitoring period the groundwater table was 2.6–4.5 m b.g.s. (Figure 3). A brief description of the sampling procedure is provided in Appendix 2. The monitoring design and test site are described in detail in Lindhardt *et al.* (2001), and the analysis methods in Kjær *et al.* (2002).

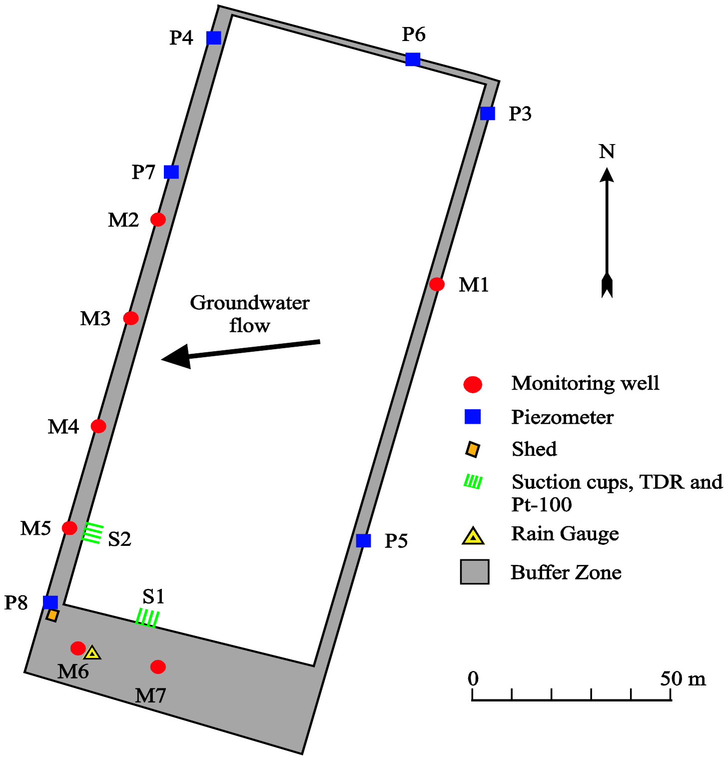


Figure 2. Overview of the **Tylstrup** site. The innermost white area indicates the cultivated land, while the grey area indicates the surrounding buffer zone. The positions of the various installations are indicated, as is the direction of groundwater flow (by an arrow). Pesticide monitoring is conducted monthly and half-yearly from suction cups and selected monitoring wells as described in Table A2.1 in Appendix 2.

2.1.2 Agricultural management

Management practice during the 2010-11 growing seasons is briefly summarized below and detailed in Appendix 3 (Table A3.1). For information about management practice during the previous monitoring periods, see previous monitoring reports available on http://pesticidvarsling.dk/publ_result/index.html.

On 4 April 2010 the field was ploughed and on 6 May planted with potatoes (cv. Kuras). On 26 May, before emergence, the field was sprayed with the herbicides aclonifen and rimsulfuron. Rimsulfuron was applied again on 8 June, when the fifth leaf of the main stem had unfolded. Cyazofamid was used against fungi six times between 15 June and 2 August. On 9 July a fungicide containing mancozeb and metalaxyl was used, of which only metalaxyl was monitored. Between 9 August and 23 August the fungicide mancozeb was again applied, but not monitored. The crop was irrigated twice, with 29 mm on 6 July and 28 mm on 27 July. The yield of potatoes, harvested on 20 October, was 470.3 hkg/ha with 27.2% DM (128.0 hkg/ha at 100% DM), yields being below the average for the year and soil type (Plantedirektoratet 2010).The field was ploughed on 17 April 2011. Spring barley (cv. TamTam), sown on the 19 April, emerged on 24 April.

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 2011 and to establish an annual water balance.

Compared to Kjær *et al.* (2011), 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 2011. Daily time series of groundwater table measured in the piezometers located in the buffer zone, soil water content measured at three different depths (25, 60 and 110 cm b.g.s.) from the two profiles S1 and S2 (Figure 2) and the bromide concentration measured in the suction cups located 1 and 2 m b.g.s. were used in the calibration and validation process. Data acquisition, model setup and results related to simulated bromide transport are described in Barlebo *et al.* (2007).

Table 2. Annual water balance for **Tylstrup** (mm y^{-1}). 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
1.7.09–30.6.10	773	867	27	424	470
1.7.10–30.6.11	773	950	57	463	544

[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). During the last four hydraulic years the level in water saturation at 25 cm b.g.s. was, however, overestimated. Moreover the initial decrease in water saturation observed during the four summer periods at 25, 60 and 110 cm b.g.s. was less well captured.

The dynamics of groundwater table were captured with some exceptions, but as with previous simulations the amplitude of the fluctuations was less well described (Figure 3B).

The resulting annual water balance is shown for each hydraulic year of the monitoring period (July–June) in Table 2. Values for precipitation and actual evapotranspiration for the most recent hydraulic year, July 2010–June 2011, were among 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, except for the dryest April monitored (Appendix 4). Artificial irrigation was medium compared to the other monitoring years, which could be the result of the very dry April. The groundwater recharge/percolation was medium to high compared to the other hydraulic years, and continuous (Figure 3B).

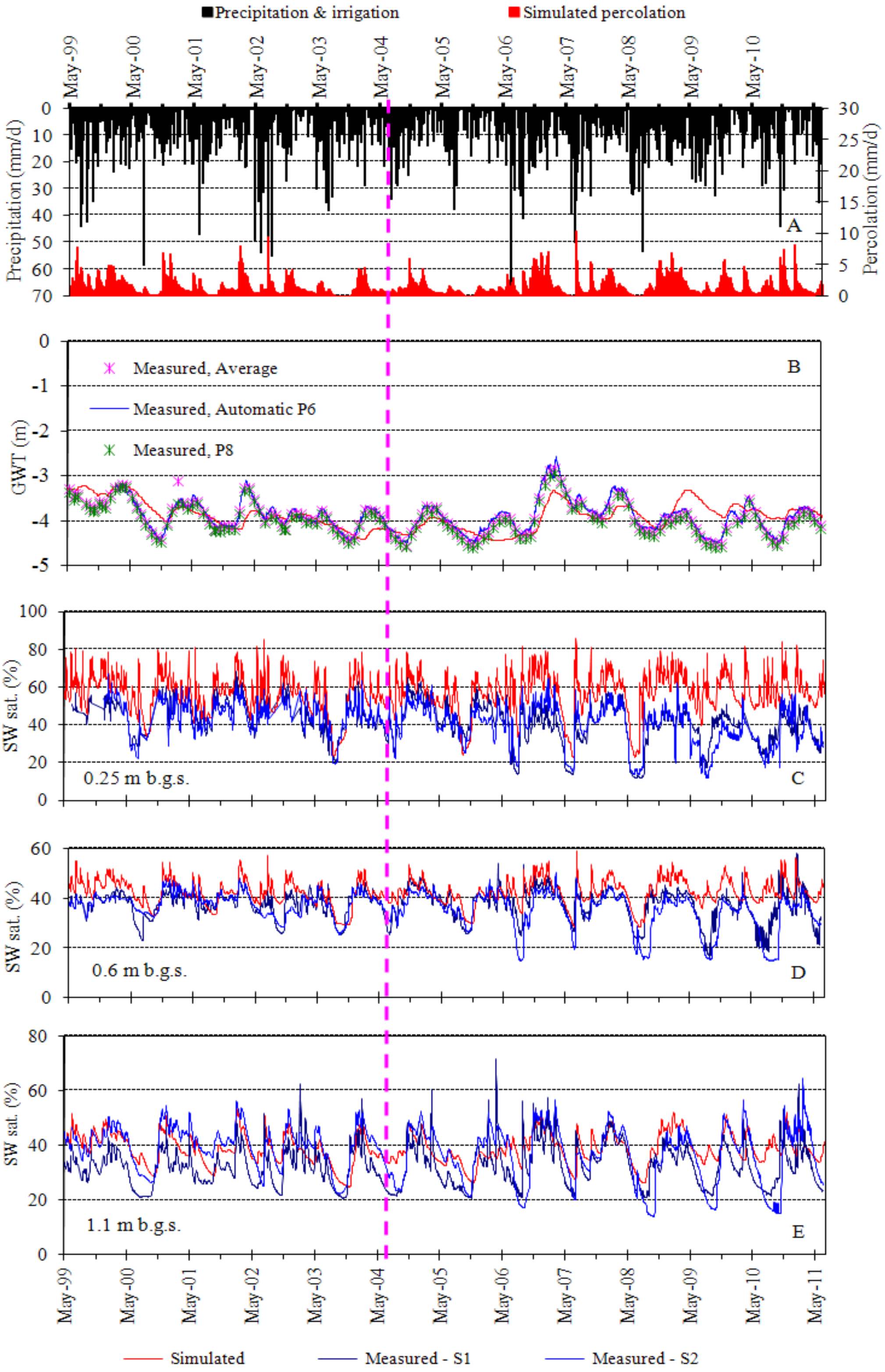


Figure 3. Soil water dynamics at **Tylstrup**: Measured precipitation, irrigation and simulated percolation 1 m b.g.s. (A), simulated and measured groundwater level GWT (B), and simulated and measured soil water saturation (SW sat.) at three different soil depths (C, D and E). The measured data in B 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 2011).

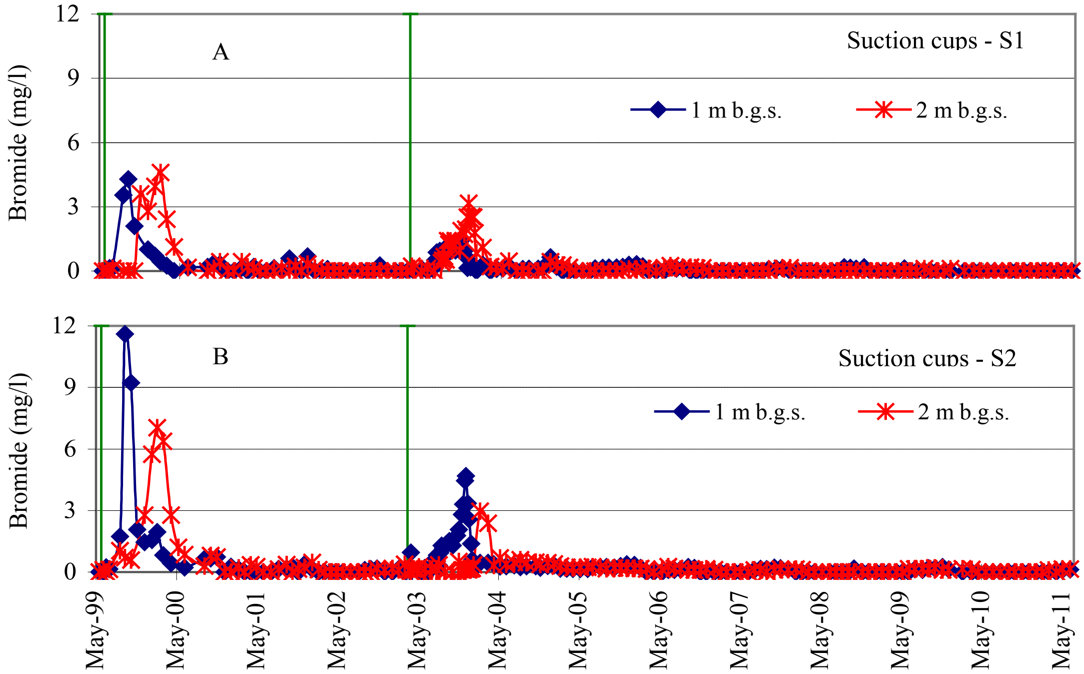


Figure 4. Measured bromide concentration in the unsaturated zone at **Tylstrup**. The measured data derive from suction cups installed 1 m b.g.s. and 2 m b.g.s. at locations S1 (A) and S2 (B) indicated in Figure 2. The green vertical lines indicate the dates of bromide applications.

2.2.2 Bromide leaching

Bromide has now been applied twice at Tylstrup. The bromide concentrations measured until April 2003 (Figure 4 and Figure 5) relate to the bromide applied in May 1999, as described further in Kjær *et al.* (2003). Unsaturated transport of the bromide applied in March 2003 is evaluated in Barlebo *et al.* (2007).

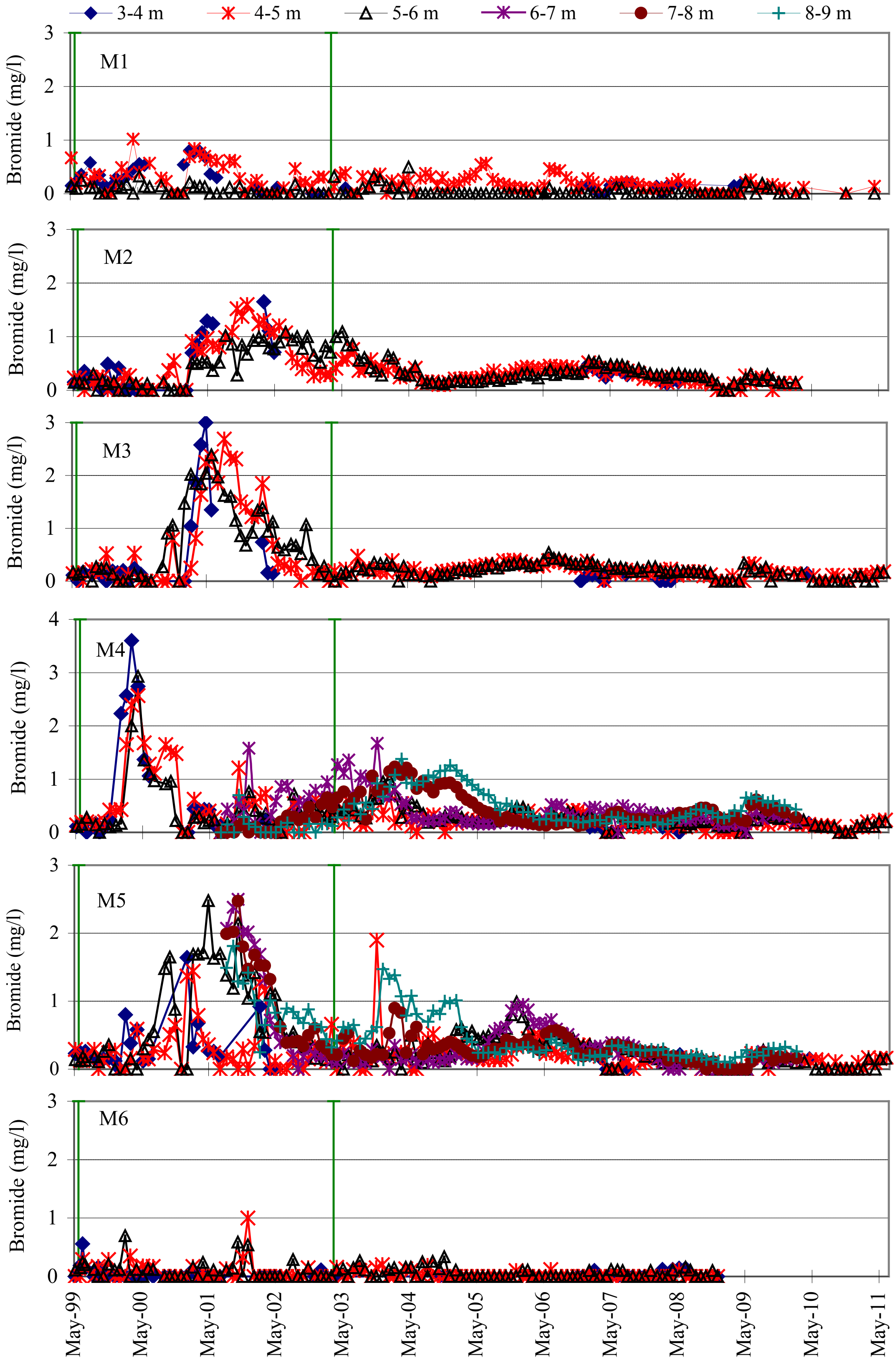


Figure 5. Bromide concentration in the groundwater at **Tylstrup.** The data derive from monitoring wells M1–M6. Monitoring at well M6 was suspended September 2008 (Appendix 2). Screen depth is indicated in m b.g.s. The green vertical lines indicate the dates of bromide applications.

2.2.3 Pesticide leaching

Monitoring at Tylstrup began in May 1999 and presently encompasses several pesticides and their degradation products, as shown in Appendix 8. Pesticide applications during the latest growing seasons are listed in Table 3 and 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 rimsulfuron (applied here as Titus) degrade rapidly. The risk of leaching is therefore associated with the degradation products PPU and PPU-desamino. In Table 3 weighted average concentrations 1 m b.g.s (Cmean) is calculated from both from both S1 and S2. When these values are reported as a range it indicated that Cmean in S1 and S2 differs from each other.Pesticides applied later than April 2011 are not evaluated in this report and hence are not included in Table 3 and Figure 6.

The current report focuses on the pesticide applied from 2009 and onwards, while leaching risk of pesticides applied before 2009 has been evaluated in previous monitoring reports (see http://pesticidvarsling.dk/publ_result/index.html). The leaching of rimsulfuront is further detailed in Kjær *et al.* (2005b), Rosenbom *et al.* (2009) and Rosenbom *et al.* (2010a).

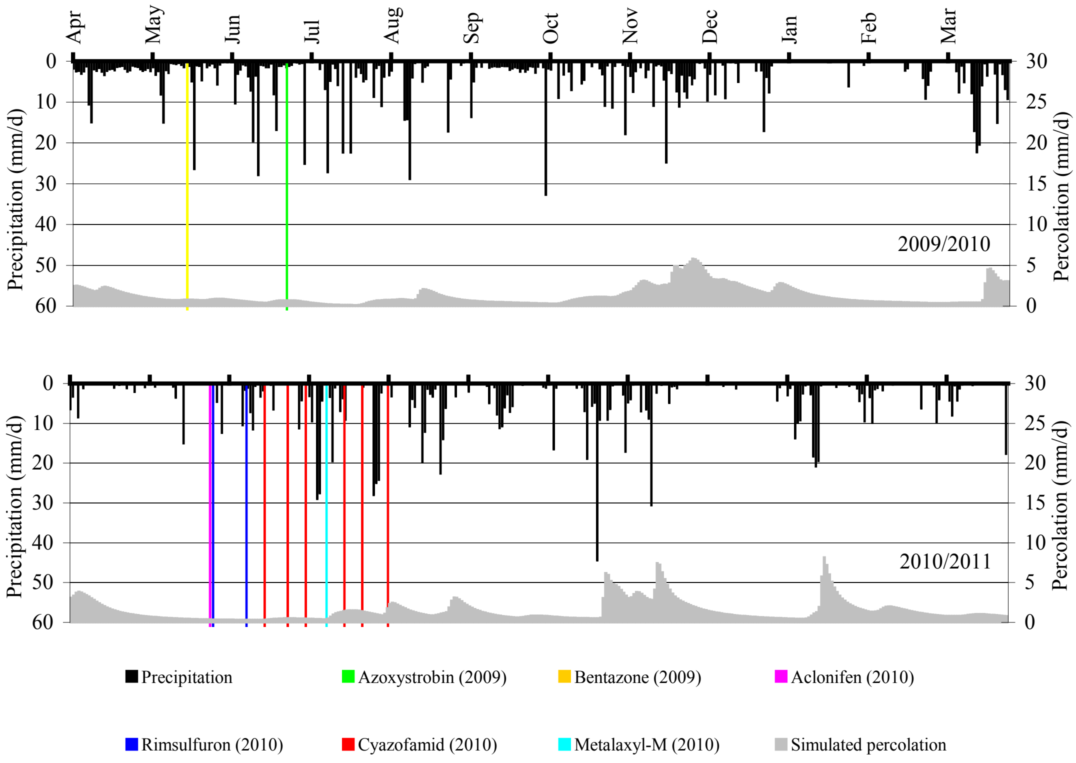


Figure 6. Application of pesticides included in the monitoring programme, precipitation and irrigation (primary axis) together with simulated percolation 1 m b.g.s. (secondary axis) at **Tylstrup** in 2009/2010 (upper) and 2010/2011 (lower).

Table 3. Pesticides analysed at **Tylstrup**. Precipitation (precip.) and percolation (percol.) are accumulated within the first year (Precip 1st year, Percol 1st year) and first month (Precip 1st month, Percol 1st year) after the first application C_{mean} refers to average leachate concentration at 1 m b.g.s. the first year after application. See Appendix 2 for calculation method and Appendix 8 (Table A8.1) for previous applications of pesticides**.**

Crop	Applied product	Analysed pesticide	Application date	End of monit.	Y 1st precip.	Y 1st percol.	M 1st precip.	M 1st percol.	C_{mean}
Winter Rape 2007	CruiserRAPS	Thiamethoxam(P)	Aug 06	Apr 08	1250	700	87	57	<0.01
		CGA 322704(M)	Aug 06	Apr 08	1250	700	87	57	<0.02
	Kerb 500 SC	Propyzamide(P)	Feb 07	Apr 09	1052	472	48	40	<0.01
		RH-24580(M)	Feb 07	Apr 09	1052	472	48	40	<0.01
		RH-24644(M)	Feb 07		1052	472	48	40	<0.01
		RH-24655(M)	Feb 07		1052	472	48	40	<0.01
	Matrigon	Clopyralid(P)	Mar 07	Apr 09	1055	488	30	24	<0.02
Winter Wheat 2008	Amistar	Azoxystrobin(P)	Jun 08	Jun 11	1316	662	141	0	<0.01
		CyPM(M)	Jun 08	Jun 11	1316	662	141	0	<0.01
	Folicur EC 250	Tebuconazole(P)	Nov 07	Mar 10	1133	461	69	43	<0.01
	Stomp	Pendimethalin(P)	Oct 07		1032	415	36	26	<0.01
Spring Barley 2009	Amistar	Azoxystrobin(P)	Jun 09	Jun 10	909	475	138	11	<0.01
		CyPM(M)	Jun 09	Jun 10	909	475	138	11	<0.01
	Basagran M75	Bentazone(P)	May 09	Jun 11*	996	488	133	22	<0.01
Potatoes 2010	Fenix	Aclonifen(P)	May 10	Jun 11*	958	491	62	12	<0.01
	Ranman	Cyazofamid(P)	Jun 10	Jun 11*	981	499	128	17	<0.01
	Ridomil Gold MZ Pepite	Metalaxyl-M(P)	Jul 10	Jun 11*	934	514	127	43	<0.01
		CGA 108906(M)	Jul 10	Jun 11*	934	514	127	43	0.03- 0.12
		CGA 62826(M)	Jul 10	Jun 11*	934	514	127	43	<0.01- 0.02
	Titus WSB	PPU(M)	May 10	Jun 11*	958	491	62	12	0.01-0.02
		PPU-desamino(M)	May 10	Jun 11*	958	491	62	12	<0.01

Systematic chemical nomenclature for the analysed pesticides is given in Appendix 1.
**Monitoring continue the following year.*

Neither the pesticides azoxystrobin and bentazone applied on spring barley in 2009 nor the degradation product CyPM leached at the Tylstrup site. Although, bentazone has been found in one sample (10 April 2006 at S1, 1 m b.g.s.) originating from the application in 2005, there were no leaching from the 2009 application (Table 3 and Figure 6). Azoxystrobin and CyPM were not detected in any of the analysed water samples (Appendix 5.1).

Neither aclonifen nor cyazofamid, both applied on potatoes in 2010, leached during the current monitoring period (Appendix 5). The final evaluation awaits an additional year of monitoring.

Leaching of metalaxyl-M applied used in potatoes in 2010 was minor at Tylstrup, and the compound was only detected in four samples collected from the unsaturated zone, concentration level ranging from 0.013 to 0.03 µg/l (Figure 7). However, two degradation products of metalaxyl-M (CGA 62826 and CGA 108906) leached from the root zone (1 m b.g.s.) the latter in average concentrations exceeding 0.1 µg/l (Table 3 and Figure 7). Both compounds were found in suction cups 1 m b.g.s. at the end of the monitoring period, indication that leaching of especially CGA 108906 had not yet ceased.

In the saturated zone neither metalaxyl-M nor CGA 62826 was found in any samples collected from the wells situated downstream the field site, whereas both compounds were found in samples collected from M1 situated upstream of the field site (Figure 8). While metalaxyl-M was detected in all seven samples (concentration 0.01–0.05 µg/l) collected from M1, CGA 62826 was only detected in two (0.02 µg/l). As the tracer test suggested that water sampled in M1 had not infiltrated at the PLAP site, but originated from the upstream neighbouring fields, detections in M1 suggest that these compound have leached from previous application occurring at these upstreams neighbouring fields, where metalaxyl have also been applied (Appendix 7).

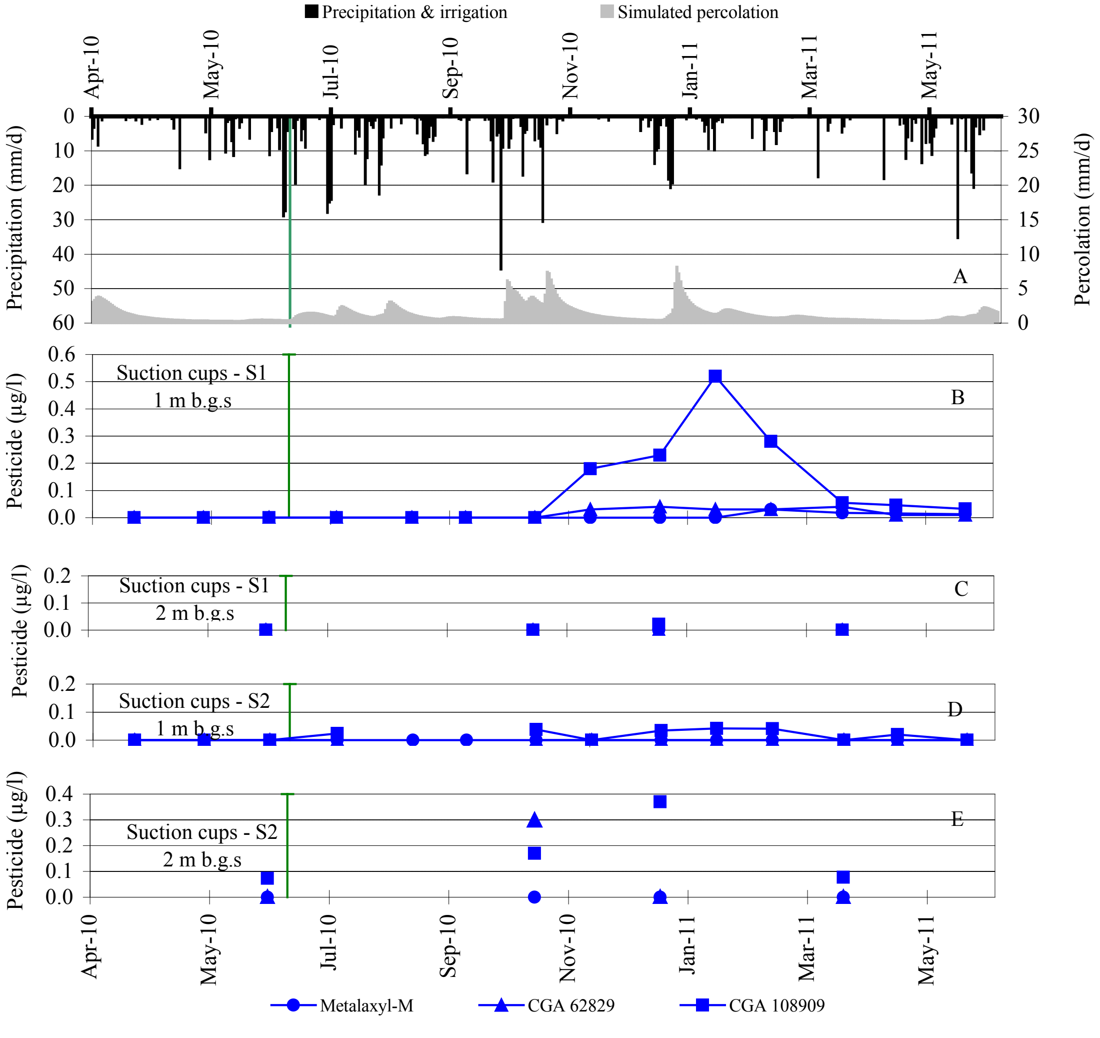


Figure 7. Precipitation, irrigation and simulated percolation 1 m b.g.s. (A) together with measured concentration of *Metalaxyl-M, CGA 62829* and *CGA 108909* (µg/l) in suction cups installed at location S1 at 1 m b.g.s. (B) and 2 m b.g.s. (C) and location S2 at 1 m b.g.s. (D) and 2 m b.g.s. (E) at **Tylstrup**. The green vertical line indicates the date of pesticide application.

CGA 108906 was found in 95% of analysed groundwater samples and 27% of the analysed sample concentrations exceed 0.1 µg/l. Similar to the other compounds GCA 108906 was also detected in samples from the upstream well of M1 and moreover present in the groundwater before metalxyl-M was applied at the PLAP field in 2010. This background concentration of CGA 108906 found in all monitoring wells makes it difficult to determine whether the elevated concentrations observed in downstream monitoring wells are due to the metalaxyl-M applied on the PLAP test site in 2010 or to previous applications on the "upstream" fields. However, the background concentration suggests that leaching of CGA 108906 occurs both from our field as well as from neighbouring field situated upstream our field site. Moreover, with a background level of CGA 108906 ranging between 0.02–0.1 µg/l, additional input via root zone leaching as that observed is likely to increase the frequency of exeedence of the 0.1 µg/l in samples collected from the groundwater monitoring wells.

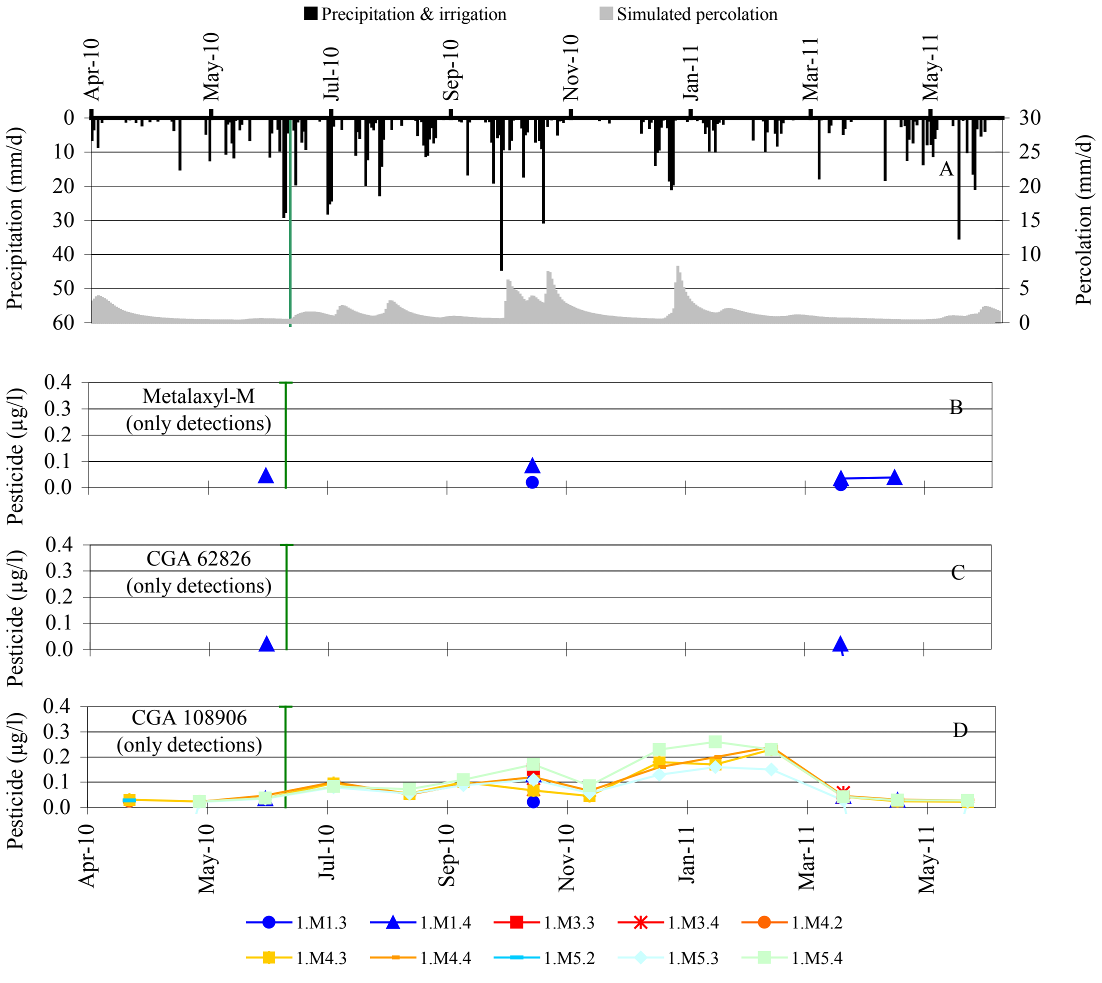


Figure 8. Precipitation, irrigation and simulated percolation 1 m b.g.s. (A) together with measured concentration of *Metalaxyl-M* (B), *CGA 62826* (C) and *CGA 108906* (D) (µg/l) in monitoring wells at **Tylstrup**. The green vertical line indicates the date of pesticide application.

When evaluating these results it should be noted that the precipitation following the application of metalaxyl-M (applied in July) amounted to 140 mm in July 2010 (97% higher than normal) and 111 mm in June (50% higher than normal). See Appendix 4 and Table 3.

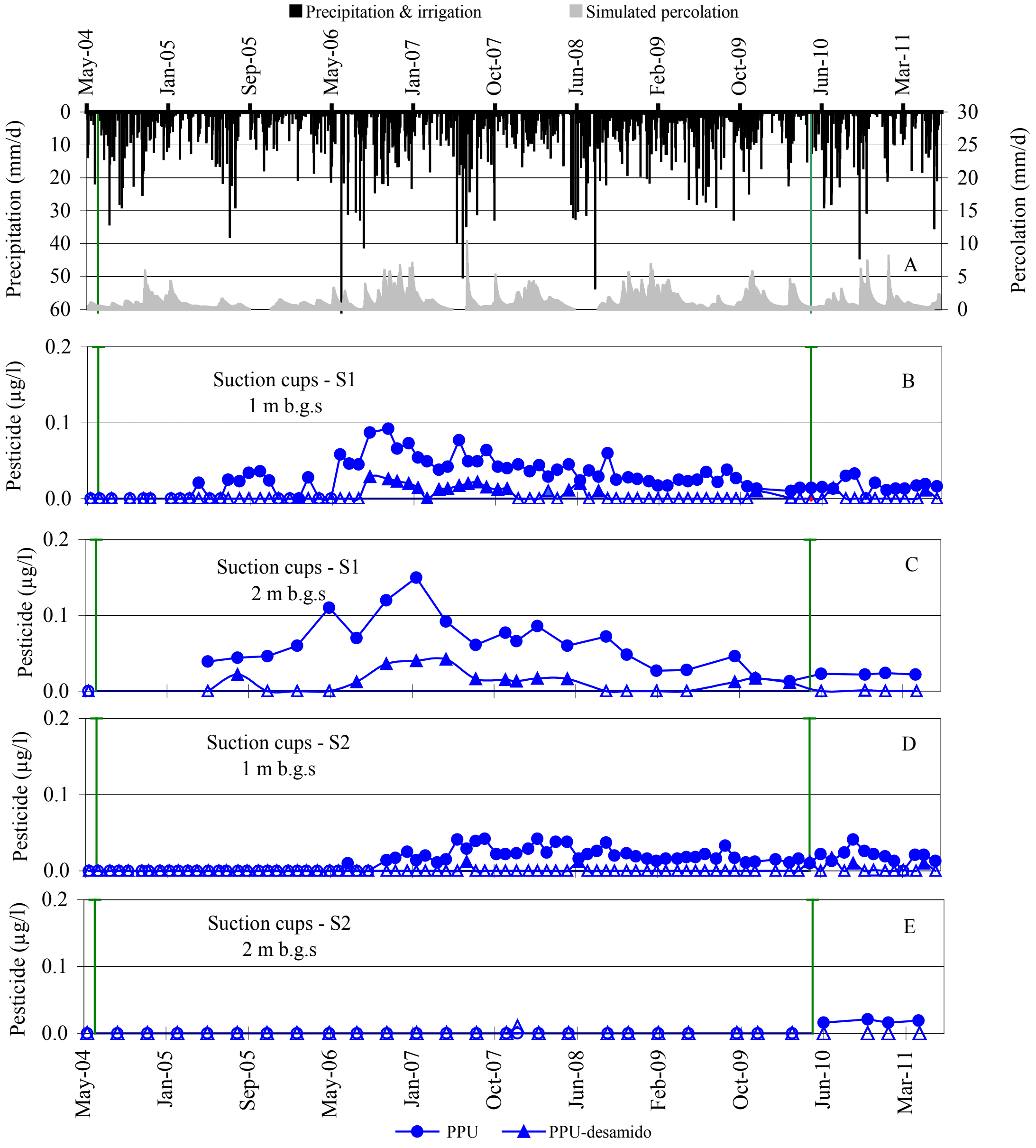


Figure 9. Precipitation, irrigation and simulated percolation 1 m b.g.s. (A) together with measured concentration of *PPU* and *PPU*–desamino (µg/l) in suction cups installed at location S1 at 1 m b.g.s. (B) and 2 m b.g.s. (C) and location S2 at 1 m b.g.s. (D) and 2 m b.g.s. (E) at **Tylstrup**. The 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). While PPU-desamino has not been detected in the groundwater, PPU was detected in two groundwater samples (see text).

Metalaxyl was on the Danish market from 1980-1995, reported maximum allowed dosage from 1984-1995 being 375 gr. a.i./ha. It re-entered the Danish marked in 2007 as Metalaxyl-M with a maximum allowed dosage of 77.6 g/ha. Since 2006 metalaxyl-M was applied at upstream neighboring fields where reported dosage did not exceed the maximum allowed dosage of 77.6 g a.i./ha. Usage data are not available from 1980-1995 but information from local farmers suggest that metalxyl during this period was applied on some of the upstream neighboring field (Appendix 7). For placing the result into regulatory context it would thus be important to judge if measured groundwater residues origin from initial high usage of 375 g a.i/ha allowed in 1980–1995 or from the current usage of 77.6 g a.i/ha allowed since 2007.

Based on available data we believe that detected residues in the groundwater are most likely to derive from current usage of metalaxyl allowed since 2007 and not the initial usage allowed from 1980–1995. With an average travel time to all monitoring wells being less than 4 years (Laier et al. in prep) it is unlikely that water sampled from these screen have infiltrated the unsaturated zone before 1995 (17 years ago). A possibility could however be that the residues originating from the initial usage of 375 g/ha (allowed in 1980-1995) were left in the soil and continued to leached during a long period of time. Should this be the case the persistency of these compounds would be very high allowing them to leach more than a decade after application. An assumption which dot not correspond the regulatory assessment where final endpoints for DT_{50} were less than 18 days Danish EPA (2007).

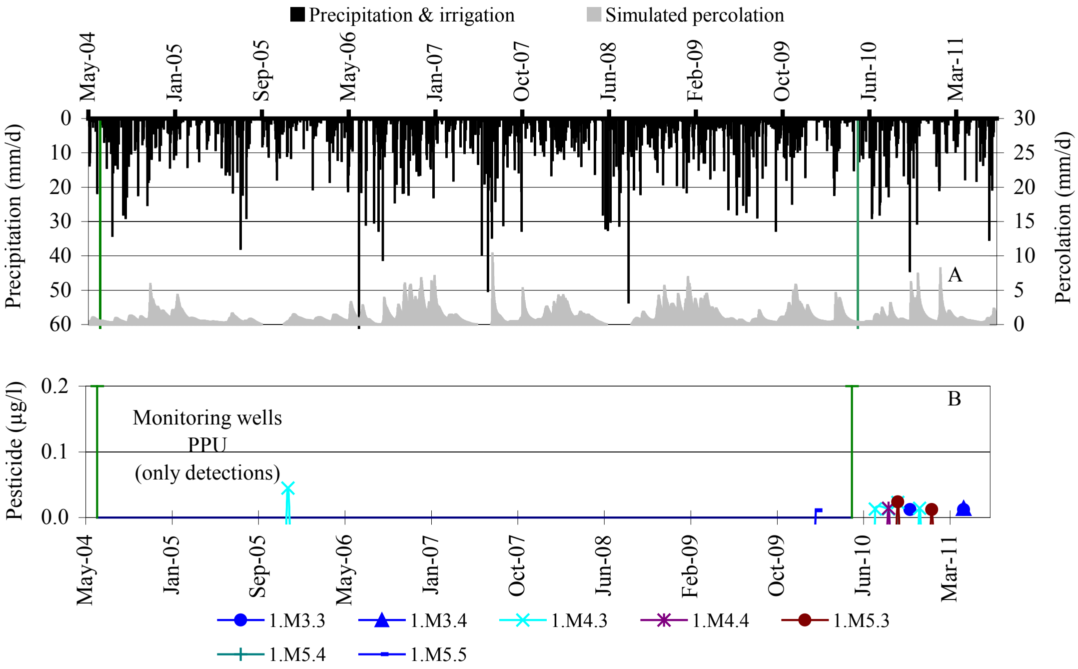


Figure 10. Precipitation, irrigation and simulated percolation 1 m b.g.s. (A) together with measured concentration of *PPU* (µg/l) in monitoring wells (B) at **Tylstrup**. The green vertical line indicates the date of pesticide application.

Rimsulfuron was applied on potatoes in 2010 in the same dosage as that used on potatoes in 2004. Rimsulfuron degrades rapidly in the soil, and the leaching risk is therefore associated with the degradation products PPU and PPU-desamino. At Tylstrup PPU was characterised by continuous leaching over a long period of time. Residues (ranging between 0.01–0.05 µg/l) of the 2004 application were thus still detected in the suction cups prior to the 2010 application. Evidence of additional leaching following the 2010 application have not yet been observed, as leachate concentration 1 m b.g.s. following the 2010 application is similar to that observed in previous year of 2009/2010 (Figure 9). During the last monitoring year (from July 2010 and onwards) frequency of PPU (Rimsulfuron metabolite) detection in the groundwater has increased markedly and PPU is found in 35% of analysed samples, concentration level being low however (0.012-0.023 µg/l, Figure 10). Final evaluation of the 2010 application awaits an additional year of monitoring; as travel time of these metabolites to the suction cups 1 m b.g.s. is know to be approximately 10 mounts (Kjær et al. 2010). The results of the 2004 application are summarised Rosenbom *et al.* (2010a).

3 Pesticide leaching at Jyndevad

3.1 Materials and methods

3.1.1 Site description and monitoring design

Jyndevad is located in southern Jutland (Figure 1). The test site covers a cultivated area of 2.4 ha (135 x 184 m) and is practically flat. A windbreak borders the eastern side of the test site. The area has a shallow groundwater table ranging from 1 to 3 m b.g.s. (Figure 12B) The overall direction of groundwater flow is towards the northwest (Figure 11). 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 2010-11 growing seasons is briefly summarized below and detailed in Appendix 3 (Table A3.2). For information about management practice during the previous monitoring periods, see previous monitoring reports available on http://pesticidvarsling.dk/publ_result/index.html.

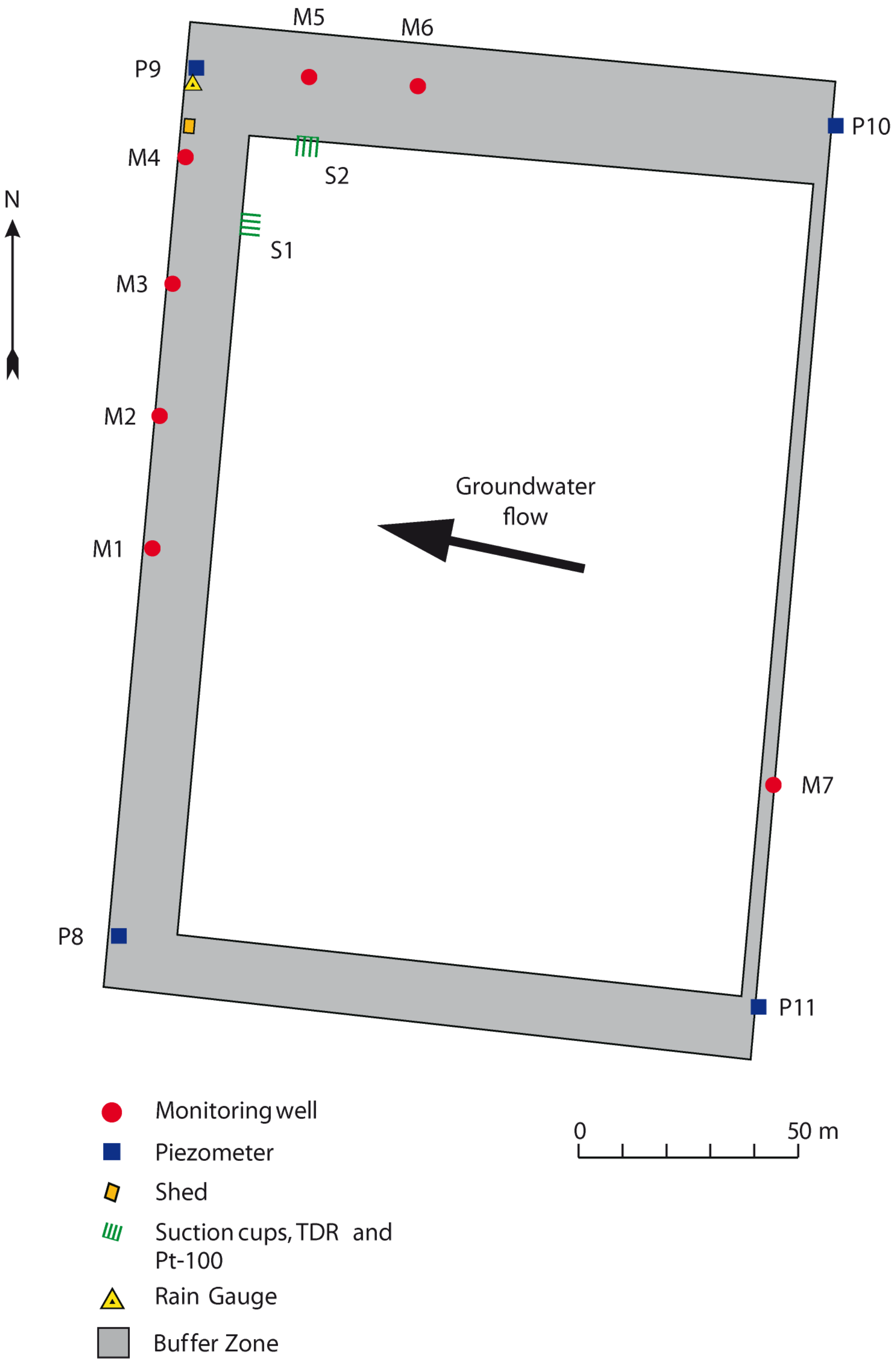


Figure 11. Overview of the **Jyndevad** site. The innermost white area indicates the cultivated land, while the grey area indicates the surrounding buffer zone. The positions of the various installations are indicated, as is the direction of groundwater flow (by an arrow). Pesticide monitoring is conducted monthly and half-yearly from selected monitoring wells and suctions cups as described in Table A2.1 in Appendix 2.

Having been ploughed on 14 April 2010, the field was planted with potatoes (cv. Kuras) on 4 May. Before the potatoes emerged the field was sprayed with the herbicides aclonifen and rimsulfuron on 27 May. Rimsulfuron was applied again on 8 June. The fungicide cyazofamid was used five times between 28 June and 9 August, whereas azoxystrobin was applied on 6 July and a combination of mancozeb and metalaxyl on 25 July. Aphids were sprayed once using lambda-cyhalothrin on 16 July. The field was irrigated three times with 25, 25 and 30 mm on 24 June, 30 June and 8 July, respectively. Neither mancozeb, azoxystrobin nor lambda-cyhalothrin was included in the monitoring. The potatoes were harvested on 19 October yielding 450 hkg/ha with 26.8% DM (120.6 hkg/ha at 100% DM), yields being below the average for the soil type and year (Plantedirektoratet, 2010). The field was ploughed on 22 March 2011 and the following day sown with spring barley (cv. Quench).

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 2011 and to establish an annual water balance.

Compared with the setup in Kjær *et al.* (2011), 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 2011. 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 11), and the bromide concentration measured in the suction cups located 1 and 2 m b.g.s (Figure 13). Data acquisition, model setup as well as results related to simulated bromide transport are described in Barlebo *et al.* (2007).

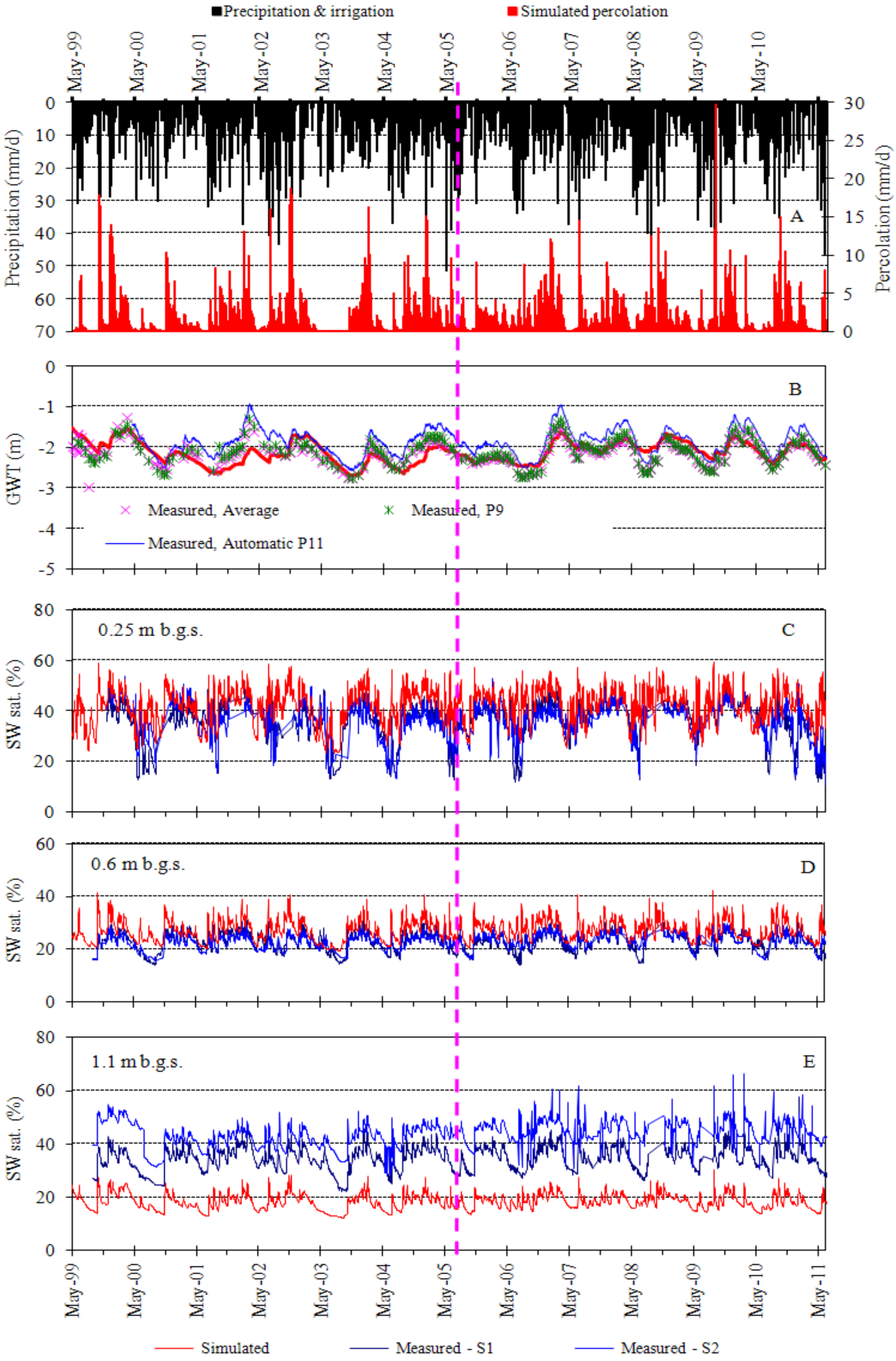


Figure 12. Soil water dynamics at **Jyndevad**: Measured precipitation, irrigation and simulated percolation 1 m b.g.s. (A), simulated and measured groundwater level (B), and simulated and measured soil water saturation (SW sat.) at three different soil depths (C, D and E). The measured data in B derive from piezometers located in the buffer zone. The measured data in C, D and E derive from TDR probes installed at S1 and S2 (Figure 8). The broken vertical line indicates the beginning of the validation period (July 2004-June 2011).

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 12). The dynamics of the simulated groundwater table were well described with MACRO 5.1 (Figure 12B). No measurements of the water saturation were obtained during the following two periods: 1 June-25 August 2009 (given a breakdown in the TDR measuring system) and 7 February-6 March 2010 (given a sensor error). As noted earlier in Kjær *et al.* (2011), the model still had some difficulty in capturing the degree of soil water saturation 1.1 m b.g.s. (Figure 12E) and also the decrease in water saturation observed during summer periods at 25 and 60 cm b.g.s. A similar decrease in water saturation is observed from December 2010 to February 2011 at 25 cm b.g.s., which is caused by precipitation falling as snow (air-temperature below zero degrees Celcius). The water flow through the soil profile will hereby be delayed – a delay, which can not be captured by the MACRO-setup.

The resulting water balance for Jyndevad for the 11 monitoring periods is shown in Table 4. Compared with the previous eleven years, the latest hydraulic year July 2010-June 2011 was characterised by having medium precipitation, high simulated actual evapotranspiration and high irrigation values. Precipitation in the latest hydraulic year was characterised by August to October and May-June being very wet, and April being the driest monitored at this site (Appendix 4). Continuous percolation 1 m b.g.s. were simulated for this hydraulic year.

Table 4. Annual water balance for **Jyndevad** (mm yr^{-1}). 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	1078	84	551	610
1.7.09–30.6.10	995	1059	80	530	610
1.7.10–30.6.11	995	1070	92	554	607

[1)] *Normal values based on time series for 1961-1990.*

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

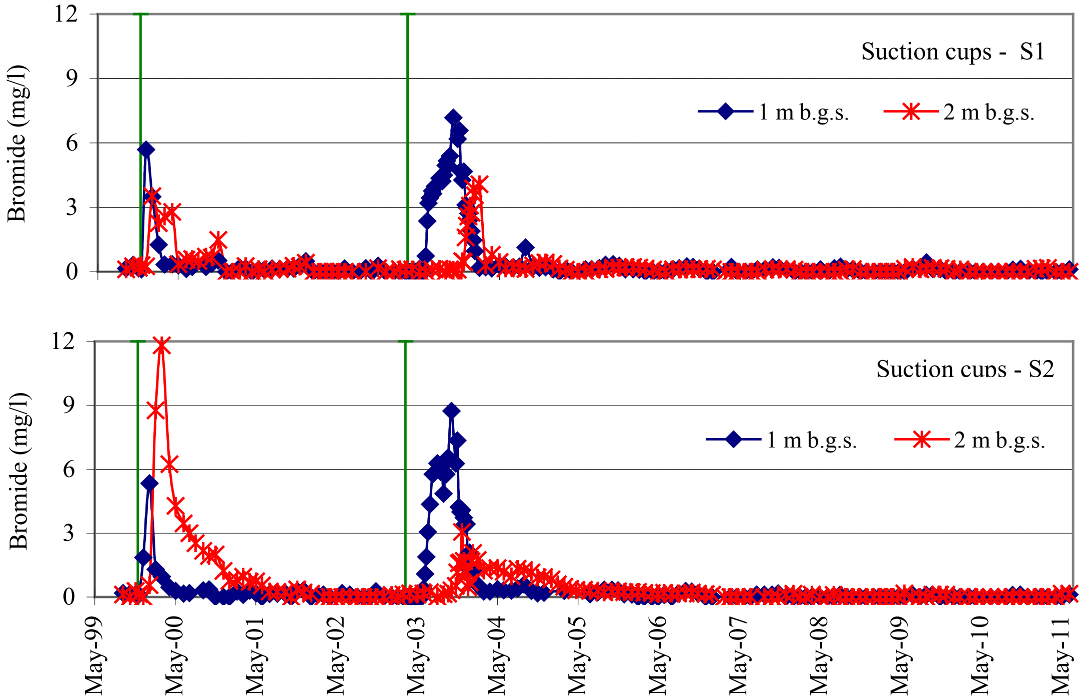


Figure 13. Bromide concentration in the unsaturated zone at **Jyndevad**. The measured data derive from suction cups installed 1 m b.g.s. (upper) and 2 m b.g.s. (lower) at locations S1 and S2 (Figure 8). The green vertical lines indicate the dates of bromide applications.

3.2.2 Bromide leaching

Bromide has now been applied twice at Jyndevad. The bromide concentrations measured until April 2003 (Figure 13 and Figure 14) relate to the bromide applied in autumn 1999, as described further in Kjær *et al.* (2003). Leaching of the bromide applied in March 2003 is evaluated in Barlebo *et al.* (2007).

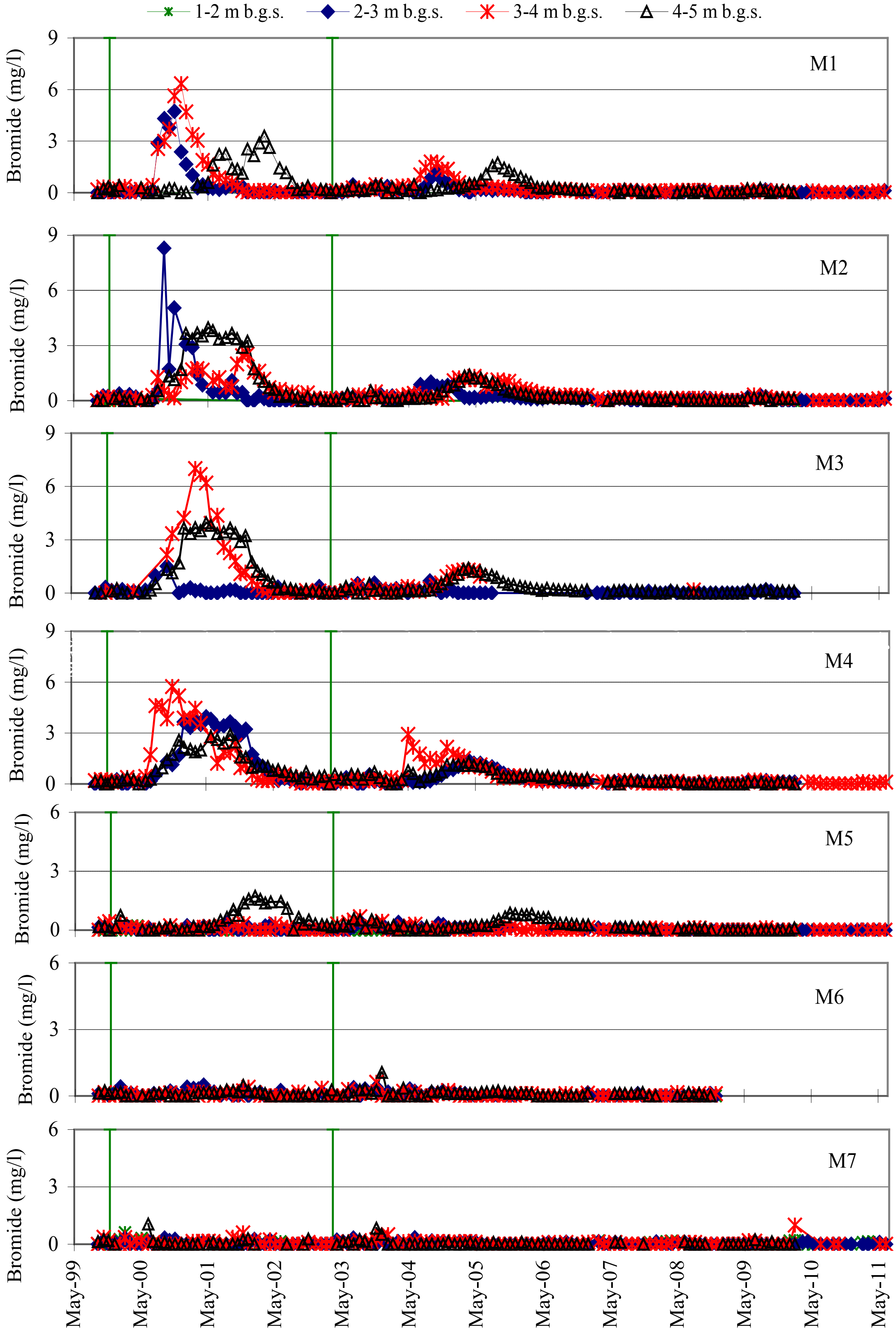


Figure 14. Bromide concentration in the groundwater at **Jyndevad**. The data derive from monitoring wells M1–M7. Monitoring at well M6 was suspended September 2008 (Appendix 2). Screen depth is indicated in m b.g.s. The green vertical lines indicate the dates of bromide applications.

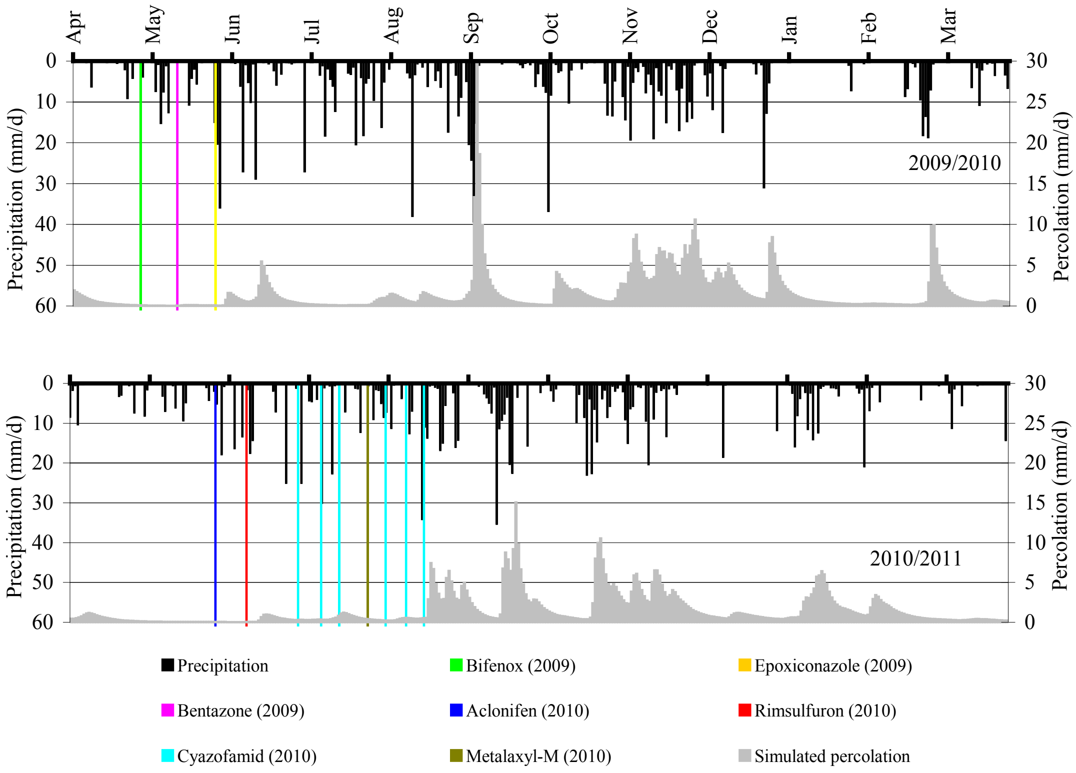


Figure 15. Application of pesticides included in the monitoring programme, precipitation and irrigation (primary axis) together with simulated percolation 1 m b.g.s. (secondary axis) at **Jyndevad** in 2009/2010 (upper) and 2010/2011 (lower).

3.2.3 Pesticide leaching

Monitoring at Jyndevad began in September 1999 and presently encompasses several pesticides and their degradation products, as indicated in Appendix 8. Pesticide application during the most recent growing seasons is listed in Table 5 and shown together with precipitation and simulated precipitation in Figure 15. 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 rimsulfuron (applied here as Titus) degrade rapidly. The leaching risk is therefore associated with the degradation products: 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). Pesticides applied later than April 2011 are not evaluated in this report and hence not included in Table 5 and Figure 16.

Table 5. Pesticides analysed at **Jyndevad**. Precipitation (precip.) and percolation (percol.) are accumulated within the first year (Precip 1st year, Percol 1st year) and first month (Precip 1st month, Percol 1st year) after the first application C_{mean} refers to average leachate concentration at 1 m b.g.s. the first year after application. See Appendix 2 for calculation method and Appendix 8 (Table A8.2) for previous applications of pesticides.

Crop	Applied product	Analysed pesticide	Application date	End of monit.	Y 1st precip.	Y 1st percol.	M 1st precip.	M 1st percol.	C_{mean}
Triticale 2007	Atlantis WG	Mesosulfuron-methyl(P)	Oct 06	Dec 09	1346	809	95	73	<0.01
		Mesosulfuron(M)	Oct 06		1346	809	95	73	<0.02
	Cycocel 750	Chlormequat(P)	Apr 07	Jun 08	1223	638	79	1	<0.01
	Opus	Epoxiconazole(P)	May 07	Dec 09	1193	644	123	6	<0.01
Winter Wheat 2008	Folicur EC 250	Tebuconazole(P)	Dec 07	Mar 10	1396	827	60	97	<0.01
	Pico 750 WG	Picolinafen(P)	Oct 07	Mar 10	1418	777	77	55	<0.01
	Pico 750 WG	CL153815(M)	Oct 07	Mar 10	1418	777	77	55	<0.01
Spring Barley 2009	Basagran M75	Bentazone(P)	May 09	Jun 11	1178	630	144	13	<0.01-0.04
	Bell	Epoxiconazole(P)	May 09	Dec 09	1181	630	164	42	<0.01
	Fox 480 SC	Bifenox(P)	Apr 09	Jun 11*	1206	630	106	3	<0.02
	Fox 480 SC	Bifenox acid(M)	Apr 09	Jun 11*	1206	630	106	3	<0.05
	Fox 480 SC	Nitrofen(M)	Apr 09	Jun 11*	1206	630	106	3	<0.01
Potatoes 2010	Fenix	Aclonifen(P)	May 10	Jun 11*	1149	567	123	10	<0.01
	Ranman	Cyazofamid(P)	Jun 10	Jun 11*	1188	627	125	16	<0.01
	Ridomil Gol MZ Pepite	Metalaxyl-M(P)	Jul 10	Jun 11*	1073	613	161	41	0.02[1]
		CGA 108906(M)	Jul 10	Jun 11*	1073	613	161	41	0.37-0.66[2]
		CGA 62826(M)	Jul 10	Jun 11*	1073	613	161	41	0.16[2]-0.19
	Titus WSB	PPU(M)	Jun 10	Jun 11*	1160	592	137	13	0.02[1]
		PPU-desamino(M)	Jun 10	Jun 11*	1160	592	137	13	<0.01[1]

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

[1] *C_{mean} is only calculated from suction cups S1(see text).*

[2] *Degradation product of metalaxyl-M.*

**Monitoring continue the following year.*

The current report focuses on the pesticides applied from 2009 and onwards, while leaching risk of pesticides applied before 2008 has been evaluated in previous monitoring reports (see http://pesticidvarsling.dk/publ_result/index.html).

In Table 6 weighted average concentrations 1 m b.g.s (C_{mean}) is calculated from both from both S1 and S2. When these values are reported as a range it indicated that C_{mean} in S1 and S2 differs from each other. During the monitoring period 2010/2011 it was unfortunately not possible to extract sufficient water from S2 to perform all pesticide analysis. For some of the compounds (metalaxyl-M, PPU, PPU-desamino) there was not sufficient data to calculate weighted leachate concentration (Figure 16 and 18), why reported 2010 values in Table 6 refers to suction cups S1 only (see note 1 in Table 5). For the same reason concentration of CGA62826 and CGGA 108906 in S2 was not measured in S2 during the first mounts after applications. In Table 6 calculation concentration of CGA62826 and CGA 108906 in S2 being 0.16 and 0.66 respectively refers to average leaching concentration from date of first analysis on 4 November 2010 until 1 July 2011 (see note 2 in Table 6).

The herbicides bifenox and bentazone and the fungicide epoxiconazole were used in the spring barley sown in 2009. Bifenox was found twice in suctions cups, in concentrations of 0.034 and 0.036 µg/l, four to six months after the application as well as in two monitoring wells five months after application, in concentrations of 0.05 and 0.033 µg/l

(Table A5.2). The metabolite bifenox acid was found once, 0.1 µg/l, in a monitoring well four months after application, while nitrofen was not detected in any analysed water sample. Bentazone was absent in all the samples from the monitoring wells (Table 20). It was, however, found frequently in samples from suction cups, reaching a maximum of 0.71 µg/l (see Figure 15 in Kjær et al 2011). None of the substances were leached in yearly average concentrations exceeding 0.1 µg/l (Table 6). Epoxiconazole did not leaching at Jyndevad, as it was never detected in any of the analysed water samples.

Aclonifen and Cyazofamid both applied on potatoes in 2010 did not leaching during the current monitoring period, as none of the compounds was found in any of the analysed water samples (Appendix 5.2). The final evaluation awaits an additional year of monitoring.

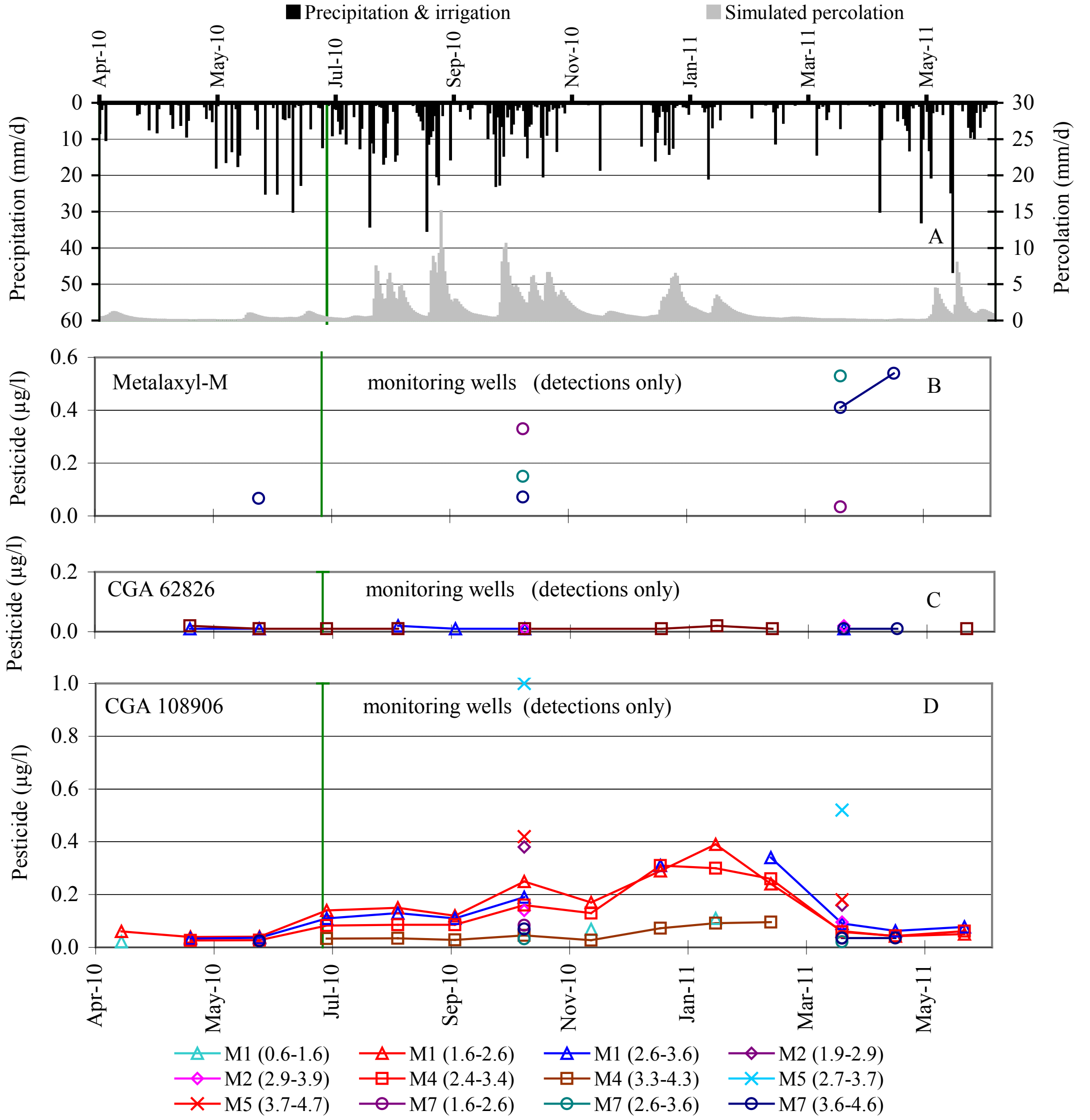


Figure 16. Precipitation, irrigation and simulated percolation 1 m b.g.s. (A) together with measured concentrations (µg/l) in downstream (M1, M2 and M4) and upstream monitoring wells (M7) of *metalaxyl-M* (B), CGA 62826 (C) and CGA 108906 (D) at Jyndevad. The numbers in parantheses indicate the depths of the analysed screens. The green vertical line indicates the date of pesticide application.

Both metalaxyl-M applied on potatoes in 2010 as well as its two degradation product for CGA 62829 and CGA 108909 leached from the root zone (1 m b.g.s.) the two latter in average concentrations exceeding 0.1 µg/l (Table 3, Figure 16 and 17). Both degradation products were found is suction cups 1 m b.g.s. in the end of the monitoring period indication that leaching had not yet ceased.

Results from the saturated zone suggested that previous application occurring at up streams neighbouring fields also have induced leaching to the groundwater of Metalaxyl-M, CGA 62829 and CGA108909. All three compound were present in groundwater before metalaxyl-M was applied to the field, they were also detected in samples collected from M7 situated upstream of the field site (Figure 16) and CGA 108909 was also found in M5 located north of the field. As the tracer test suggested that water sampled in M7 and M5 (uppermost three filters) had not infiltrated at the PLAP site (Figure 14), but originated from the upstream neighbouring fields where metalaxyl have also been applied (Appendix 7). Moreover, CGA108909 was found in all groundwater samples collected 27 July. As this sampling was done only 2 days after application and precipitation during this period amounted to only 0.5 mm these detections are likely to occur from previous applications as well.

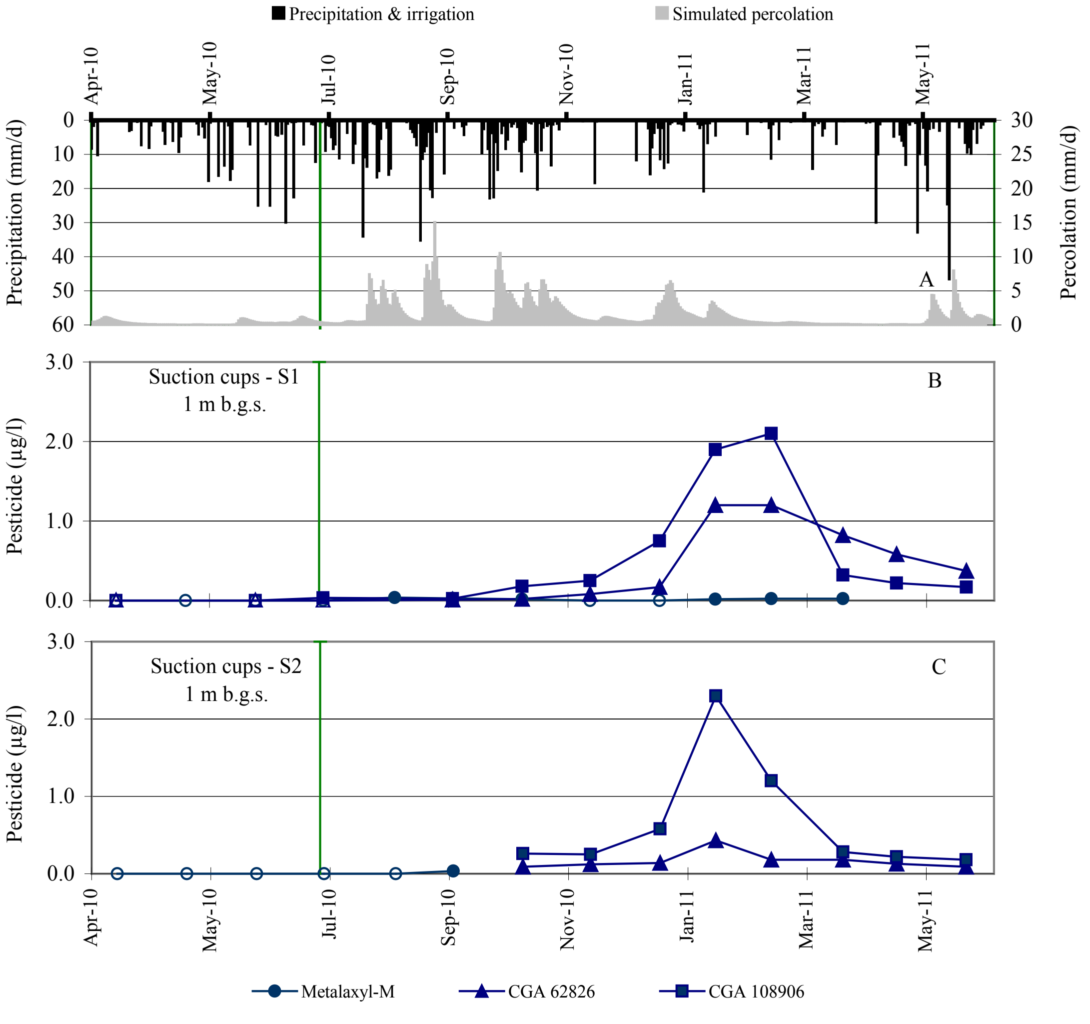


Figure 17. Precipitation, irrigation and simulated percolation 1 m b.g.s. (A) together with measured concentrations of *Metalaxyl-M,* CGA 62826 and CGA 108906. The green vertical line indicates the date of pesticide application.

The background concentration of CGA 108909 found in all monitoring wells makes it difficult to determine whether the elevated concentrations observed in downstream monitoring wells during winter 2010/2011 are due to the metalaxyl-M applied on the PLAP test site in 2010 or to previous application on the "upstream" fields (Figure 7). However, with a background level of CGA 108909 ranging between 0.014–0.14 µg/l additional input via root zone leaching is likely to increase groundwater concentration and by this the frequency of exeedance of the 0.1 µg/l in collected groundwater samples.

In total CGA 108909 was found in 90% of analysed groundwater samples and 38% of analysed samples had concentration exceeding 0.1 µg/l. CGA 108909 was found in 30% of analysed groundwater samples, concentration being less than 0.1 µg/l however. Metalaxyl was only detected in the upstream well M7, but in high concentration reaching 0.54 µg/l.

When evaluating these results it should be noted that the precipitation following the application of metalaxyl-M (applied on 25 July 2010) amounted to 180 mm in August 2010 (99% higher than normal) and 149 mm in September 2010 (47% higher than normal). See Appendix 4 and Table 4.

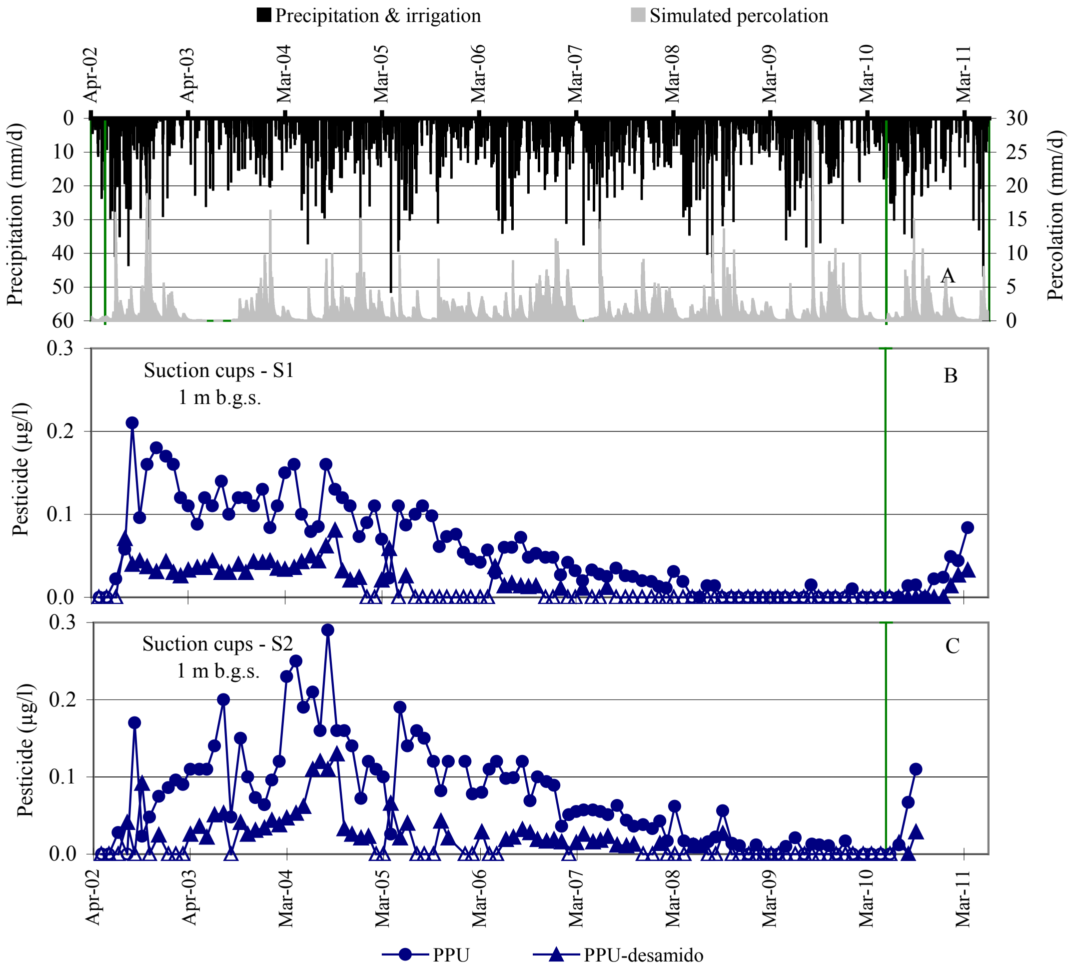


Figure 18. Precipitation, irrigation and simulated percolation 1 m b.g.s. (A) together with measured concentrations of *PPU* and *PPU-desamino (*µg/l) in suction cups installed 1 m b.g.s. at location S1 (B) and S2 (C) at **Jyndevad**. The green vertical line indicates the date of pesticide application. Open symbols indicate concentrations below the limit of detection (0.02 µg/l prior to July 2006 and 0.01 µg/l thereafter).

Metalaxyl was on the Danish market from 1980-1995, reported maximum allowed dosage from 1984-1995 being 375 gr. a.i./ha. It re-entered the Danish marked in 2007 as Metalaxyl-M with a maximum allowed dosage of 77.6 g/ha. Since 2006 metalaxyl-M was applied at upstream neighboring fields where reported dosage did not exceed the maximum allowed dosage of 77.6 g a.i./ha but evidence of higher dosage used in the period 1988 1993 was also reported (Appendix 7). For placing the result into regulatory context it would thus be important to judge if measured groundwater residues origin from initial high usage of 375 g a.i/ha allowed in 1980-1995 or from the current usage of 77.6 g a.i/ha allowed since 2007.

Based on available data we believe that detected residues in the groundwater are most likely to derive from current usage of metalaxyl allowed since 2007 and not the initial usage allowed from 1980–1995. With an average travel time to all monitoring wells being less than 3 years (Laier et al. in prep) it is unlikely that water sampled from these screen have infiltrated the unsaturated zone before 1995 (17 years ago). A possibility could however be that the residues originating from the initial usage of 375 g/ha (allowed in 1980-1995) were left in the soil and continued to leached during a long period of time.

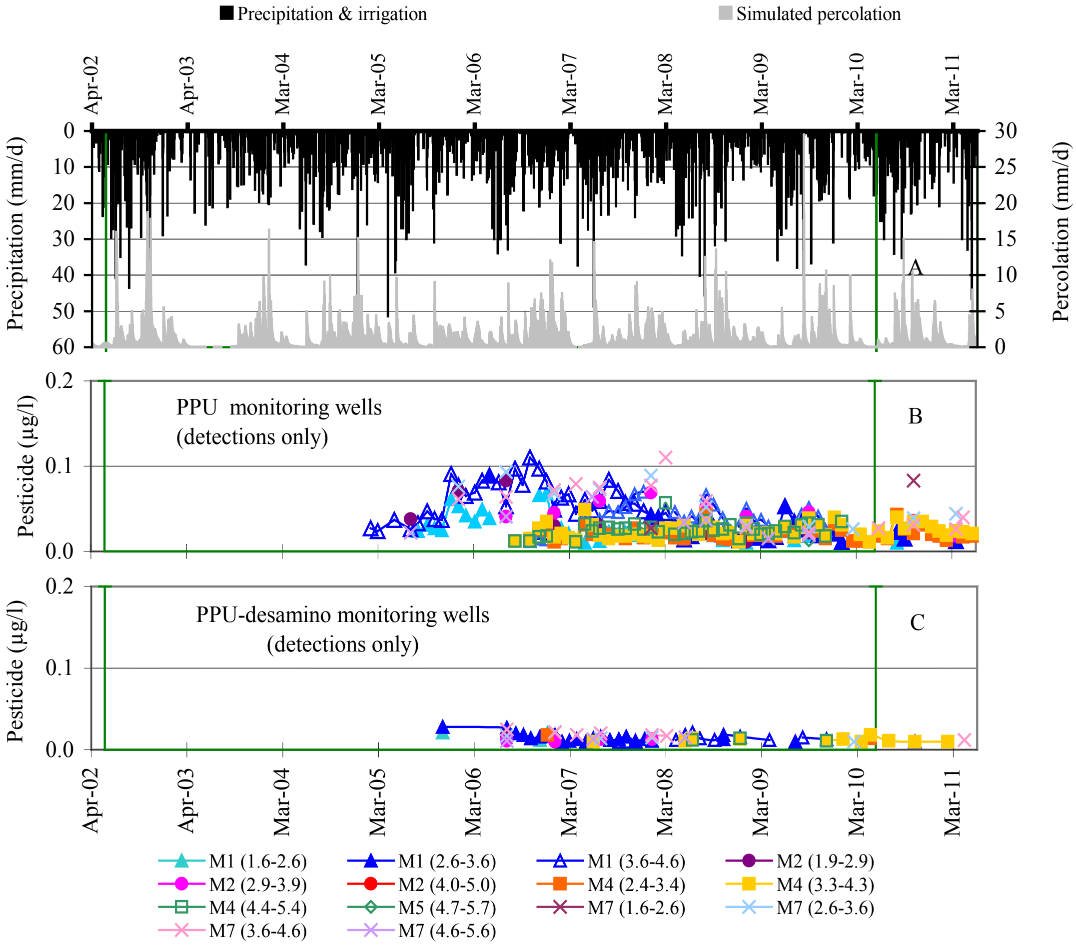


Figure 19. Precipitation, irrigation and simulated percolation 1 m b.g.s. (A) together with measured concentrations (µg/l) in downstream (M1, M2 and M4) and upstream monitoring wells (M7) of *PPU* (B) and *PPU-desamino* (C) at **Jyndevad.** The numbers in parentheses indicate the depths of the analysed screens. The green vertical lines indicates the date of pesticide application.

Should this be the case the persistency of these compounds would be very high allowing them to leach more than a decade after application. An assumption which dot not correspond the regulatory assessment where final endpoints for DT_{50} were less than 18 days Danish EPA (2007).

Rimsulfuron was applied on potatoes in 2010 in the same dosage as that used on potatoes in 2002. Rimsulfuron degrades rapidly in the soil, and the leaching risk is therefore associated with the degradation products PPU and PPU-desamino. Following the 2002 application both compounds were characterised by continuous leaching over a long period of time. Average yearly concentrations of especially PPU reaching 0.1 µg/l were seen as long as three years after 2002 application (Rosenbom et al 2010a). Although the concentration decreased during the 2009/2010, PPU could occasional still be found in low concentrations. Additional leaching was observed after the 2010 application, concentration of PPU reaching 0.084 µg/l and 0.11 µg/l were seen in suction cups S1 and S2 respectively (Figure 18). Final evaluation of the 2010 application awaits an additional year of monitoring, as the leaching period of these metabolites extent the current monitoring period (Figure 18). During the last monitoring year PPU were however still frequently found in the groundwater (frequency of detection being 59% and concentration level being less that 0.1µg/l), whereas detection frequency of PPU-desmino was decreased down to 10% (Figure 19).

The results of the 2002 application are summarized in Rosenbom *et al.* (2010a).

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 20). 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 2010-2011 growing seasons is briefly summarized below and detailed in Appendix 3 (Table A3.3). For information about management practice during the previous monitoring periods, see previous reports available on http://pesticidvarsling.dk/publ_result/index.html.

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

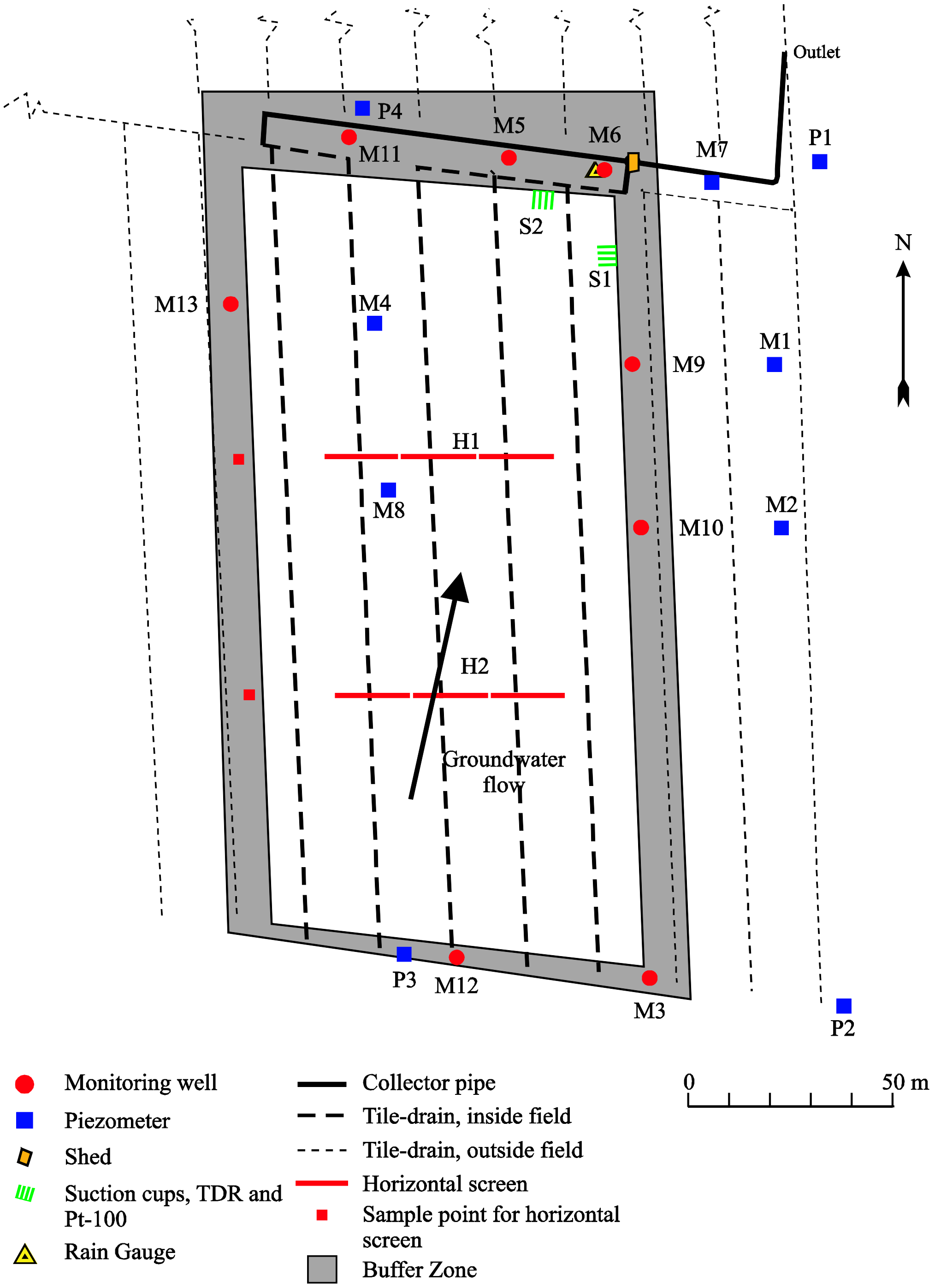


Figure 20. Overview of the **Silstrup** site. The innermost white area indicates the cultivated land, while the grey area indicates the surrounding buffer zone. The positions of the various installations are indicated, as is the direction of groundwater flow (by an arrow). Pesticide monitoring is conducted weekly from the drainage system (during period of continuous drainage runoff) and monthly and half-yearly from selected groundwater monitoring wells as described in Table A2.1 in Appendix 2.

4.1.3 Model setup and calibration

Compared with the setup in Kjær *et al.* (2011), 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 2011. 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 20), and the measured drainage flow. Data acquisition, model setup and results related to simulated bromide transport are described in Barlebo *et al.* (2007). Given impounding of water in the drainage water monitoring well, estimates for the measured drainage on 11 December 2006, 13-14 December 2006, 28 February 2007, 23 October 2011, 13 November 2011 and 11 December 2011 were based on expert judgement. Additionally, TDR-measurements at 25 cm b.g.s. in the period 15 December 2009–20 March 2010 were discarded given freezing soils (soil temperatures at or below zero degrees Celsius). The soil water content is measured with TDR based on Topp calibration (Topp *et al.*, 1980), which will underestimate the total soil water content at the soil water freezing point as the permittivity of frozen water is much less than that of liquid water (Flerchinger *et al.*, 2006).

4.2 Results and discussion

4.2.1 Soil water dynamics and water balances

The model simulations were largely consistent with the observed data, thus indicating a reasonable model description of the overall soil water dynamics in the unsaturated zone (Figure 21). As in Kjær *et al.* (2011), 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 21B and 21C). The first drainage flow period of the past year was well captured by the model, whereas the magnitude of the second drainage flow period was not captured (Figure 21C). The last period can be characterised by frozen soil and precipitation in the form of snow – a situation, which MACRO has difficulties in describing. Additionally, drainage flow (q) is calculated by means of continuous measurements of the water height (h) at a V-notch in the drainage well and a q/h relationship. At events with extreme water flow it may happen that the discharge pipe has inadequate capacity to discharge the water, so that water will rise above the V-notch plate in the drainage well. This was the case during the snowmelt occurring on 11 December 2011, why adequate water sampling was not possible. At these events the q/h relationship is not valid, and the drainage flow is estimated at a water height (h) corresponding to the maximum height (h) of the V-notch plate, which could have resulted in an overestimation of the measured drainage flow. As in the previous monitoring periods, the overall trends in soil water content were described reasonably well (Figure 21D, 21E and 21F), although the model describe the topsoil as being more wet during the summer period than measured by the upper TDR probes (Figure 21D).

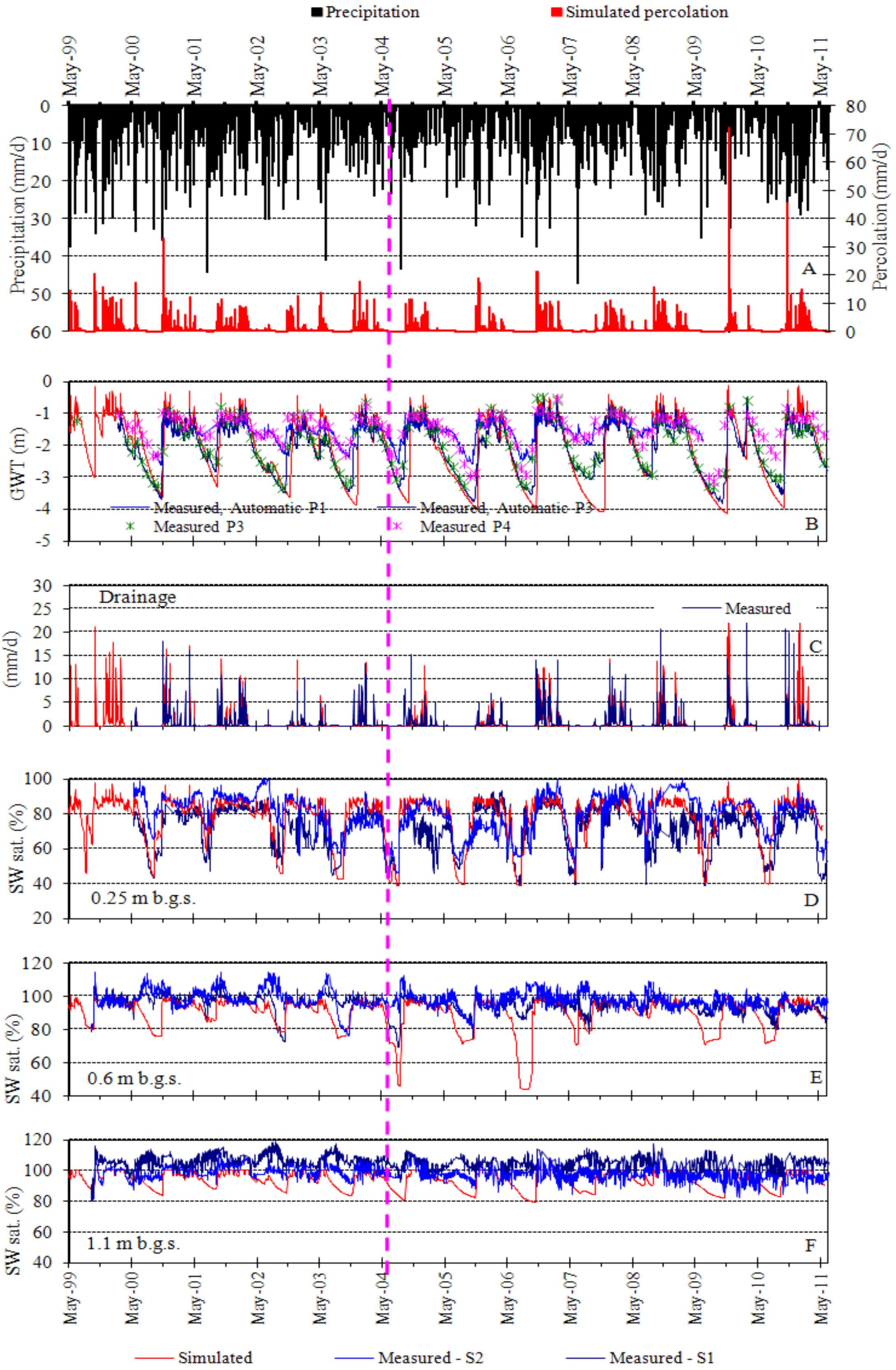


Figure 21. Soil water dynamics at **Silstrup**: Measured precipitation and simulated percolation 1 m b.g.s. (A), simulated and measured groundwater level GWT (B), simulated and measured drainage flow (C), and simulated and measured soil water saturation (SW sat.) at three different soil depths (D, E and F). The measured data in B derive from piezometers located in the buffer zone. The measured data in D, E and F derive from TDR probes installed at S1 and S2 (Figure 16). The broken vertical line indicates the beginning of the validation period (July 2004-June 2011)**.**

Table 6. 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
1.7.09–30.6.10	976	835	402	203	225	230
1.7.10–30.6.11	976	1063	399	172	569	492

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.

The resulting water balance for Silstrup for the entire monitoring period is shown in Table 6. Compared with the previous 12 years, the recent hydraulic year July 2010-June 2011 was characterised by having the third highest precipitation, the lowest simulated actual evapotranspiration, and the medium measured drainage. Precipitation of this year was characterised by the wettest January monitored at Silstrup in January with more than 150 mm, and April being very dry (Appendix 4). Due to this precipitation pattern, the simulated percolation pattern of the year July 2010-June 2011 continuous percolation was simulated from medio September until June (Figure 21A). The climatic setting of this year gave rise to two long periods with the groundwater table just fluctuating at the drainage level, however, only causing medium measured drainage compared to the other hydrological years included in PLAP (Figure 21B and 21C).

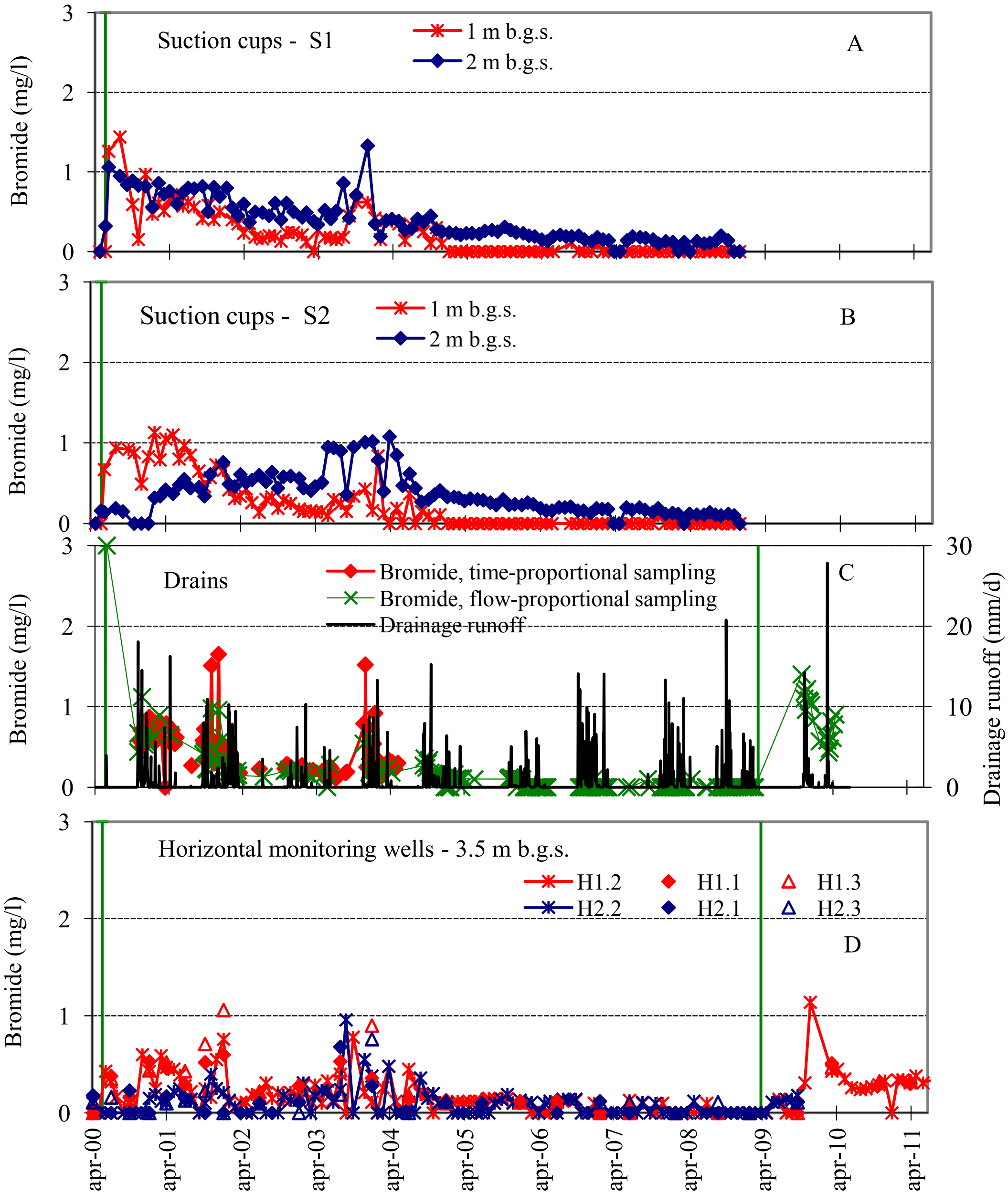


Figure 22. Bromide concentration at **Silstrup**. A and B refer to suction cups located at S1 and S2 (see Figure 16). The bromide concentration is also shown for drainage runoff (C) and the horizontal monitoring wells H1 and H2 (D). In March 2009, bromide measurements in the suction cups were suspended (Appendix 2). The green vertical lines indicate the dates of bromide applications.

4.2.2 Bromide leaching

The bromide concentrations shown in Figure 22 and Figure 23 relate to the bromide applied in May 2000, as described in previous reports (Kjær *et al.* 2003 and Kjær *et al.* 2004) and further evaluated in Barlebo *et al.* (2007). In Marts 2009, bromide measurements in the suction cups and monitoring wells M6 and M11 were suspended. In April 2009, 31.5 kg/ha potassium bromide was applied for the second time.

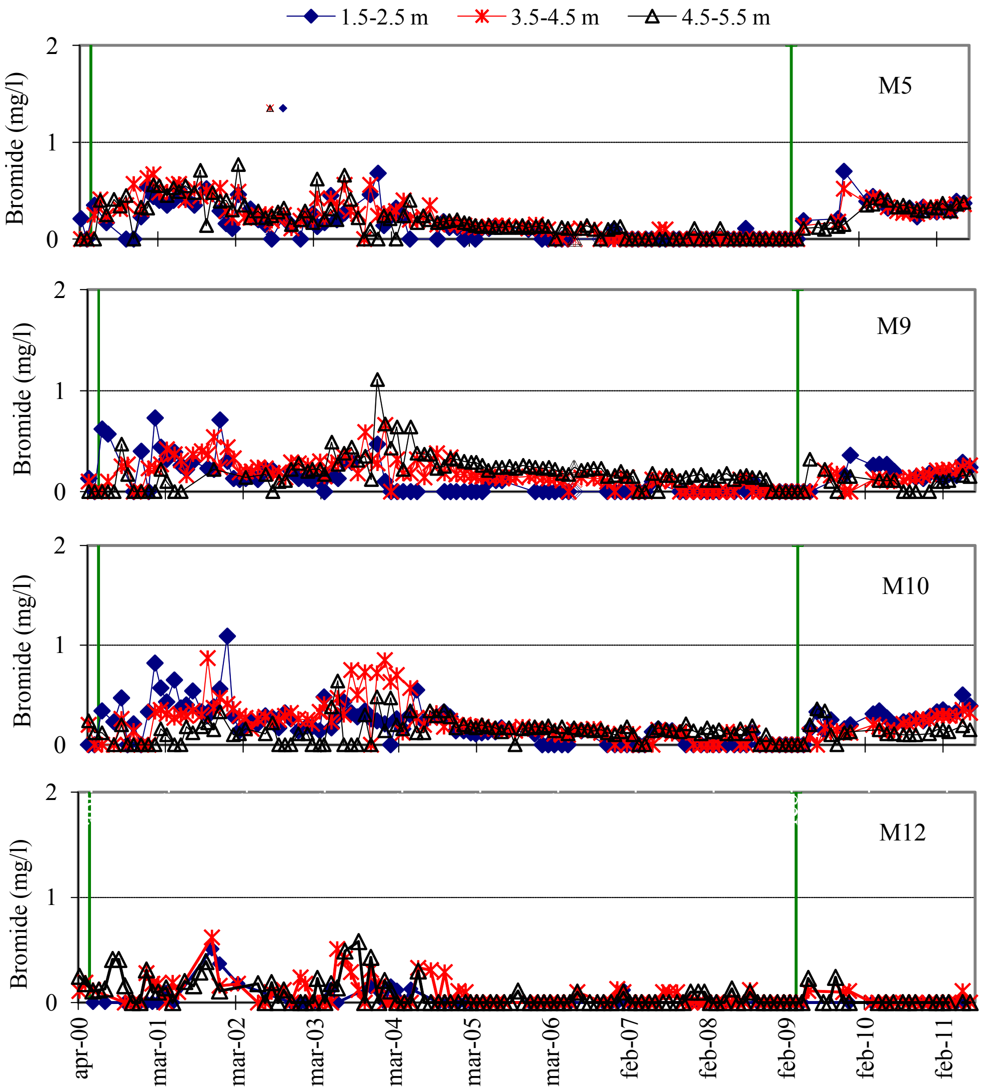


Figure 23. Bromide concentration at **Silstrup**. The data derive from the vertical monitoring wells (M5–M12). In September 2008, monitoring wells M6 and M11 were suspended (Appendix 2). Screen depth is indicated in m b.g.s. The green vertical lines indicate the date of bromide applications.

4.2.3 Pesticide leaching

Monitoring at Silstrup began in May 2000 and presently encompasses several pesticides and their degradation products, Appendix 8. Pesticide application during the most recent growing seasons, 2009/2010 and 2010/2011, is listed in Table 7 and shown together with precipitation and simulated percolation in Figure 24. It should be noted that precipitation in Table 7 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 2011 are not evaluated in this report and hence not included in Table 7.

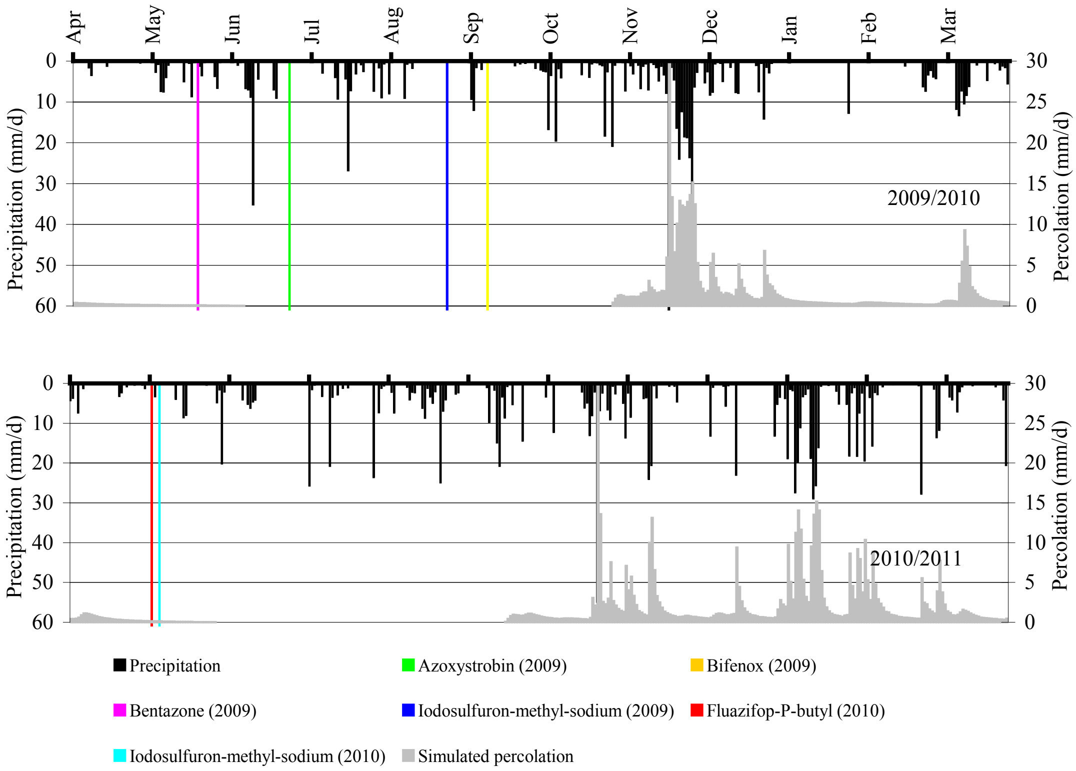


Figure 24. Application of pesticides included in the monitoring programme, precipitation and irrigation (primary axis) and simulated percolation 1 m b.g.s. (secondary axis) at **Silstrup** in 2009/2010 (upper) and 2010/2011 (lower).

It should also be noted that as fluazifop-P-butyl (Fusilade Max) degrade rapidly, the leaching risk is associated with their respective degradation products 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).

The current report focuses on the pesticides applied from 2009 and onwards, while the leaching risk of pesticides applied in 2008 and before has been evaluated in previous monitoring reports (see http://pesticidvarsling.dk/publ_result/index.html).

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 25B) nor groundwater (Figure 25D). When applying fluazifop-P-butyl in July 2008 and including its degradation product TFMP in the monitoring programme, a different picture emerged (Figure 25C and Figure 25D). At the onset of the drainage flow on 11 September 2008, a concentration of 0.52 µg/l TFMP was found. Concentrations remained above 0.1 µg/l throughout the period of drainage runoff. Further, TFMP was found in the screens of the vertical monitoring wells M5.1 (1.5 to 2.5 m b.g.s) and M5.2 (2.5 to 3.5 m b.g.s.) more than one month prior to the detection in the drainage water, in concentrations of 0.11 and 0.064 µg/l, respectively (Figure 25C).

Table 7. Pesticides analysed at Silstrup. Precipitation (precip.) and percolation (percol.) are accumulated within the first year (Precip 1st year, Percol 1st year) and first month (Precip 1st month, Percol 1st year) after the first application. C_{mean} refers to average leachate concentration at 1 m b.g.s. the first year after application. See Appendix 2 for calculation method and Appendix 8, Table A8.3 for previous applications of pesticides.

Crop	Applied product	Analysed pesticide	Application date	End of monit.	Y 1st precip.	Y 1st percol.	M 1st precip.	M 1st percol.	C_{mean}
Winter Wheat 2007	Cycocel 750	Chlormequat(P)	Apr 07	Jun 08	966	382	30	3	<0.01
	Hussar OD	Iodosulfuron-methyl(P)	Apr 07	Oct 10	966	382	30	3	<0.01
		Metsulfuron-methyl(P)	Apr 07	Oct 10	966	382	30	3	<0.01
	Opus	Epoxiconazole(P)	Jun 07	Apr 09	947	407	173	0	<0.01
	Stomp Pentagon	Pendimethalin(P)	Sep 06	Apr 08	1166	508	111	0	0,04
Fodder Beet 2008	Fusilade Max	Fluazifop-P(M)	Jul 08	Jun 11*	985	494	105	21	<0.01
		TFMP(M)	Jul 08	Jun 11*	985	494	105	21	0,24
	Goliath	Metamitron(P)	May 08	Jun 11*	969	498	43	4	0,01
		Desamino-metamitron(M)	May 08	Jun 11*	969	498	43	4	0,02
	Safari	Triflusulfuron-methyl(P)	Maj 08	Jun 10	969	498	43	4	<0.01
		IN-D8526(M)	May 08	Jun 10	969	498	43	4	<0.01
		IN-E7710(M)	May 08	Jun 10	969	498	43	4	<0.01
		IN-M7222(M)	May 08	Jun 10	969	498	43	4	<0.02
	Tramat 500 SC	Ethofumesate(P)	May 08	Dec 10	979	497	68	3	<0.01
Spring Barley 2009	Amistar	Azoxystrobin(P)	Jun 09	Jun 11*	835	390	61	0	0,01
		CyPM(M)	Jun 09	Jun 11*	835	390	61	0	0,06
	Fighter 480	Bentazone(P)	May 09	Jun 11	876	391	85	1	0,03
Red Fescue 2010	Fox 480 SC	Bifenox(P)	Sep 09	Jun 11*	888	390	56	0	<0.02
		Bifenox acid(M)	Sep 09	Jun 11*	888	390	56	0	2,26
		Nitrofen(M)	Sep 09	Jun 11*	888	390	56	0	<0.01
	Fusilade Max	Fluazifop-P(M)	May 10	Jun 11*	1027	520	53	2	<0.01
		TFMP(M)	May 10	Jun 11*	1027	520	53	2	<0.02
	Hussar OD	Iodosulfuron-methyl(P)	Aug 09	Dec 10	898	390	27	0	<0.01
		Metsulfuron-methyl(M)	Aug 09	Dec 10	898	390	27	0	<0.01
		Triazinamin (M)	Aug 09	Dec 10	898	390	27	0	<0.01
	Hussar OD	Iodosulfuron-methyl(P)	May 10	Dec 10	1024	520	49	1	<0.01
		Metsulfuron-methyl(P)	May 10	Dec 10	1024	520	49	1	<0.01

Systematic chemical nomenclature for the analysed pesticides is given in Appendix 1.
**Monitoring continue the following year.*

With the groundwater table minimum 1.6 m b.g.s., the root zone being relatively dry, and with percolation 1 m b.g.s. in July-August 2008 (Figure 21 and Figure 25A), this indicates pronounced macro pore transport bypassing the tile drainage system.

During the summer of 2009 there was no drainage flow. However, at the onset of flow in the autumn of 2009, TFMP was still present (Figure 25C), the last detection being 0.023 µg/l on 2 December 2009. Since 18 March 2009 there has been no exceedance of the 0.1 µg/l in the drainage water, and since 1 April 2009 in the groundwater. The most recent detection of TFMP was 0.03 µg/l on 1 December 2009. The average leaching concentration in drainage water within the first year of application of fluazifop-p-butyl, amounted to 0.24 µg/l of TFMP (Table 7). Maximum concentration of TFMP in the groundwater at Silstrup was 0.29 µg/l (Table 18).

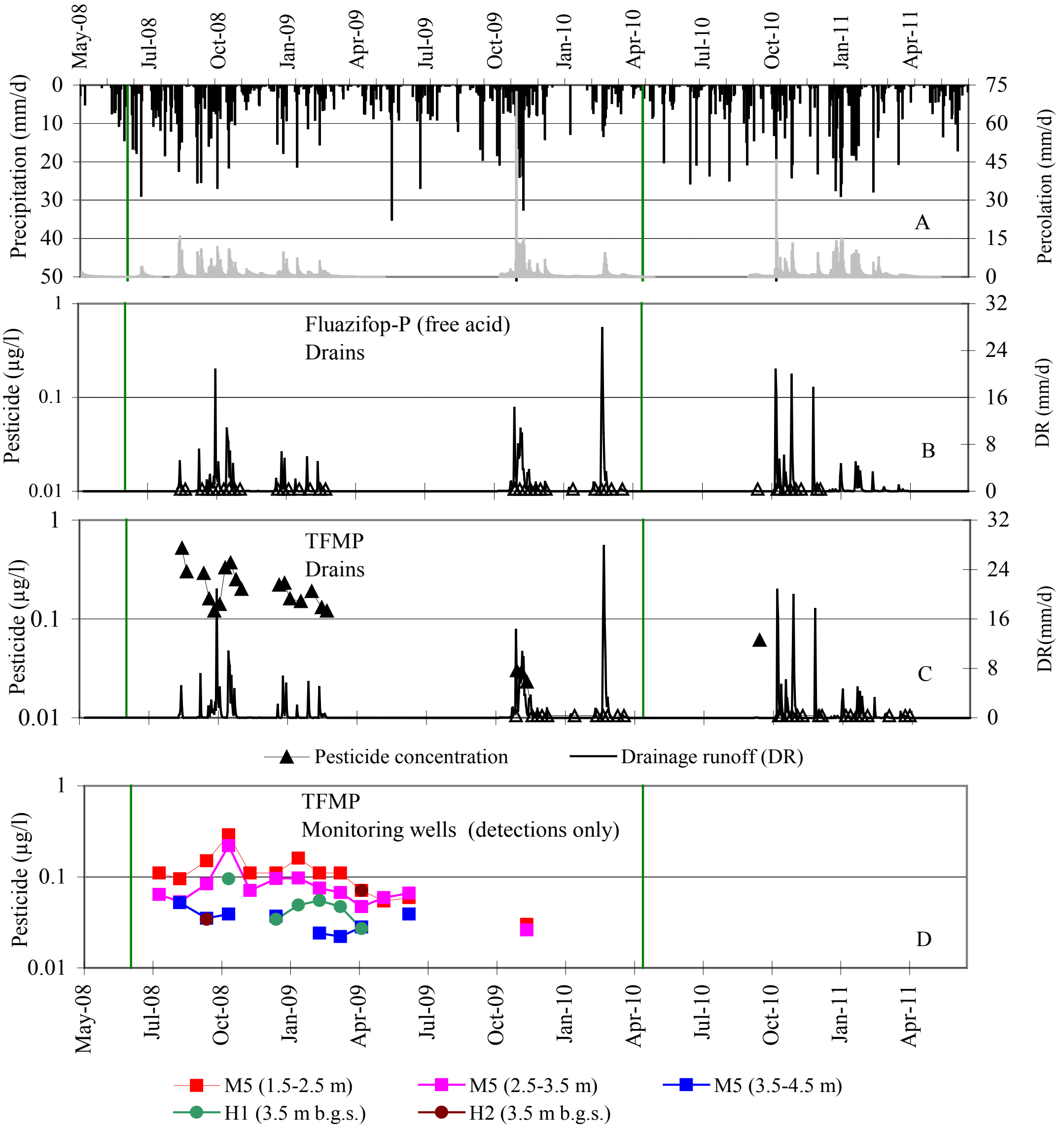


Figure 25. Precipitation and simulated percolation 1 m b.g.s. (A) together with the concentration of fluazifop-P (free acid) (B) and TFMP (C) in the drainage runoff, and the concentration of TFMP (D) in the groundwater monitoring screens at **Silstrup**. The green vertical lines indicate the dates of fluazifop-P-butyl applications. Values below the detection limit of 0.01 µg/l are shown as 0.01µg/l (all graphs) and further represented by open symbols in A, B and C.

An application of fluazifop-P-butyl on 2 May 2010 did not cause any detections of its metabolite fluazifop-P (free acid) in drainage water, in line with observations following the 2008 application (Figure 25B). Another metabolite, TFMP, was found just once 30 September, in a diminutive amount of drainage water (Figure 25C), concentration being 0.061µg/l. TFMP was this year not found at all in the groundwater (Figure 25D) thereby deviating from results following the application of fluazifop-P-butyl in 2008. An explanation may lye in the differences in applied dosage as well as the precipitation and percolation patterns before as well as after the two applications. Autumn 2008 the Danish EPA enforced considerable restriction on the application of fluazifop-P-buthyl by reducing maximum allowed dosage by 50%. Dosage used in 2010 was thus 50% lower than that in 2008, thereby minimising the risk of leaching.

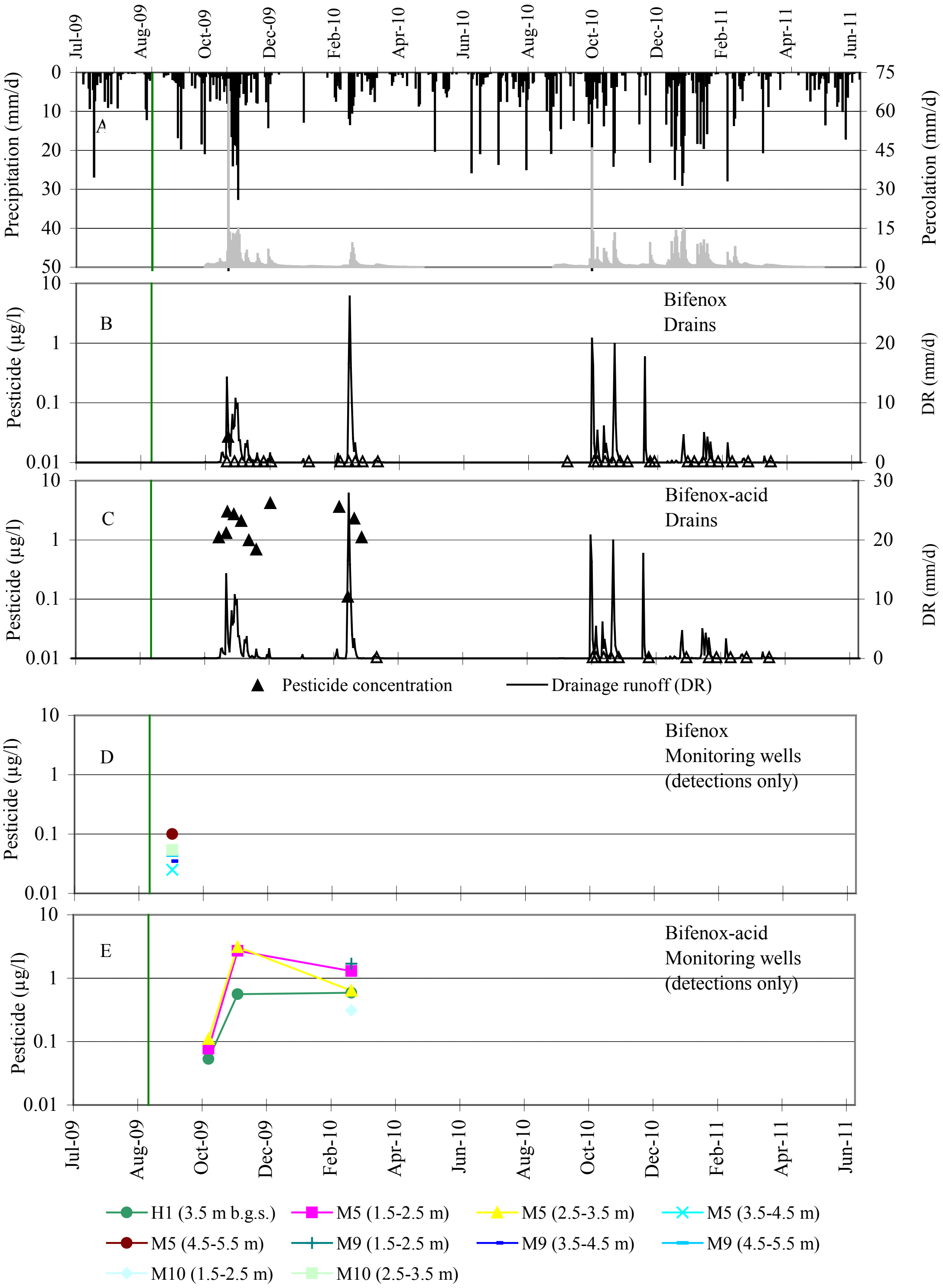


Figure 26. Precipitation and simulated percolation 1 m b.g.s. (A) together with the concentration of bifenox (B) and bifenox-acid (C) in the drainage runoff, and the concentration of bifenox (D) and bifenox-acid (E) in the groundwater monitoring screens at **Silstrup**. The green vertical line indicates the date of bifenox application. Values below the detection limit of 0.01 µg/l are shown as 0.01 µg/l (all graphs) and further represented as open symbols in B and C.

In 2008 preferential flow transferred the pesticide from the surface firstly to groundwater and secondly to the tile drains. Although both the accumulated amount of precipitation within the first month following the spraying was as well as the total precipitation was higher in 2010 than 2008 (Table 7), the amount of percolation in the first month following the 2008 spraying was double that of n 2010 spraying. As is seen from Figure 25A, there was virtually neither percolation nor drainage flow for a period of approximately 4.5 months following the 2010 spraying.

Since the application of the herbicide bifenox in the spring barley on 9 September 2009, there has been a single detection in drainage water sampled on 19 November 2009 (Figure 26B) and in samples from 5 groundwater screens in three different wells on 30 September (Figure 26D), whereof one reached 0.1 µg/l. The degradation product bifenox acid was found in groundwater in the screens of both horizontal and vertical wells (Figure 26E). Four of the five detections from the horizontal wells exceeded 0.1 µg/l, maximum, concentrations being 0.86 µg/l. Concentrations found in the vertical wells were even higher, amounting to 3.1 µg/l. The bifenox acid appeared in the groundwater before it was found in drainage water, in this case seven days earlier. Since the aforementioned detections neither bifenox nor bifenox acid has been found in any of the water samples.

Bentazone applied on 19 May 2009 had also been applied in May 2003. Although the amount of active ingredient was the same in both years, the 2003 application was followed by concentrations that were above 0.1 µg/l in both drainage and groundwater (Kjær et all, 2005), as opposed to the 2009 application where 0.1 µg/l was never exceeded (Figure 27B, 27E and Table 9). These results may reflect the importance of different climatic conditions following a spraying.

Azoxystrobin, applied on 24 June 2009, as well as it metabolite CyPM were found in drainage water (Figure 27C and 27D). The concentrations of the metabolite were generally higher than those of the parent compound. All concentrations but one of CyPM were below 0.1 µg/l. Average yearly concentrations in drainage water amounted to 0.01 and 0.06 for azoxystrobin and CyPM, respectively (Table 7), which is about the same as for the two previous applications in 2004 and 2005 (Table 7). Whereas there were no detections of azoxystrobin in the groundwater, CyPM could be found in both horizontal and vertical wells, concentrations ranging between 0.013 and 0.086 µg/l and 0.011 and 0.1 µg/l, respectively. Leaching pattern of Azoxystrobin and CYPM is given in Flindt Jørgensen et al 2011.

When evaluating the leaching occurring during the 2009/2010 drainage season (Figure 25–27) it should be noted that the large drainage event that took place during the snowmelt on 12 March 2010 (28 mm/d) could not be sampled due to technical problems caused by the extreme intensity of the drainage runoff. Likewise the drainage runoff could not be measured, and the estimated value for this day is likely to be overestimated (see section 4.2.1 for details).

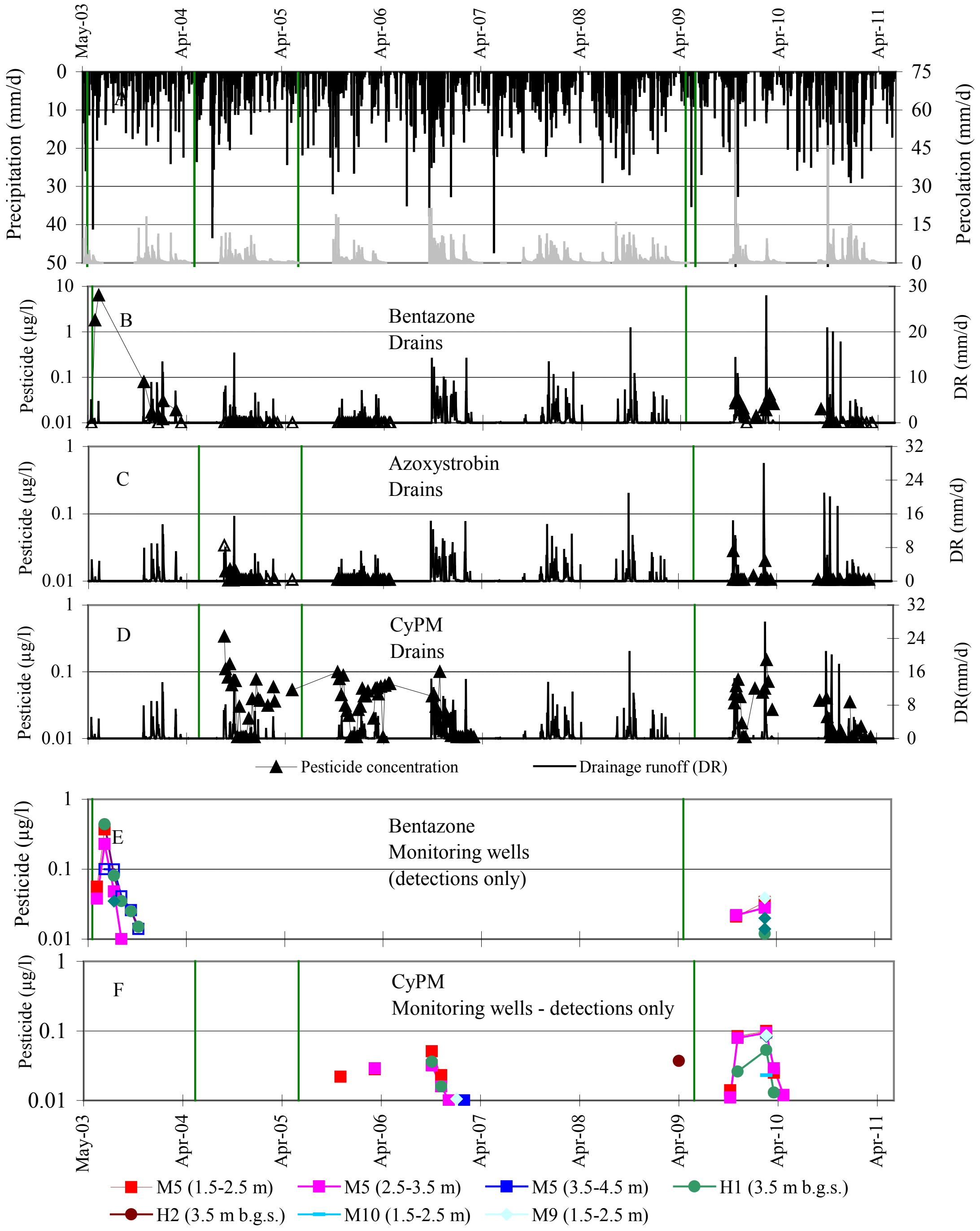


Figure 27. Precipitation and simulated percolation 1 m b.g.s. (A) together with the concentration of bentazone (B), azoxystrobin (C) and CyPM (D) in the drainage runoff, and the concentration of bentazone (E) and CyPM (F) in the groundwater monitoring screens at **Silstrup**. The green vertical lines indicate the dates of bentazone and azoxystrobin applications. Values below the detection limit of 0.01 µg/l are shown as 0.01µg/l (all graphs) and further represented as open symbols in B.

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 28). The site is highly heterogeneous with considerable variation in both topsoil and aquifer characteristics (Lindhardt *et al.*, 2001). Such heterogeneity is quite common for this geological formation, however. Based on three profiles excavated in the buffer zone bordering the field the soil was classified as Abrupt Argiudoll, Aqua Argiudoll and Fragiaquic Glossudalf (Soil Survey Staff, 1999). The topsoil is characterised as sandy loam with a clay content of 10–20%, and an organic carbon content of 1.7–7.3%. A C-horizon of low permeability also characterises the site. The saturated hydraulic conductivity in the C-horizon is 10^{-8} m/s, which is about two orders of magnitude lower than at the other loamy sites (Table 1). The geological structure is complex comprising a clay till core with deposits of different age and composition (Lindhardt *et al.*, 2001). A brief description of the sampling procedure is provided in Appendix 2. The monitoring design and test site are described in detail in Lindhardt *et al.* (2001) and the analysis methods in Kjær *et al.* (2002). Please note that the geological conditions only allowed one of the planned horizontal wells to be installed.

5.1.2 Agricultural management

Management practice during the 2010-11 growing seasons is briefly summarized below and detailed in Appendix 3 (Table A3.4). For information about management practice during the previous monitoring periods, see previous monitoring reports available on http://pesticidvarsling.dk/publ_result/index.html.

On the 24 August 2009 the field was ploughed and rotor-harrowed and sown with winter rape (cv. Cabernet). The following day the herbicide clomazone was applied but not included in the monitoring. The herbicide bifenox was used on 30 September when four leaves had unfolded. Pesticide treatment was applied on 9 October using cypermethrin, but the substance was not monitored. Due to poor overwintering of the winter rape, the field was partially resown on 20 April 2010 using the spring rape variety Pluto.

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

On the same day the seedbed was prepared and the field was sown with winter wheat (cv. Frument). On the 25 September the crop emerged, whereas on the 30 September, when first leaf was through the coleoptiles, the herbicide tribenuron-methyl was sprayed.

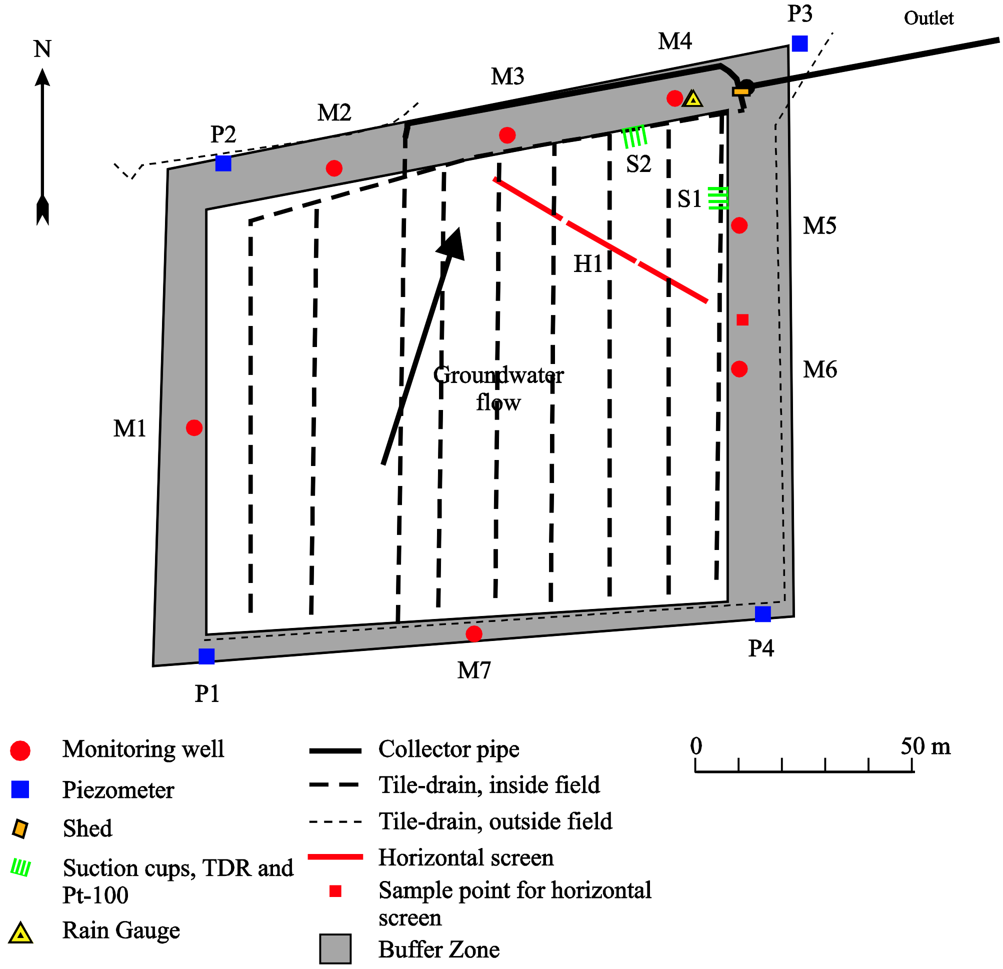


Figure 28. Overview of the **Estrup** site. The innermost white area indicates the cultivated land, while the grey area indicates the surrounding buffer zone. The positions of the various installations are indicated, as is the direction of groundwater flow (by an arrow). Pesticide monitoring is conducted weekly from the drainage system (during period of continuous drainage runoff) and monthly and half-yearly from selected groundwater monitoring wells as described in Table A2.1 in Appendix 2.

5.1.3 Model setup and calibration

The numerical model MACRO (version 5.1, Larsbo *et al.,* 2005) was applied to the Estrup site covering the soil profile to a depth of 5 m b.g.s., always including the groundwater table. The model is used to simulate the water flow in the unsaturated zone during the monitoring period from July 2000-June 2011 and to establish an annual water balance.

Compared to the setup in Kjær *et al.* (2011), a year of validation was added to the MACRO setup for the Estrup site. The setup was subsequently calibrated for the monitoring period May 1999-June 2004 and validated for the monitoring period July 2004-June 2011. 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 28). The TDR probes installed at the other depths yielded unreliable data with saturations far exceeding 100% and unreliable soil water dynamics with increasing soil water content during the drier summer periods (data not shown). No explanation can presently be given for the unreliable data, and they have been excluded from the analysis. The data from the soil profile S2 have also been excluded due to a problem with water ponding above the TDR probes installed at S2, as mentioned in Kjær *et al.* (2003). Finally, TDR-measurements at 25 cm b.g.s. in February 2010 were discarded given freezing soils (soil temperatures at or below zero degrees Celsius). The soil water content is measured with TDR based on Topp calibration (Topp *et al.*, 1980), which will underestimate the total soil water content at the soil water freezing point as the permittivity of frozen water is much less than that of liquid water (Flerchinger *et al.*, 2006).

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

5.2 Results and discussion

5.2.1 Soil water dynamics and water balances

The model simulations were generally consistent with the observed data (which were limited compared to other PLAP sites, as noted above), indicating a good model description of the overall soil water dynamics in the unsaturated zone (Figure 29). 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 29B). Also here the simulated groundwater table did not seem as sensitive to these short periods of low precipitation and tended not to drop as much as the measured values. Since the subsoil TDR data are limited, a more detailed study of soil water dynamics in these layers is difficult. However, the overall soil water saturation at 25 and 40 cm b.g.s. was captured (Figure 29D and 29E), except for the drop in water saturation at 25 cm b.g.s. in April-June 2011. Nothing special is noted for the groundwater table in the latest monitoring period (July 2010-June 2011). As in previous years (Kjær *et al.*, 2011), the simulated groundwater table often fluctuates slightly above the drain depth during periods of drainage flow.

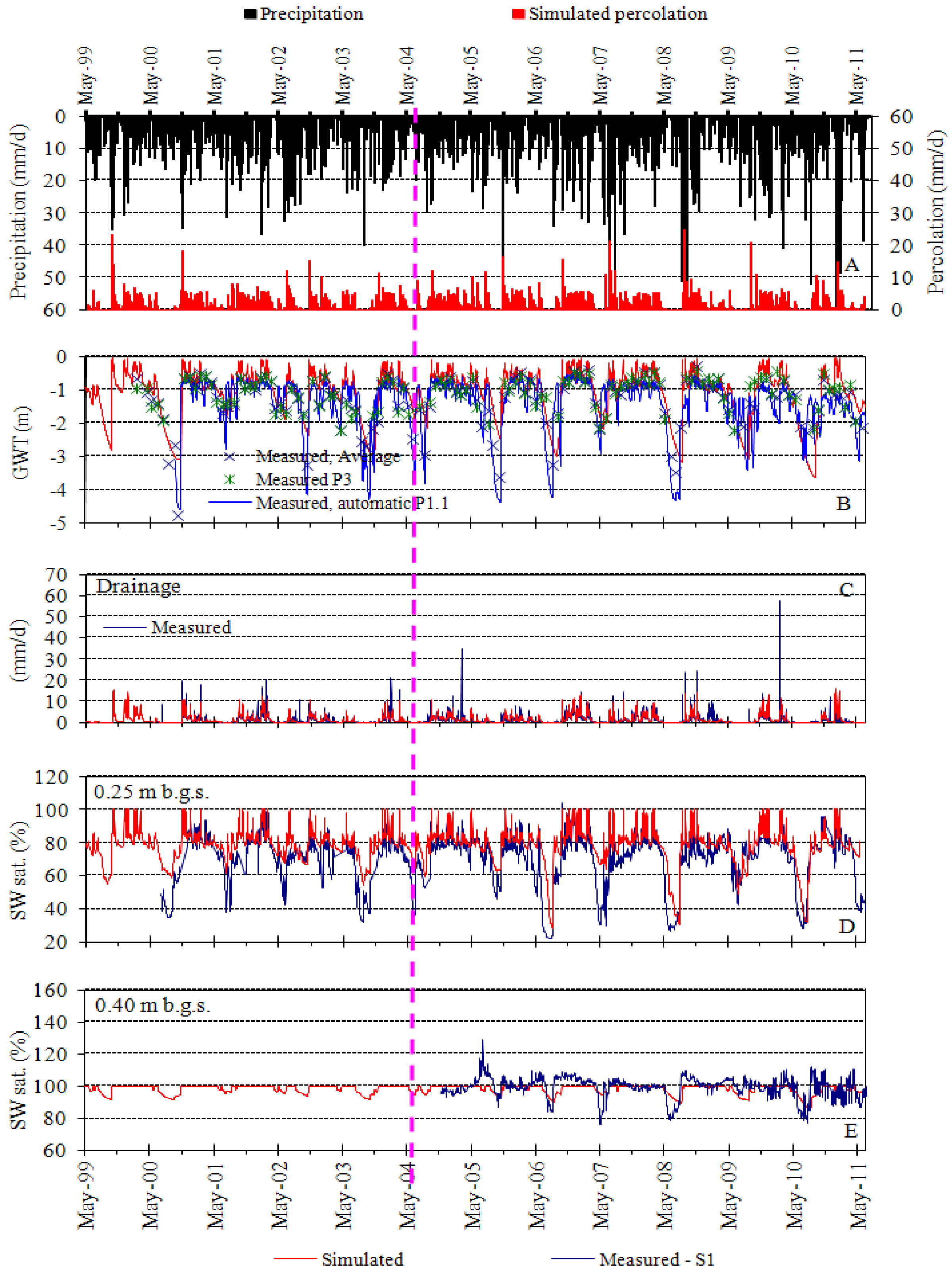


Figure 29. Soil water dynamics at **Estrup**: Measured precipitation and simulated percolation 0.6 m b.g.s. (A), simulated and measured groundwater level (B), simulated and measured drainage flow (C), and simulated and measured soil saturation (SW sat.) at two different soil depths (D and E). The measured 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 2011).

Table 8. 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
1.7.09–30.6.10	968	1190	533	499	523	158
1.7.10–30.6.11	968	1158	486	210	341	462

[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 29C) matched the measured drainage flow quite well during fall 2010. Drainage flow measured in connection with snowmelt was either not captured by MACRO as on the 11 December 2010 or overestimated in magnitude during spring 2011. In the latter case the initiation of fluctuations in the drainage flow was captured. The periods preceding these drainage periods can be characterised by frozen soil and precipitation in the form of snow – a situation which MACRO has difficulties in describing. Drainage runoff over the whole monitoring period was high compared to that of the other two till sites investigated in the PLAP. This was due to a significantly lower permeability of the C-horizon than of the overlying A and B horizons (see Kjær *et al.* (2005c) for details).

The resulting water balance for Estrup for the entire monitoring period is shown in Table 10. Compared with the previous eleven years, the latest hydraulic year July 2010-June 2011 was characterised by having the fourth-highest precipitation, the medium simulated actual evapotranspiration and lowest measured drainage. With MACRO not being able to capture drainage flow in connection with snowmelt resulted that the simulated drainage flow was largely overestimated. Precipitation in this year was characterised by January-February being very wet and Marts-April being very dry (Appendix 4). Due to this precipitation pattern, the simulated percolation pattern of the year July 2010-June 2011 resulted in continuously percolation from the end of August 2010 until the end of June 2011 (Figure 29A).

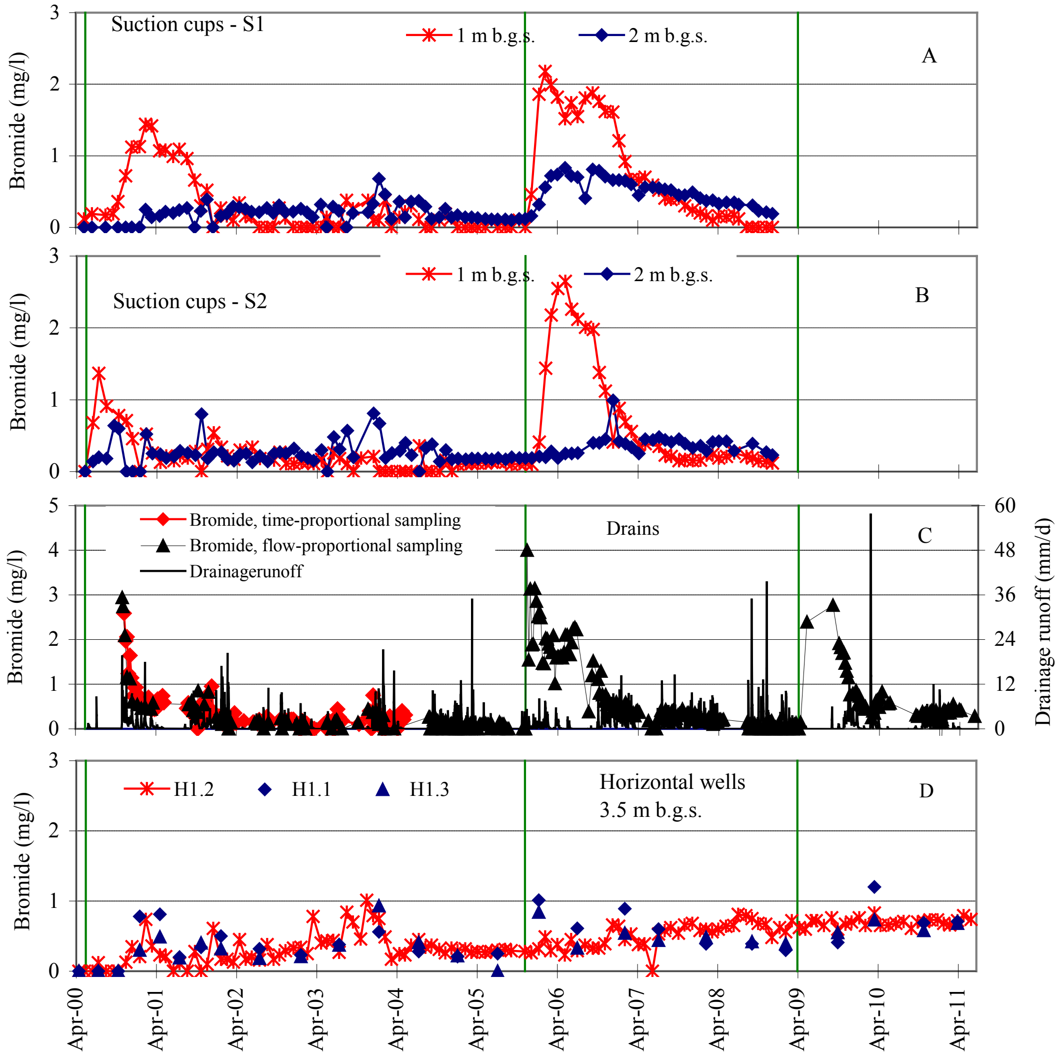


Figure 30. Bromide concentration at **Estrup**. A and B refer to suction cups located at S1 and S2, respectively. The bromide concentration is also shown for drainage runoff (C) and the horizontal monitoring well H1 (D). In September 2008, bromide measurements in the suction cups were suspended (Appendix 2). The green vertical lines indicate the dates of bromide applications.

5.2.2 Bromide leaching

Bromide has now been applied three times at Estrup. The bromide concentrations measured up to October 2005 (Figure 30 and Figure 31) relate to the bromide applied in spring 2000, as described further in Kjær *et al.* (2003) and Barlebo *et al.* (2007). In March 2009, bromide measurements in the suction cups and monitoring wells M3 and M7 were suspended.

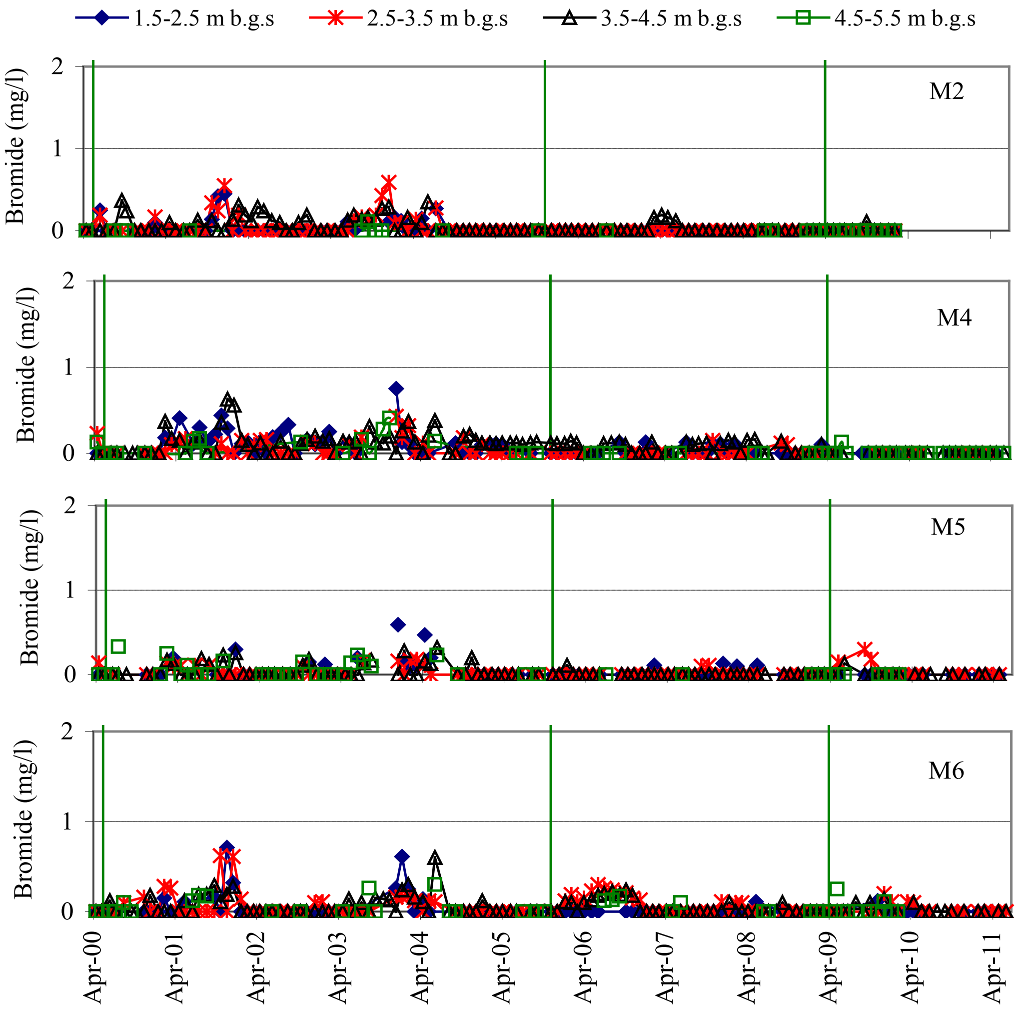


Figure 31. Bromide concentration at **Estrup**. The data derive from the vertical monitoring wells (M2–M6). Screen depth is indicated in m b.g.s. In September 2008, monitoring wells M3 and M7 were suspended (Appendix 2). The green vertical lines indicate the dates of bromide applications.

5.2.3 Pesticide leaching

Monitoring at Estrup began in May 2000. Pesticides and degradation products monitored so far can be seen from Table 9 (2007-2011) and Appendix 8, Table A8.4 (2000-2007). Pesticide application during the most recent growing seasons (2007/2010 and 2010/2011) is shown together with precipitation and simulated precipitation in Figure 32. 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 2011 are not evaluated in this report and hence not included in Table 9.

Table 9. Pesticides analysed at Estrup. Precipitation (precip.) and percolation (percol.) are accumulated within the first year (Precip 1st year, Percol 1st year) and first mount (Precip 1st month, Percol 1st year) after the first application C_{mean} refers to average leachate concentration at 1 m b.g.s. the first year after application. See Appendix 2 for calculation method and Appendix 8, (Table A8.4) for previous applications of pesticides.

Crop	Applied product	Analysed pesticide	Application date	End of monit.	Y 1st precip	Y 1st percol	M 1st precip	M 1st percol	C_{mean}
Winter Wheat 2007	Atlantis WG	Mesosulfuron-methyl(P)	Oct 06	Jul 08	1420	305	90	29	0.01
		Mesosulfuron(M)	Oct 06		1420	305	90	29	<0.02
	Cycocel 750	Chlormequat(P)	Apr 07	Jul 08	1261	287	31	0	<0.01
	Opus	Epoxiconazole(P)	May 07	Jul 08	1154	299	154	29	0.02
Winter Wheat 2008	Amistar	Azoxystrobin(P)	Jun 08	Jun 11*	1093	232	88	0	0.06
		CyPM(M)	Jun 08	Jun 11*	1093	232	88	0	0.48
	Folicur EC 250	Tebuconazole(P)	Nov 07	Mar 10	1325	275	103	31	0.44
	Pico 750 WG	Picolinafen(P)	Oct 07	Mar 10	1253	267	76	24	0.03
		CL153815(M)	Oct 07	Mar 10	1253	267	76	24	0.24
	Roundup Max	Glyphosate(P)	Sep 07	Jun 11*	1200	261	113	29	0.19
		AMPA(M)	Sep 07	Jun 11*	1200	261	113	29	0.13
Spring Barley 2009	Amistar	Azoxystrobin(P)	Jun 09	Jun 11*	1215	235	60	0	0.04
		CyPM(M)	Jun 09	Jun 11*	1215	235	60	0	0.41
	Basagran M75	Bentazone(P)	May 09	Jun 11	1222	238	83	4	0.05
	Fox 480 SC	Bifenox(P)	May 09	Jun 11*	1243	246	87	16	<0.02
		Bifenox acid(M)	May 09	Jun 11*	1243	246	87	16	0.16
		Nitrofen(M)	May 09	Jun 11*	1243	246	87	16	<0.01
Winter Rape 2010	Biscaya OD 240	Thiacloprid(P)	May 10	Jun 11*	1083	196	43	0	<0.01
		M34(M)	May 10	Jun 11*	1083	196	43	0	<0.02
		Thiacloprid sulfonic acid(M)	May 10	Jun 11*	1083	196	43	0	<0.1
		Thiacloprid-amide(M)	May 10	Jun 11*	1083	196	43	0	<0.01
Winter Wheat 2011	Express ST	Triazinamin-methyl(M)1)	Sep 10	Jun 11*	823	176	97	31	0.01

Systematic chemical nomenclature for the analysed pesticides is given in Appendix 1.
1)Degradation product of tribenuron-methyl. The parent degradte to rapidly to be detected by monitoring.
**Monitoring continue the following year.*

The current report focuses on pesticides applied from 2009 and onwards, while leaching risk of pesticides applied in 2008 and before has been evaluated in previous monitoring reports (see http://pesticidvarsling.dk/publ_result/index.html).

Azoxystrobin has now been applied four times at Estrup: 22 June 2004, 29 June 2006, 13 June 2008 and 4 June 2009 (Figure 33). The last application before then was in June 1998 (Lindhardt *et al.*, 2001). Following all four applications azoxystrobin and the metabolite CyPM leached to the depth of the drainage system at the onset of drainage due to infiltration of excess rain. Concentrations in drainage water of both parent and metabolite are shown in Figure 33. 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.

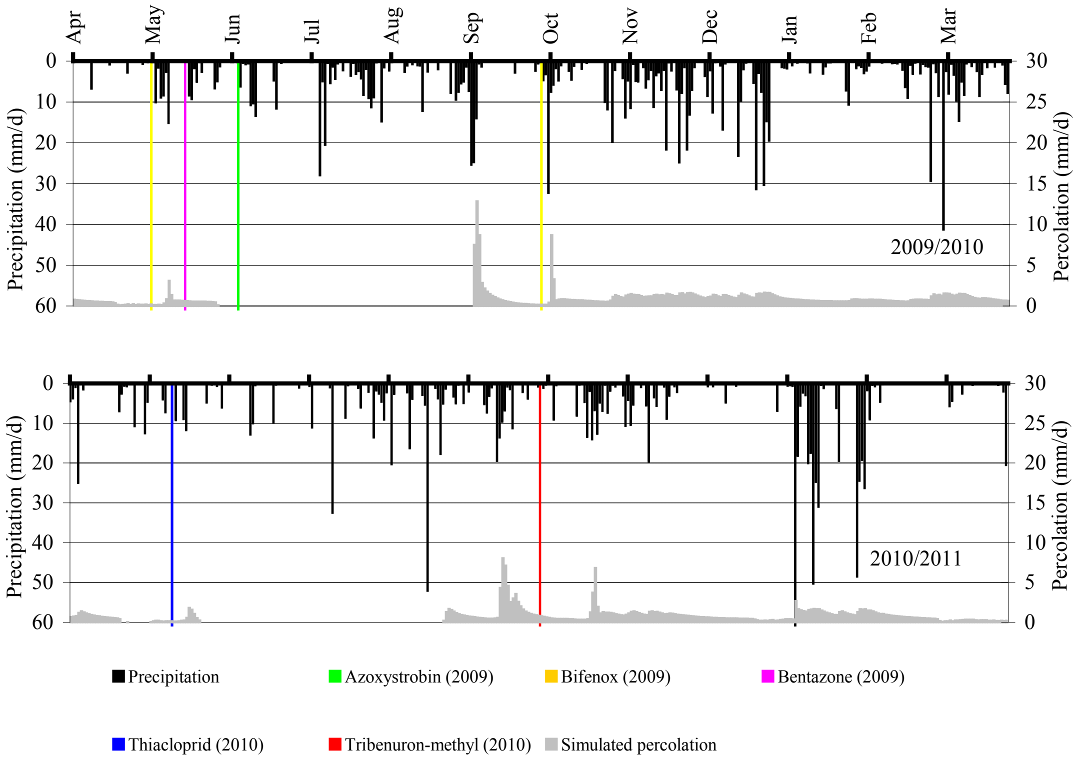


Figure 32. Application of pesticides included in the monitoring programme and precipitation (primary axis) together with simulated percolation 0.6 m b.g.s. (secondary axis) at **Estrup** in 2009/2010 (upper) and 2010/2011 (lower).

Within the year of application as well as the following year, the average concentrations of CyPM in drainage water were higher than of azoxystrobin (Figure 33B and 33C), indicating its higher persistence. Differences in persistence for the two substances is further underlined by the fact that only one of 467 groundwater samples contained azoxystrobin (0.011 µg/l–data not shown) whereas 11 contained CyPM, maximum concentration being 0.09 µg/l, Figure 33D and Table A5.4. The leaching pattern of Azoxystrobin and CyPm is further described in Jørgensen et al 2012.

The herbicide bifenox was used on 1 May and on 30 September 2009. Less than two weeks later 0.15 µg/l of bifenox was detected in the drainage water (Figure 34B). Following the second application, bifenox was found twice, this time in concentrations less than 0.1 µg/l. The metabolite bifenox acid was found in connection with a small drain flow event on 9 September 2009 at a concentration of 1.9 µg/l (Figure 34C), whereas bifenox was below the detection limit of 0.01 µg/l. Following the application in September there were only two detections of bifenox, both less than 0.1 µg/l (Figure 34B), whereas eight out of ten bifenox acid detections were above 0.1 µg/l (Figure 34C). Bifenox acid leached from the root zone to the drainage system in an average concentration of 0.16 µg/l in the drainage water, whereas the figure for bifenox was <0.02 µg/l (Table 9). Neither bifenox nor bifenox acid was found in the groundwater monitoring screens.

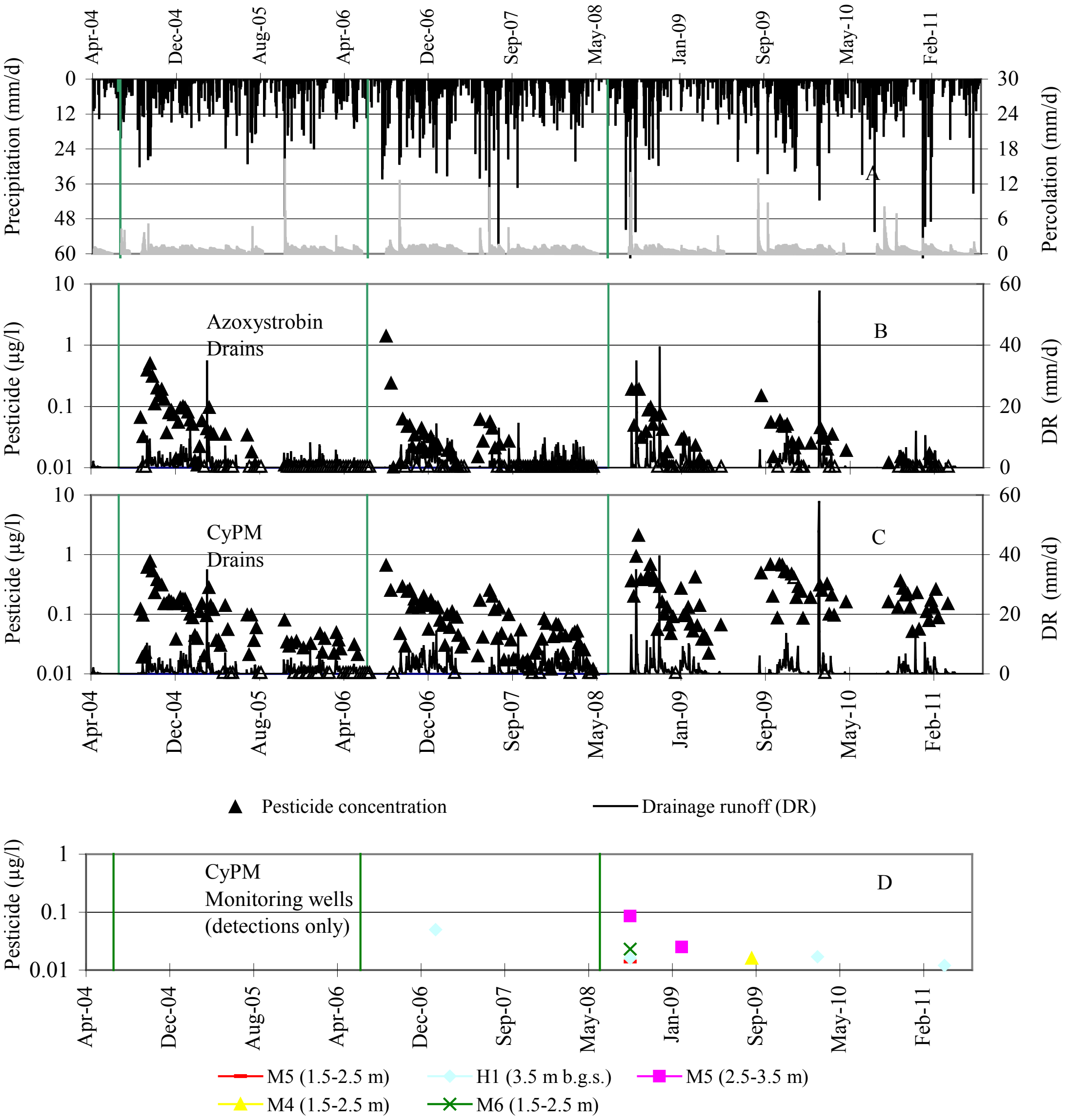


Figure 33. Precipitation and simulated percolation 0.6 m b.g.s. (A) together with concentration of azoxystrobin (B) and CyPM (C) in the drainage runoff (DR on the secondary axis) at **Estrup**. Detections of CyPM in groundwater monitoring screen are indicated in D. Azoxystrobin was only detected once in groundwater monitoring screens (see text). The green vertical lines indicate the dates of applications. Open symbols in B and C indicate values below the detection limit of 0.01 µg/l.

The highest concentration in drainage water of bentazone following the 14 May 2009 application was 0.16 µg/l in connection with a small drain flow event in September 2009 (Figure 34D). None of the subsequent concentrations were above 0.1 µg/l and the average yearly concentrations amounted to 0.05 µg/l (Table 9). The second year following the application bentazone was still leaching to the drainage water (Figure 34), 11 of 17 samples containing bentazone in the range 0.011 to 0.025 µg/l. t Within the first year after application bentazone was found four times in groundwater monitoring screens; concentrations did, however, not exceed 0.1 µg/l (Table A5.4, Appendix 5).

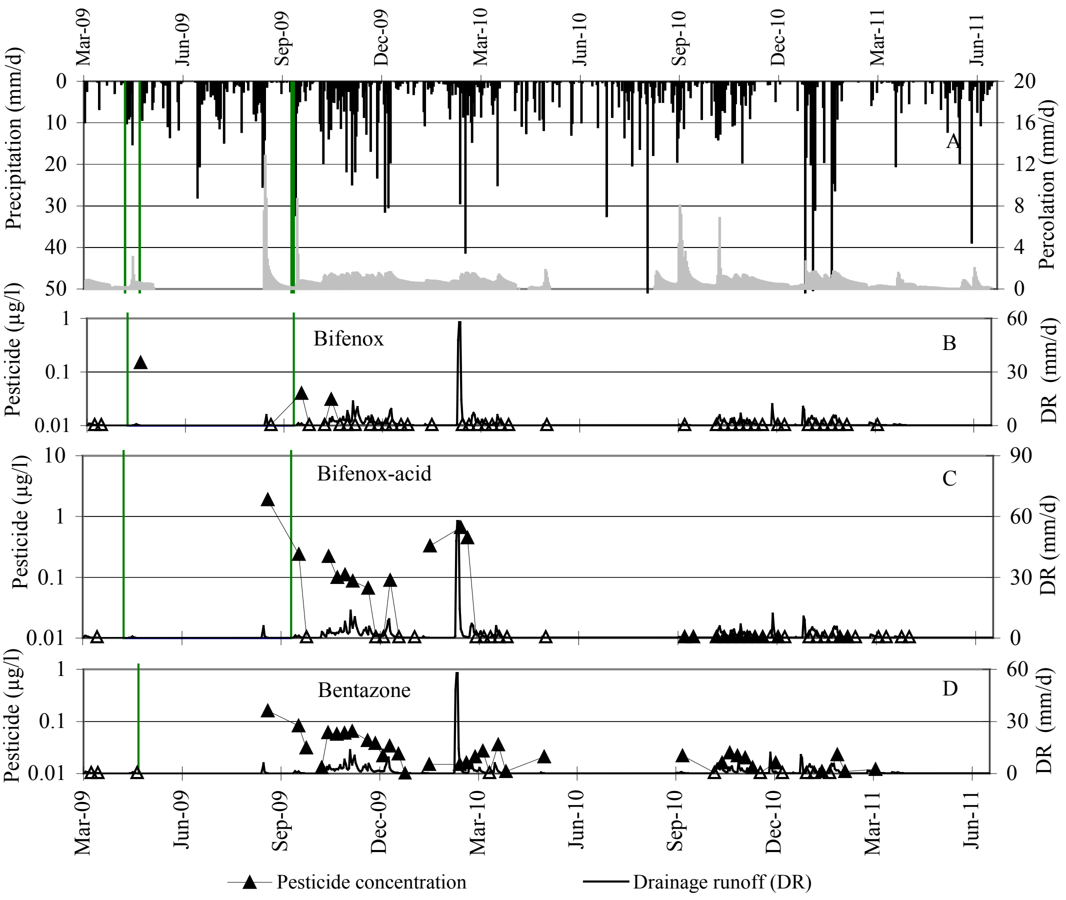


Figure 34. Precipitation and simulated percolation (A) together with concentration of bifenox (B), bifenox-acid (C) and bentazone (E) in the drainage runoff (DR on the secondary axis) at **Estrup** in 2004/2010. The green vertical lines indicates the dates of applications. Open symbols indicate values below the detection limit of 0.01 µg/l. While bifenox and bifenox-acid were not detected in any samples from groundwater monitoring, bentazone was detected in four samples (see text).

The herbicide glyphosate has now been applied at Estrup in 2000, 2002, 2005 and 2007 (Figure 35). Following all applications, both glyphosate and AMPA could be found in the drainage water. Out of 418 drainage water samples analysed for glyphosate and AMPA in the period 31 October 2000-7 February 2011, the concentrations of glyphosate and AMPA exceeded 0.1 µg/l in 89 and 98 samples, respectively (Figure 35B and 35C). During that period AMPA never exceeded 0.1 µg/l (Figure 35E and Table A5.4 in Appendix 5), whereas glyphosate did so in three samples, of which two were taken on 7 July 2005 from two different wells, concentrations being 0.67 and 0.59 µg/l, and one on 13 January 2010 from a third well with a concentration of 0.17 µg/l (Figure 35D and Table A5.4 in Appendix 5). In relation to the data shown in Figure 35 it should be noted that the quality program of the program has indicated possible analytical problems with the quantification of glyphosate in a number of ground water samples. The results from the external quality assurance reveal that in the period June 2007 to July 2010 the concentration of glyphosate may have been underestimated by a factor of up to ~2 as compared to previous periods A modification of the analytical procedure has been implemented in the analysis to address this problem (for further details see section 7.2.2.).

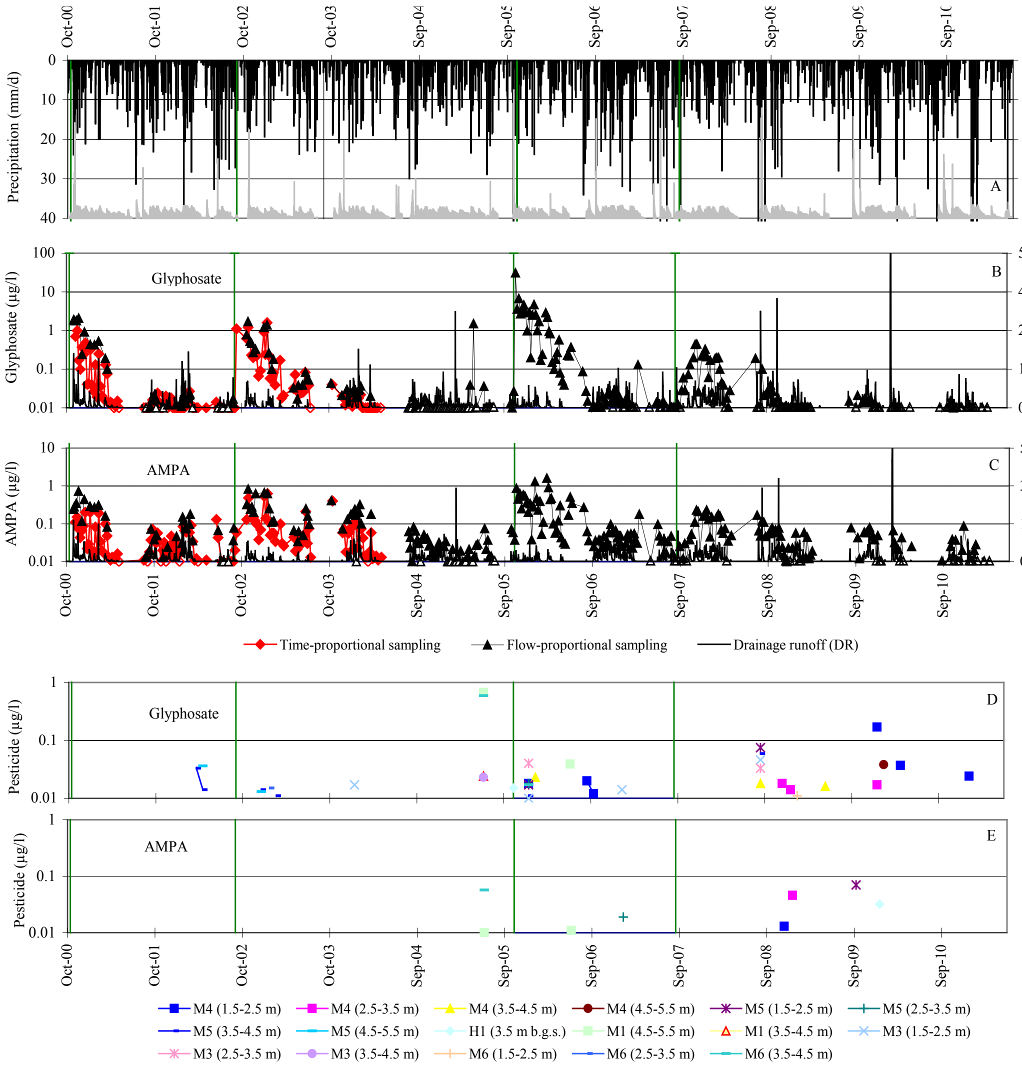


Figure 35. Precipitation and simulated percolation 0.6 m b.g.s. (A) together with the concentration of glyphosate (B) and AMPA (C) in the drainage runoff (DR on the secondary axis) at **Estrup**. Data represent a nine-year period including four applications of glyphosate as indicated by the green vertical lines. Open symbols indicate values below the detection limit of 0.01 µg/l. Detection of glyphosate and AMPA in groundwater monitoring wells is shown in D and E. In the period June 2007 until July 2010, marked with the red outlined box, analytical problems caused the concentration of glyphosate to be underestimated (see text for details).

When comparing the three-year periods following the application of glyphosate in September 2002 and the four year period following the September 2007 application, a pattern of longevity/persistence seems to emerge, in particular regarding AMPA (Figure 35B and Figure 35C). This long-term leaching of AMPA may indicate that AMPA is retained within the soil and gradually released over a very long time, as described in Kjær *et al.* (2005a), or that glyphosate is retained within the soil and then gradually degraded into AMPA. With an increased detection of glyphosate in the groundwater samples at Estrup following high precipitation events in September 2005 (nearly three years after latest application), September 2008 and January 2010 (one and two and a half years after the latest application, respectively), evidence of the latter pattern seems also to be recognizable.

It is remarkable that detections of particularly glyphosate in groundwater monitoring wells seem to increase over the years (Figure 35D). Within the first four years, detections of glyphosate were scarce, and AMPA is not found at all (Figure 35E). Following these four years there is an increase in the first 3 years, particularly in detections and concentrations of glyphosate. A similar tendency was observed for AMPA, although detections are less frequent and the concentrations comparatively lower. In this respect it should be noted that there had been no application of glyphosate for at least seven years prior to the 2000 application (Lindhardt *et al.*, 2001). A single detection in the most recent year, where there had not been sprayed, was of glyphosate, Figure 35E.

Thiacloprid, a pesticide, was applied on 10 May 2010. Neither samples of drainage nor groundwater have contained the substance or any of its three metabolites thiacloprid-amide (M2), thiacloprid sulfonic acid (M30) or thiacloprid sulfonic acidamide (M34).

Instead of the herbicide tribenuron-methyl, applied 30 September 2010 which degrades rapidly its metabolite, triazinamin-methyl (INL5296) has been analyzed for. The metabolite was not found in any of the 46 groundwater samples taken. However, it was detected in 2 out of 19 drainage water samples, concentrations being 0.042 µg/l on 28 October 2010 and 0.025 µg/l on 4 November 2010 (data not shown).

Pesticide leaching at Estrup is mostly confined to the depth of the drainage system. Apart from AMPA, CyPM, bentazone, desethyl-terbuthylazine, deisopropylatrazine, and glyphosate having been detected in 8, 11, 16, 7, 27 and 42 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 macro pores (see Kjær *et al.*, 2005c, for details). An indication thereof are the long periods with groundwater table beyond drainage depth in which an increasing lateral transport to the drainage system and decreased leaching to the deeper groundwater will occur.

6 Pesticide leaching at Faardrup

6.1 Materials and methods

6.1.1 Site description and monitoring design

Faardrup is located in southern Zealand (Figure 36). 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 37). Based on three profiles in the buffer zone bordering the field, the soil was classified as Haplic Vermudoll, Oxyaquic Hapludoll and Oxyaquic Argiudoll (Soil Survey Staff, 1999). The topsoil is characterised as sandy loam with 14–15% clay and 1.4% organic carbon. Within the upper 1.5 m numerous desiccation cracks coated with clay are present. The test field contains glacial deposits dominated by sandy till to a depth of about 1.5 m overlying a clayey till. The geological description shows that small channels or basins filled with melt water 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 36). 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 37 and Figure 40), 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).

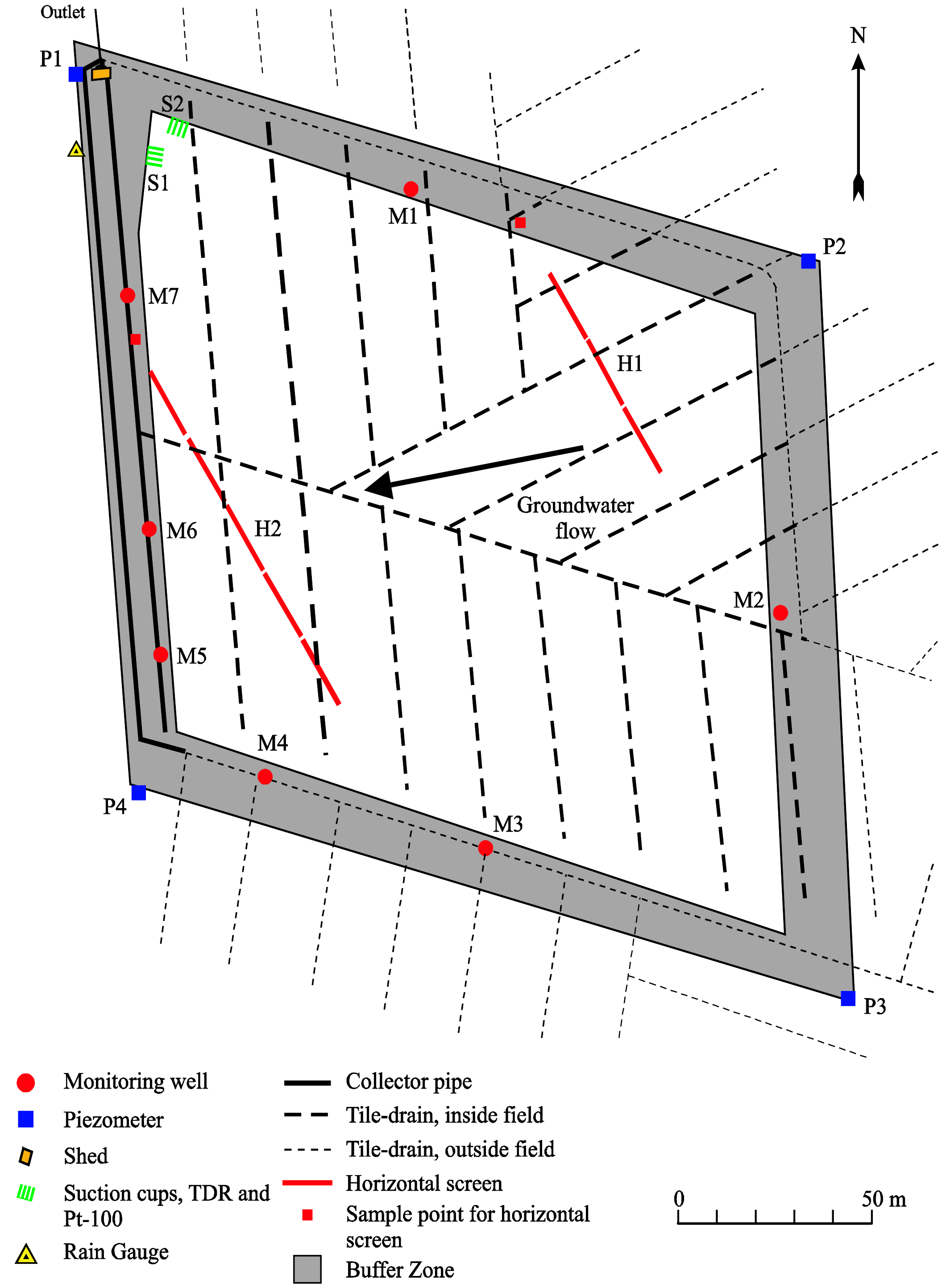


Figure 36. Overview of the **Faardrup** site. The innermost white area indicates the cultivated land, while the grey area indicates the surrounding buffer zone. The positions of the various installations are indicated, as is the direction of groundwater flow (by an arrow). Pesticide monitoring is conducted weekly from the drainage system (during period of continuous drainage runoff) and monthly and half-yearly from selected groundwater monitoring wells as described in Table A2.1 in Appendix 2.

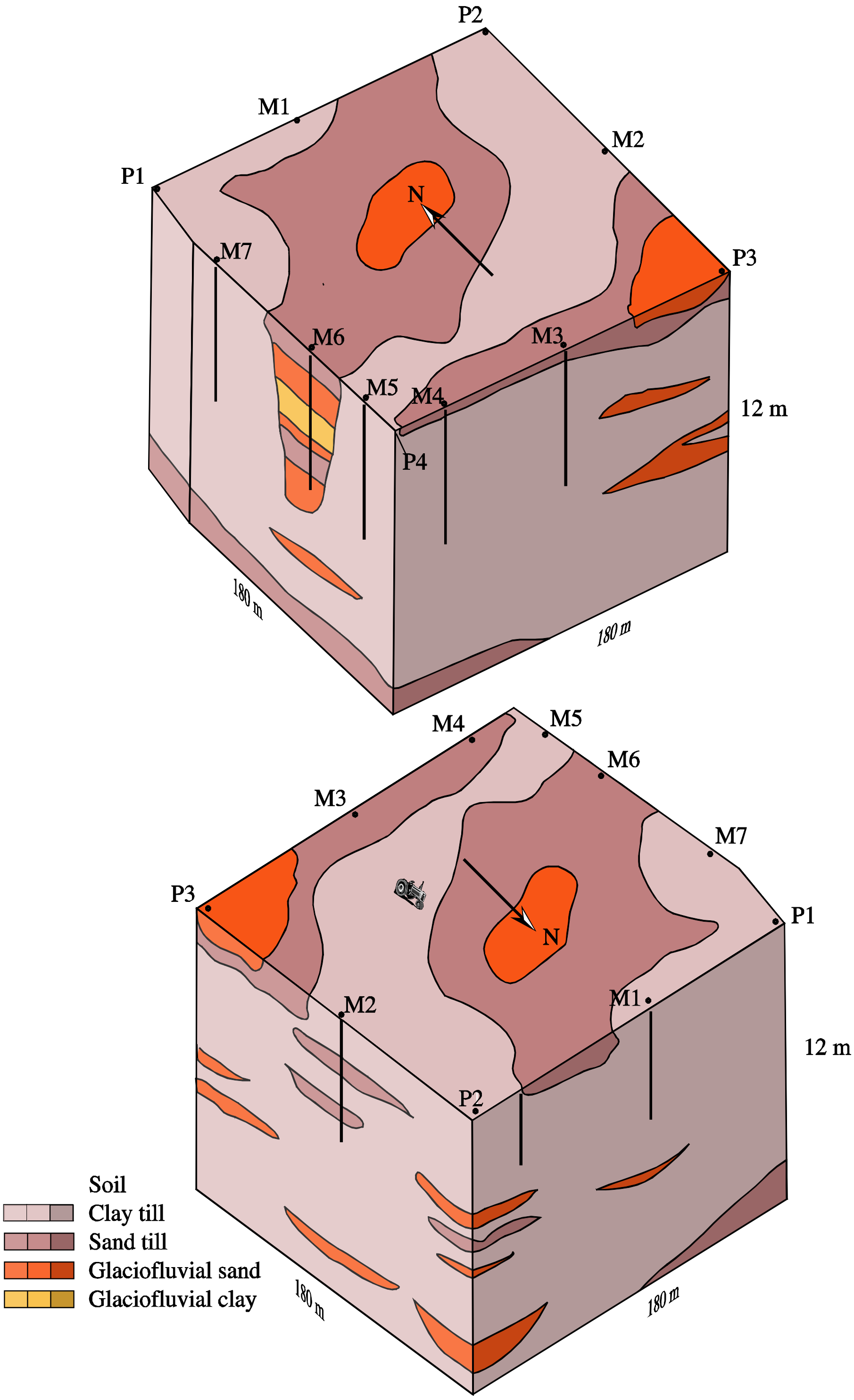


Figure 37. Geological description of **Faardrup** (Lindhardt *et al.*, 2001).

6.1.2 Agricultural management

Management practice during the 2010-11 growing seasons is briefly summarized below and detailed in Appendix 3 (Table A3.5). For information about management practice during the previous monitoring periods, see previous monitoring reports available on http://pesticidvarsling.dk/publ_result/index.html.

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

The red fescue was sprayed with bifenox, a herbicide, on 25 October 2010, where the grass plants were having between 4 and 8 detectable tillers whereas others where at the end of tillering.

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 2011 and to establish an annual water balance.

Compared to the setup in Kjær *et al.* (2011), 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 2011. 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 36) and measured drainage flow. Data acquisition and model setup are described in Barlebo *et al.* (2007).

Table 10. 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	35	206
1.7.01–30.6.02	626	810	514	197	201	99
1.7.02–30.6.03	626	636	480	49	72	107
1.7.03–30.6.04	626	685	505	36	19	144
1.7.04–30.6.05	626	671	469	131	55	72
1.7.05–30.6.06	626	557	372	28	16	158
1.7.06–30.6.07	626	796	518	202	212	77
1.7.07–30.6.08	626	645	522	111	65	12
1.7.08–30.6.09	626	713	463	46	20	204
1.7.09–30.6.10	626	624	415	54	43	155
1.7.10–30.6.11	626	694	471	133	184	90

[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 2010-June 2011 were generally well described by the model (Figure 38D, 38E and 38F). However, for the summer period 2011 the model largely underestimated the drop in measured water saturation at 60 and 110 cm b.g.s. (Figure 38E and 38F). Especially, the measured drop at 110 cm depth looks unrealistic and will be checked. Drainage flow generated by snowmelt on the 11 December 2010 and 8 January 2011 was not captured by the MACRO-model.

The resulting water balance for Faardrup for the 12 monitoring periods is shown in Table 10. Compared with the previous eleven years, the latest hydraulic year July 2010-June 2011 was characterised by having the medium precipitation, the medium simulated actual evapotranspiration, and the fourth-highest measured and simulated drainage. Precipitation in this year was characterised by July-November 2010 being very wet and December-February being very dry (Appendix 4). Due to this precipitation pattern, the duration of the simulated percolation period of the year July 2010-June 2011 was represented by continuous percolation throughout the period August-May (Figure 38A). Compared to the other years, the climate this year gave rise to long periods, where the groundwater table was a bit higher than the drainage level, causing long-term contributions to the drains (Figure 38B and 38C).

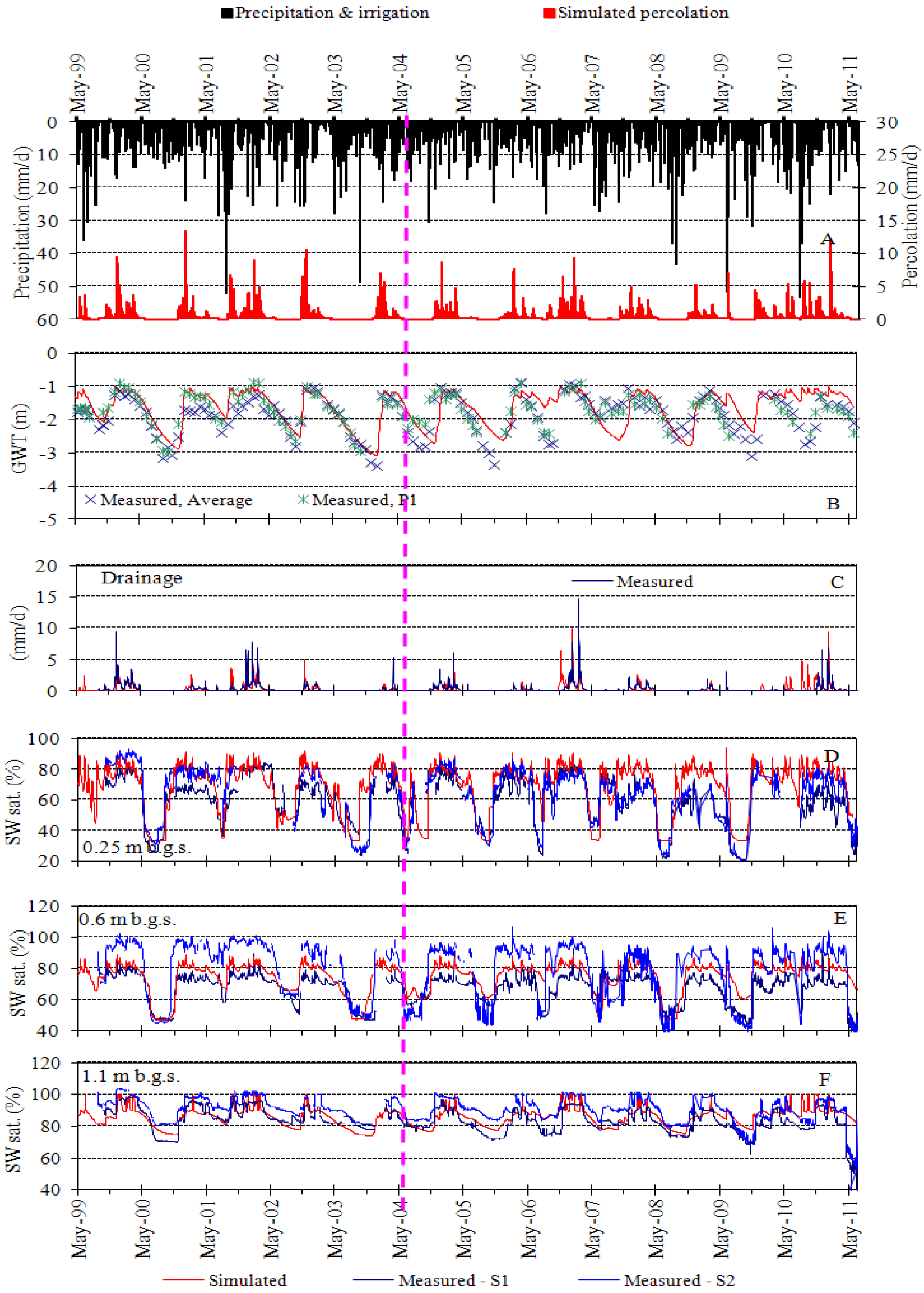


Figure 38. Soil water dynamics at **Faardrup**: Measured precipitation and simulated percolation 1 m b.g.s. (A), simulated and measured groundwater level GWT (B), simulated and measured drainage flow (C) and simulated and measured soil water saturation (SW sat.) at three different soil depths (D, E and F). The measured data in B derive from piezometers located in the buffer zone. The measured data in D, E and F derive from TDR probes installed at S1 and S2 (Figure 32). The broken vertical line indicates the beginning of the validation period (July 2004-June 2011).

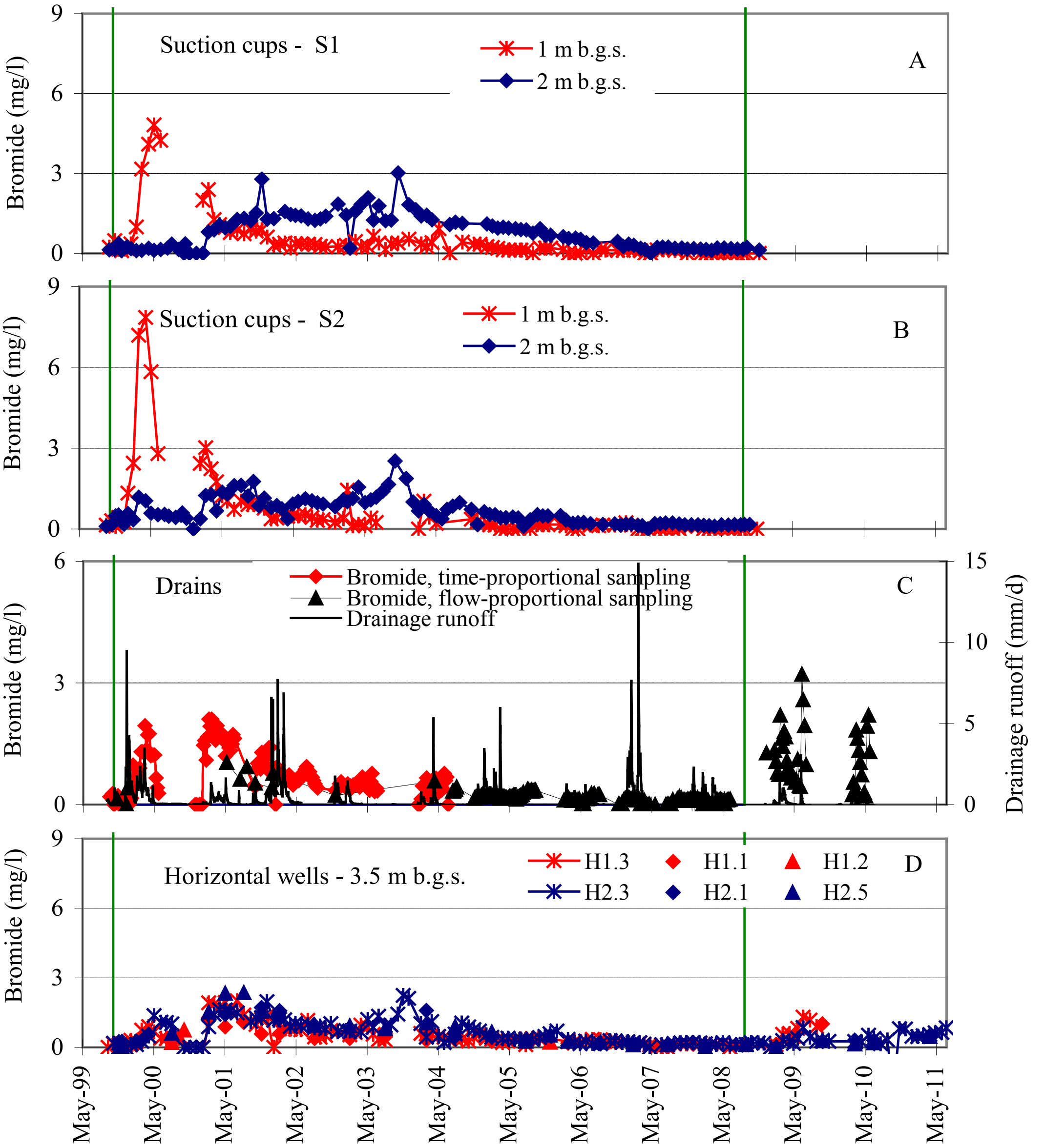


Figure 39. Bromide concentrations at **Faardrup**. A and B refer to suction cups located at S1 and S2. The bromide concentration is also shown for drainage runoff (C) and the horizontal monitoring wells (D). In September 2008, bromide measurements in the suction cups were suspended. The green vertical lines indicate the dates of bromide applications.

6.2.2 Bromide leaching

The bromide concentration shown in Figure 39 and Figure 40 relates primarily to the bromide applied in May 2000, as described further in Kjær *et al.* (2003), and further evaluated in Barlebo *et al*. (2007). In August 2008, 30 kg/ha potassium bromide was applied for the second time. In September 2008, bromide measurements in the suction cups and monitoring wells M2 and M7 were suspended. A drastic increase in bromide concentration in M4 and M5 was detected in May-June 2009 (Figure 40).

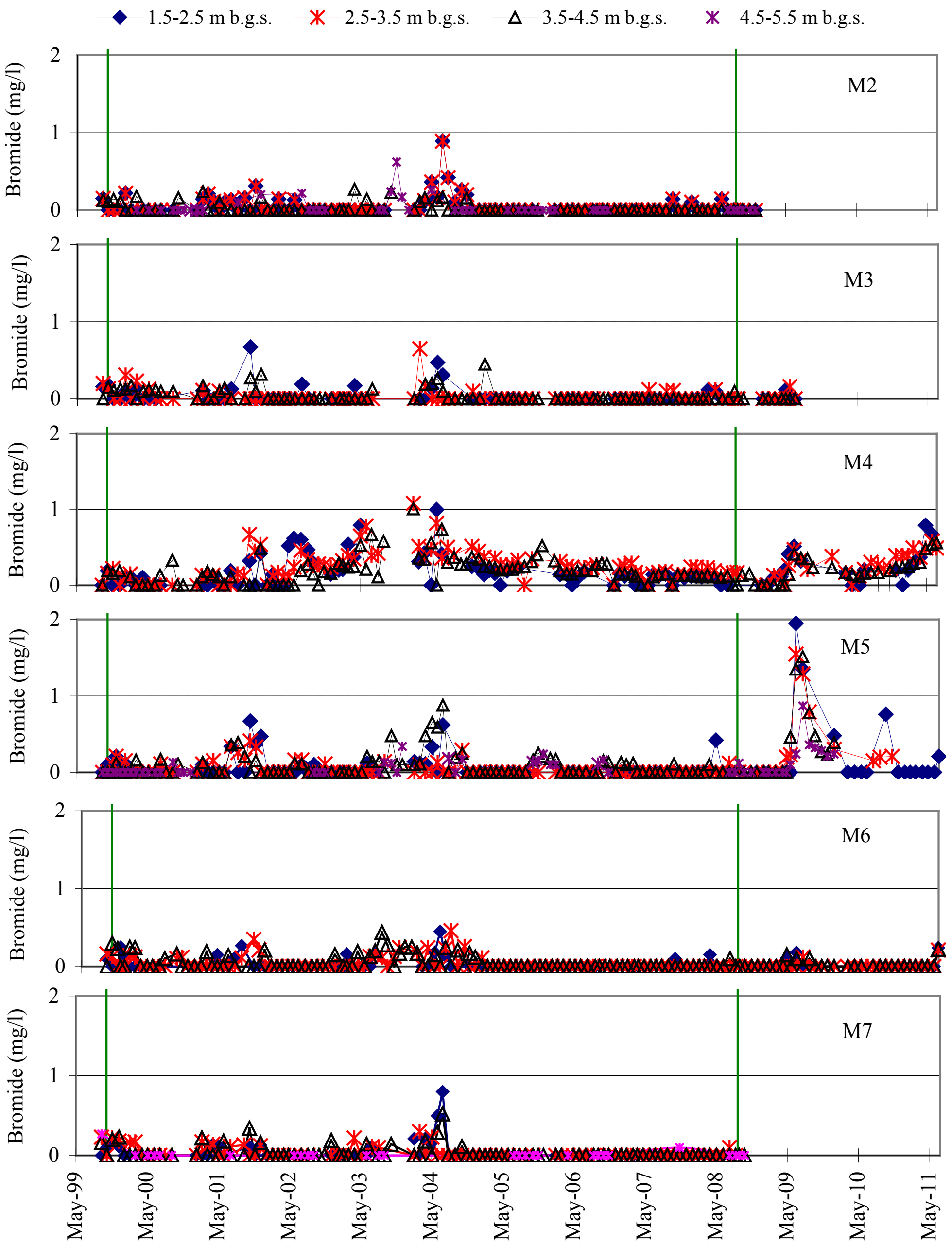


Figure 40. Bromide concentrations at **Faardrup**. The data derive from the vertical monitoring wells (M2–M7). Screen depth is indicated in m b.g.s. In September 2008, monitoring wells M2 and M7 were suspended (Appendix 2). The green vertical line indicate the dates of bromide applications.

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 11 and in Appendix 8, Table A8.5.

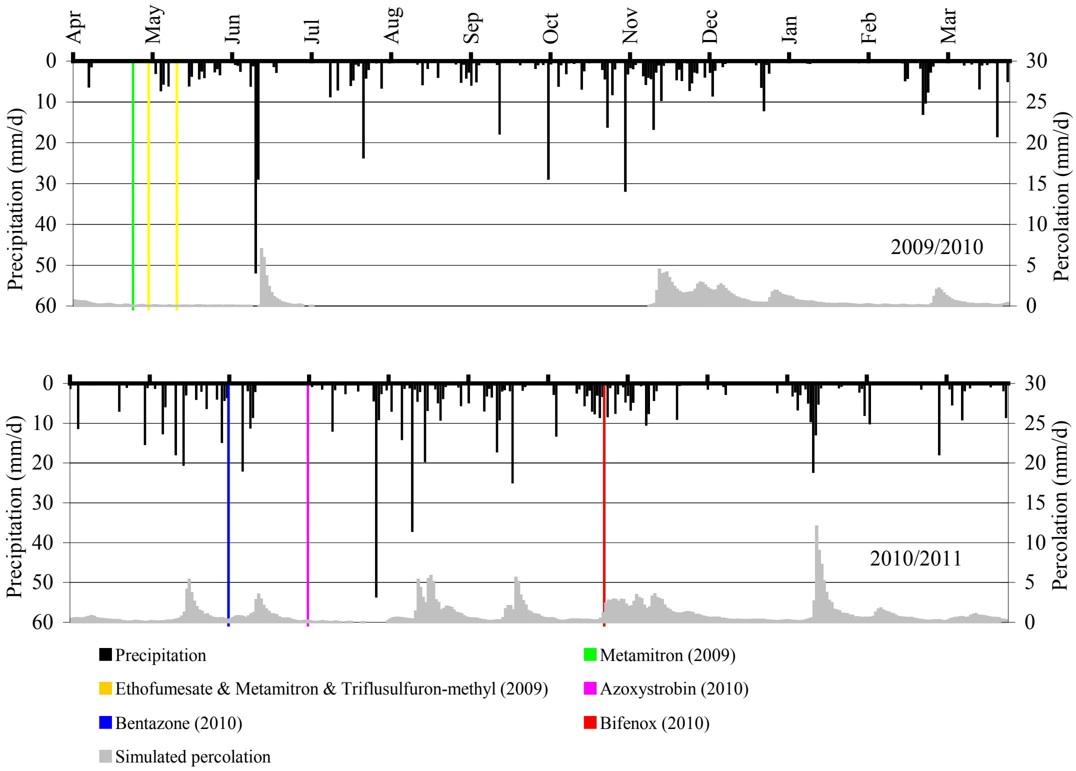


Figure 41. Application of pesticides included in the monitoring programme and precipitation (primary axis) together with simulated percolation (secondary axis) at **Faardrup** in 2009/2010 (upper), in 2010/2011 (lower).

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 41. 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. tribenuron-methyl (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 (Appendix 8, Table A8.5).

Table 11. Pesticides analysed at Faardrup. Precipitation (precip.) and percolation (percol.) are accumulated within the first year (Precip 1st year, Percol 1st year) and first mount (Precip 1st month, Percol 1st year) after the first application C_{mean} refers to average leachate concentration at 1 m b.g.s. the first year after application. See Appendix 2 for calculation method and Appendix 8 (Table A8.5) for previous applications of pesticides.

Crop	Applied product	Analysed pesticide	Application date	End of monit.	Y 1st precip.	Y 1st percol.	M 1st precip.	M 1st percol.	C_{mean}
Spring Barley 2006	Opus	Epoxiconazole(P)	Jun 06	Jun 08	790	306	17	3	<0.01
	Starane 180 S	Fluroxypyr(P)	May 06	Jun 08	708	333	37	17	<0.02
Winter Rape 2007	CruiserRAPS	Thiamethoxam(P)	Aug 06	Jul 08	806	294	57	23	<0.01
		CGA 322704(M)	Aug 06	Jul 08	806	294	57	23	<0.02
	Kerb 500 SC	Propyzamide(P)	Feb 07	Mar 09	735	199	64	46	0.01
		RH-24580(M)	Feb 07	Mar 09	735	199	64	46	<0.01
		RH-24644(M)	Feb 07		735	199	64	46	<0.01
		RH-24655(M)	Feb 07	Mar 09	735	199	64	46	<0.01
Winter Wheat 2008	Folicur 250	Tebuconazole(P)	Nov 07	Dec 09	693	158	64	56	<0.01
	Stomp SC	Pendimethalin(P)	Oct 07	Dec 09	673	180	51	24	<0.01
Sugar Beet 2009	Ethosan	Ethofumesate(P)	Apr 09	Jun 11	609	146	50	2	0.01
	Goliath	Metamitron(P)	Apr 09	Jun 11	609	146	42	2	0.02
		Desamino-metamitron(M)	Apr 09	Jun 11	609	146	42	2	0.06
	Safari	Triflusulfuron-methyl(P)	Apr 09	Jun 11	609	146	50	2	<0.01
		IN-D8526(M)	Apr 09	Jun 11	609	146	50	2	<0.01
		IN-E7710(M)	Apr 09	Jun 11	609	146	50	2	<0.01
		IN-M7222(M)	Apr 09	Jun 11	609	146	50	2	<0.02
Spring Barley and Red Fescue 2010	Fighter 480	Bentazone(P)	Jun 10	Jun 11*	693	327	49	29	<0.01
	Fox 480 SC	Bifenox(P)	Oct 10	Jun 11*	351	190	75	72	0.02
		Bifenox acid(M)	Oct 10	Jun 11*	351	190	75	72	2.54
		Nitrofen(M)	Oct 10	Jun 11*	351	190	75	72	0.01

Systematic chemical nomenclature for the analysed pesticides is given in Appendix 1.
**Monitoring continue the following year.*

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

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

Metamitron, ethofumesate and triflusulfuron were applied April 2009 (Figure 41) and so far neither of the pesticides nor their metabolites have been detected in water samples from Faardrup.

Bentazone, bifenox and fluazifop-Pbutyl were applied in 2010 and in 2011 (Table 13).

Bentazone was found in one water sample (0.013 µg/l) from a drain in January 2011, but bentazone was also found in small concentrations in 5 water samples in 2010. 2 of these water samples originated from the drain system and 3 from the horizontal well.

Bifenox was applied in October 2010 and found in 6 water samples collected from drains from November 2010 to December 2010. Al concentrations were below 0.1 µg/l.

The metabolite bifenox-acid was found in 7 samples in 2010 from the same drain, but in high concentrations from 0.23-6.9, and in one ground water sample from the horizontal well H2 in a concentration of 0.19 µg/l (Figure 42). In January to April 2011 the metabolite was found in high, but decreasing concentrations in 9 water samples the drain (8.3 to 0.11 µg/l). The 2010 average concentration in the drain for bifenox-acid and bifenox was 2.54 µg/l and 0.02 µg/l respectively.

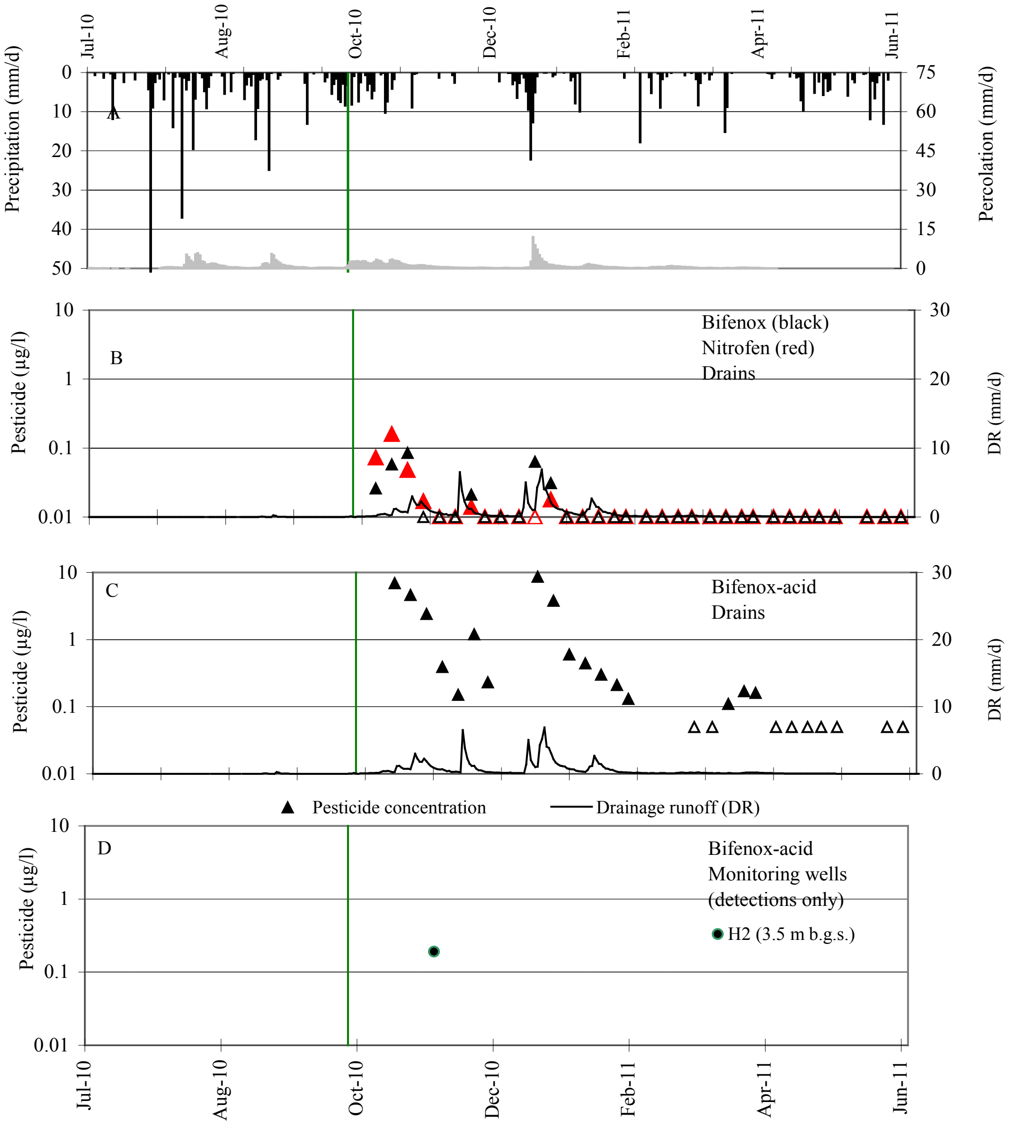


Figure 42. Precipitation and simulated percolation 0.6 m b.g.s. (A) together with concentration of bifenox and nitrofen (B) and bifenox-acid (C) in the drainage runoff, and the detections of bifenox-acid (E) in the groundwater monitoring screens at **Faardrup**. The green vertical line indicate the date of bifenox application. Open symbols in B and C represent values below the detection limit of 0.01 µg/l (bifenox and nitrofen) and 0.05 µg/l (bifenox-acid).

Another metabolite from bifenox - nitrofen - was found in the same drain in 5 water samples in concentrations from 0.014 to 0.16 in 2010 and in one water sample from 2011. 24 water samples were analyzed in 2010 and 60 samples in 2011. The samples originated both from ground water and drain water.

From Figure 42 it can be seen that the precipitation in July before the application in October was large, which could indicate that the soil was more or les saturated below the root zone (Figure 38), during application.

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 2010 to June 2011 are presented below, while those for the preceding monitoring periods are given in previous monitoring reports (available on http://pesticidvarsling.dk/publ_result/index.html).

7.1 Materials and methods

All pesticide analyses were carried out at commercial laboratories selected on the basis of a competitive tender. In order to assure the quality of the analyses, the call for tenders included requirements as to the laboratory's quality assurance (QA) system comprising both an internal and an external control procedure. In addition to specific quality control under the PLAP, the laboratory takes part in the proficiency test scheme employed by the Danish Environmental Protection Agency when approving laboratories for the Nationwide Monitoring and Assessment Programme for the Aquatic and Terrestrial Environments (NOVANA).

7.1.1 Internal QA

With each batch of samples the laboratory analysed one or two control samples prepared at each laboratory as part of their standard method of analysis. The pesticide concentration in the internal QA samples ranged between 0.03–0.11 µg/l. Using these data it was possible to calculate and separate the analytical standard deviation into within-day (S_w), between-day (S_b) and total standard deviation (S_t). Total standard deviation was calculated using the following formula (Wilson 1970, Danish EPA 1997):

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

7.1.2 External QA

Every four months, two external control samples were analysed at the laboratories along with the various water samples from the five test sites. Two stock solutions of different concentrations were prepared from two standard mixtures in ampoules prepared by Dr. Ehrenstorfer, Germany (Table 14). Fresh ampoules were used for each set of standard solutions. The standard solutions were prepared two days before a sampling day and stored in darkness and cold until use. For the preparation of stock solutions 150 µl (low level) or 350 µl (high level) of the pesticide mixture was pipetted into a preparation glass containing 10 ml of ultrapure water. The glass was closed and shaken thoroughly and shipped to the staff collecting the samples. The staff finished the preparation of control samples in the field by quantitatively transferring the standard solution to a 3.0 l measuring flask. The standard solution was diluted and adjusted to the mark with groundwater from a groundwater well. After a thorough mixing, the control sample was transferred to a sample bottle and transported to the laboratories together with the regular samples. In the present report period the final concentrations in the solutions shipped for analysed in the laboratories were in the range 45 to 50 µg/l for low level spikes and 105 to 117 µg/l for high spike levels. 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 or blanks.

Table 12. Pesticide concentrations in both the original ampoules and in the resulting high-level and low-level external control samples used in in the period 1.7.2010-30.6.2011.

Compound	Ampoule Concentration (µg/l)	Ampoule	High-level control (µg/l)	Low-level control (µg/l)
AMPA	1000	2	0.117	0.050
Aclonifen	900	1	0.105	0.045
Bentazone	900	1	0.105	0.045
Bifenox acid	900	1	0.105	0.045
CGA 62826	900	1	0.105	0.045
CyPM	900	1	0.105	0.045
Cyazofamid	900	1	0.105	0.045
Ethofumesate	900	1	0.105	0.045
Glyphosate	1000	2	0.117	0.050
IN-E7710	900	1	0.105	0.045
Metamitron	900	1	0.105	0.045
Metsulfuron-methyl	900	1	0.105	0.045
PPU	900	1	0.105	0.045
TFMP	900	1	0.105	0.045
Thiacloprid-amide	900	1	0.105	0.045

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 random and systematic 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, 12 out of 21 compounds had ratios above 2, and the highest S_b/S_w ratio in this group was observed for desamino-metamitron (4.2) and diflufenican (3.9). When all compounds are considered, a particularly high S_b/S_w ratio is apparent for CGA 108906, PPU-desamino and PPU. Such relatively high ratios can be caused by very low within-day standard deviations, i.e. within each laboratory day, the variation on the analysis is small compared to the other compounds, whereas the variation between days is comparable to the other compounds analysed. This is not the case for the three high ratio compounds CGA 108906, PPU-desamino and PPU. For these compounds it is apparent that the high S_b/Sw ratio is caused by relatively high between-day deviation (S_b).

The total standard deviations (St) of the various analyses of pesticides and degradation products lie within the range 0.001-0.111 µg/l, the highest value being observed for CGA 108906 (max St for compounds other than CGA 108906 was 0.061 µg/l). In general, the data suggest that the analytical procedure used for the quantification of the compounds with high Sb/Sw ratio and/or high St, and in particular the compound CGA 108906, may benefit from a critical review and possible optimisation of within day variation. Excluding the CGA 108906 data, the overall mean St was 0.012 µg/l and in the same range as observed in previous report periods.

Table 13. Internal QA of pesticide analyses carried out in the period 1.7.2010-30.6.2011. 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 α=0.05 was used.

Compound	Normal distribution α=0.05	Significant Sb Between day contribution ANOVA α=0.05	Sw (µg/l)	Sb (µg/l)	St (µg/l)	Ratio Sb/Sw	N	Conc. (µg/l)
AE-05422291*	yes	-	0.001	0.003	0.003	sb/sw	4	0.05
AE-05422291*	yes	-	0.001	0.003	0.003	sb/sw	4	0.05
AE-B107137*	yes	yes	0.005	0.006	0.008	sb/sw	4	0.10
AMPA*		yes	0.009	0.002	0.010	sb/sw	26	0.03
Aclonifen	yes	-	0.003	0.005	0.006	sb/sw	17	0.05
Azoxystrobin		yes	0.060	0.013	0.061	sb/sw	43	0.05
Bentazone		-	0.005	0.004	0.006	sb/sw	60	0.05
Bifenox	yes	-	0.003	0.008	0.008	sb/sw	53	0.05
Bifenoxacid		-	0.012	0.028	0.030	sb/sw	45	0.10
Boscalid		yes	0.001	0.000	0.001	sb/sw	3	0.05
CGA108906*		-	0.007	0.110	0.111	sb/sw	15	0.10
CGA62826*		-	0.006	0.016	0.017	sb/sw	15	0.10
CyPM*		-	0.003	0.010	0.010	sb/sw	21	0.05
Desamino-metamitron*	yes	-	0.003	0.012	0.012	sb/sw	24	0.05
Diflufenican	yes	-	0.001	0.002	0.002	sb/sw	4	0.05
Diketo-metribuzin*	yes	-	0.003	0.007	0.008	sb/sw	9	0.05
Ethofumesate		-	0.002	0.004	0.004	sb/sw	24	0.05
Fluazifop-P*		yes	0.015	0.013	0.020	sb/sw	4	0.05
Fluazifop-P(free-acid)*		-	0.002	0.003	0.004	sb/sw	7	0.05
Glyphosate		yes	0.005	0.003	0.006	sb/sw	25	0.03
IND8526*	yes	-	0.001	0.002	0.002	sb/sw	8	0.05
INE7710*	yes	-	0.002	0.005	0.005	sb/sw	8	0.05
IN-D8526*	yes	-	0.003	0.006	0.007	sb/sw	16	0.05
IN-E7710*	yes	-	0.002	0.006	0.006	sb/sw	16	0.05
IN-M7222*	yes	-	0.004	0.007	0.007	sb/sw	24	0.05
Iodosulfuron-methyl	yes	-	0.002	0.006	0.006	sb/sw	11	0.05
M34*		-	0.025	0.042	0.048	sb/sw	22	0.10
Metalaxyl-M		-	0.001	0.004	0.004	sb/sw	17	0.05
Metamitron		-	0.006	0.010	0.012	sb/sw	41	0.05
Metrafenone	yes	yes	0.001	0.002	0.003	sb/sw	4	0.05
Metsulfuron-methyl	yes	-	0.004	0.006	0.007	sb/sw	11	0.05
Nitrofen		-	0.002	0.007	0.007	sb/sw	53	0.05
PPU*		-	0.005	0.034	0.034	sb/sw	18	0.05
PPU-desamino*		-	0.002	0.019	0.019	sb/sw	18	0.05
TFMP*	yes	-	0.004	0.008	0.009	sb/sw	11	0.05
Thiacloprid		-	0.002	0.005	0.005	sb/sw	28	0.05
Thiaclopridsulfonicacid	yes	-	0.018	0.022	0.028	sb/sw	22	0.10
Thiacloprid-amide*	yes	-	0.004	0.007	0.008	sb/sw	28	0.05
Triazinamin	yes	-	0.006	0.009	0.011	sb/sw	10	0.11
Triazinamin-methyl*	yes	-	0.003	0.004	0.005	sb/sw	24	0.05

**Degradation product.*

7.2.2 External QA

As part of the quality control a set of blanks made from HPLC water are analysed to evaluate the possibility of false positive findings in the programme. From these results it can be concluded that contamination of samples during collection, storage and analysis is not likely to occur. In a total of 28 blank samples consisting of HPLC water no detection of the compounds analysed were made. As a consequence, samples analysed in the monitoring program and found to contain pesticides or their degradation products are thus regarded as true positive findings.

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

Table 14. Externally spiked samples. Average recovery (%) of the nominal concentration at low/high concentration level indicated for each site. For each compound n_{low} and n_{high} refer to the total number of samples being spiked at low and high concentrations, respectively. Bold font is used for recoveries outside the range 70% to 120%.

	Tylstrup		Jyndevad		Silstrup		Estrup		Faardrup		Average	n_{low}/n_{high}
	Low	High	Low	High	Low	High	Low	High	Low	High		
Ethofumesate					104%	114%			108%	107%	109	4/8
Glyphosate							**59%**	**58%**			**59**	3/6
Metamitron					104%	104%			96%	100%	100	4/8
AMPA*							74%	70%			72	3/6
Bentazone	85%	90%	92%	90%	89%	90%	103%	97%	100%	97%	94	15/30
PPU*	**63%**	77%	**149%**	113%							101	6/12
CyPM*	120%	107%			97%	89%	112%	114%			107	9/18
IN-E7710*									117%	123%	120	3/6
TFMP*					**132%**	111%			103%	114%	117	5/10
Bifenox acid*			**133%**	98%		75%	111%	81%	**170**%	111%	108	11/16
CGA 62826*	88%	79%	88%	79%							84	6/12
Cyazofamid	86%	78%	89%	86%							85	6/12
Aclonifen	75%	71%	85%	80%							78	6/12
Thiacloprid-amide*							117%	114%			116	3/6
Ethofumesate					104%	114%			108%	107%	109	4/8

**Degradation produkt.*

A total of 36 samples were spiked in this reporting period, Whereas the recovery of the most spiked compounds in the samples is generally good (i.e. in the range 70% to 120%), the broad range of average recoveries indicates that for some compounds there may be reason for concern. For some samples a small background content may be present in the water used for spiking, and in particular for low levels QC samples such content can cause a elevated recovery percentage. For this reason, the QC data must be considered as a whole, and used to keep track on possible changes in the quality of the program from period to period. In the present reporting period, no alarming QC data was registered, but the data points to the need for keeping track on particular compounds, e.g. bifenox and PPU.

In previous reports a somewhat low levels was observed for recovery of bifenox acid at Jyndevad and Estrup. In the present reporting period, such low recoveries were not observed, indicating that a more robust analytical method has been implemented in the program, even if a high recovery was observed for a low level spike at Faardrup (170%) and for PPU a similar high recovery is observed for low spiking levels at Jyndevad (see below for possible background in the water used for spiking).

In previous reporting periods, low recoveries were observed. In the current period the PPU levels observed at Tylstrup are still to the lower end yet acceptable, whereas the levels at Jyndevad must be considered as high. In general, the most extreme recoveries (low and high) are found for the low level spikings (0.05 ppb), indicating that the analytical procedure is more suitable for the high level spiking range close to the residue limit of 0.1 ppb.

This finding and the low overall recoveries for glyphosate indicate that there may still be some aspects of the procedures used for monitoring of glyphosate that can be optimised. Based on previous findings of low recovery of glyphosate, the analytical procedures used in the current monitoring period were optimised. As reported previously, there was a shift from GC/MS to LC/MS analytical procedure was made in June 2007. Concern for the QC aspects caused an evaluation of the analytical procedures used in the programme and as a consequence some analytical details were adjusted. As reflected by the current results of the internal QC the analytical procedure performs well on in-house spiked samples (Table 15). However, it seems there are still some elements of the sampling handling and analytical procedure that needs evaluation, as the external QC program demonstrates low overall recoveries at 59% when QC samples from the field site are analysed (Table 16). It is known that the LC based method is sensitive to a number of matrix components, possible due to the derivatization step in the method used, but even if these procedures have been optimised, there is still a nee for further investigations into the possible cause for the low overall recoveries of glyphosate.

All the compounds included in the spiking procedure (Table 14) were detected in the laboratory. Additionally, a number of compounds were measured at the threshold of detection of the analytical procedure (i.e. close to 0.01 µg/l). The occurrence of a number of false positives is expected when analysing environmental matrices and these findings do not cause a general concern in relation to the reliability of the analytical procedures used in the programme.

At the sites Tylstrup and Jyndevad the compound PPU was frequently found at levels close to the detection limit, an observation that needs to be taken into consideration when evaluating the recovery data (Table 14). In the programme, the water matrixs used for spiking were analysed. The high recovery of bifenox acid at Faardrup (170%) could not be explained by background content. In contrast, a background content was observed at one occasion for the compound PPU (level 0.03 µg/l) and this can explain the rather high recovery observed for low level spiking of PPU at Jyndevad. However, in general, the analysis of the water used for spiking showed no or were low levels of background content (i.e. in the range of the detection limit) and these findings do not cause concern for the overall quality of the programme.

During the 2010/2011 monitoring period a total of five pesticides and nine degradation products were detected in samples from the experimental fields. The external and internal QA data relating to these particular pesticides/degradation products are of special interest. These data (when available) are illustrated in Appendix 6.

7.3 Summary and concluding remarks

The QA system showed that:

- The internal QA indicates that the reproducibility of the pesticide analyses was good with total standard deviation (S_t) in the range 0.001-0.061 µg/l except for the compound CGA 108906 having a relatively large S_t of 0.111.

- As demonstrated by the external QA, recovery was generally good in externally spiked samples. Low recovery of glyphosate was, however, observed in some samples, causing low overall recovery. These results will be used in the ongoing optimization of the procedures used in the programme.

- Based on the results from analysis of blank ‘HPLC water samples’ shipped together with the true monitoring samples it is concluded that contamination of samples during collection, storage and analysis is not likely to occur.

8 Summary of monitoring results

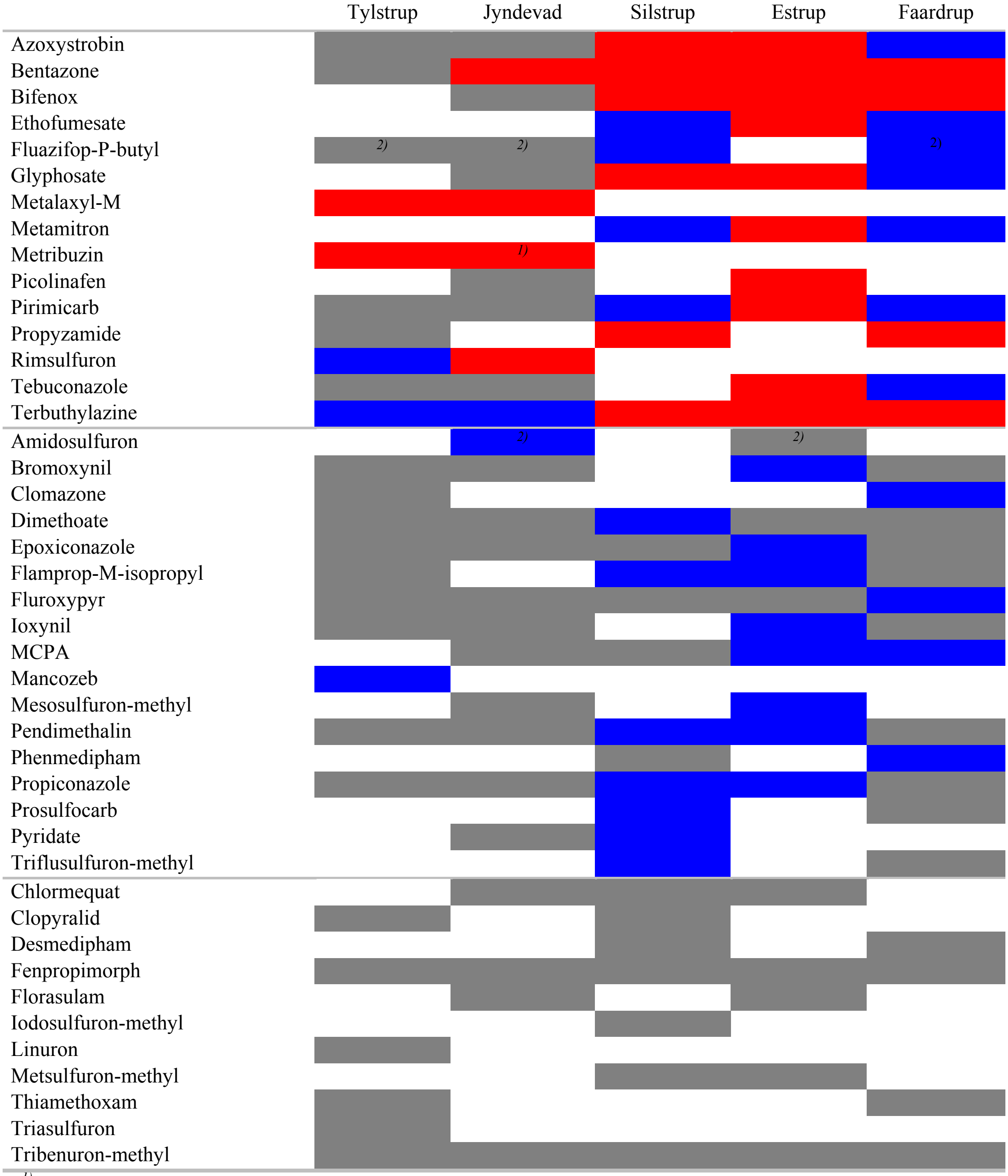
This section summarizes the monitoring data from the entire monitoring period, i.e. both data from the two most recent monitoring years (detailed in this report) and data from the previous monitoring years (detailed in previous reports available on http://pesticidvarsling.dk/publ_result/index.html). 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 15). Pronounced leaching in 1 m b.g.s. is defined as root zone leaching (1 m b.g.s.) exceeding an average concentration of 0.1 µg/l within the first season after application.

On sandy and loamy soils, leaching is determined as the weighted average concentration in soil water and drainage water, respectively (Appendix 2).

The monitoring data from the groundwater monitoring screens is divided into three categories: no detection of the pesticide (or its degradation products), detections of the pesticide (or its degradation products) not exceeding 0.1 µg/l, and detections of the pesticide (or its degradation products) exceeding 0.1 µg/l (Table 17). 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. Up to 2011 16 of the applied pesticides (or their degradation products) exhibited pronounced root zone leaching and 12 of these were also detected in the groundwater monitoring screens in concentrations exceeding 0.1 µg/l.

- Azoxystrobin, and in particular its degradation product CyPM, leached from the root zone (1 m b.g.s.) in high average concentrations at the loamy sites Silstrup and Estrup. CyPM leached into the drainage water in average concentrations exceeding 0.1 µg/l at both the Silstrup and Estrup sites, while azoxystrobin only leached in concentrations exceeding 0.1 µg/l at Estrup (Table 15 and 16). 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 17 and 18). However, detection of CyPM in groundwater monitoring wells has gradually increased over time with highest numbers of detection found after the latest applications (2009 at Silstrup, Figure 27 and 2008 at Estrup, Figure 33). Apart from one sample, however, concentrations detected were all below 0.1 µg/l. In 2010 and 2011 CyPM continued to enter the drain water especially in Silstrup in high concentrations. 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 15. Leaching **1 m b.g.s.** of pesticides or their degradation products at the five PLAP sites. The colours indicate the degree of leaching. Pesticides applied in spring 2011 are not included in the table.



	Tylstrup	Jyndevad	Silstrup	Estrup	Faardrup
Azoxystrobin	▒	▒	🟥	🟥	🟦
Bentazone	▒	🟥	🟥	🟥	🟥
Bifenox		▒	🟥	🟥	🟥
Ethofumesate			🟦	🟥	🟦
Fluazifop-P-butyl	▒ 2)	▒ 2)	🟦		🟦 2)
Glyphosate		▒	🟥	🟥	🟦
Metalaxyl-M	🟥	🟥			
Metamitron			🟦	🟥	🟦
Metribuzin	🟥	🟥 1)			
Picolinafen		▒		🟥	
Pirimicarb	▒	▒	🟦	🟥	🟦
Propyzamide	▒		🟥		🟥
Rimsulfuron	🟦	🟥			
Tebuconazole	▒	▒		🟥	🟦
Terbuthylazine	🟦	🟦	🟥	🟥	🟥
Amidosulfuron		🟦 2)		▒ 2)	
Bromoxynil	▒	▒		🟦	▒
Clomazone	▒				🟦
Dimethoate	▒	▒	🟦	▒	▒
Epoxiconazole	▒	▒	▒	🟦	▒
Flamprop-M-isopropyl	▒		🟦	🟦	▒
Fluroxypyr	▒	▒	▒	▒	🟦
Ioxynil	▒	▒		🟦	▒
MCPA		▒	▒	🟦	🟦
Mancozeb	🟦				
Mesosulfuron-methyl		▒		🟦	
Pendimethalin	▒	▒	🟦	🟦	▒
Phenmedipham			▒		🟦
Propiconazole	▒	▒	🟦	🟦	▒
Prosulfocarb			🟦		▒
Pyridate		▒	🟦		
Triflusulfuron-methyl			🟦		▒
Chlormequat		▒	▒	▒	
Clopyralid	▒		▒		
Desmedipham			▒		▒
Fenpropimorph	▒	▒	▒	▒	▒
Florasulam		▒		▒	
Iodosulfuron-methyl			▒		
Linuron	▒				
Metsulfuron-methyl			▒	▒	
Thiamethoxam	▒				▒
Triasulfuron	▒				
Tribenuron-methyl	▒	▒	▒	▒	▒

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 16. Number of samples from **1 m b.g.s**. in which the various pesticides and their degradation products were detected at each site with maximum concentration (µg/l) in parentheses. The table encompasses pesticides/degradation products detected in either several (more than three) consecutive samples or in a single sample in concentrations exceeding 0.1 µg/l. The pesticide and metabolites are mentioned if analyzed under compound. Pesticides applied in spring 2011 are not included.

Parent	Compound	Tylstrup	Jyndevad	Silstrup	Estrup	Faardrup
Azoxystrobin	Azoxystrobin	0	0	10(0.03)	106(1.4)	0
	CyPM	0	0	73(0.34)	203(2.1)	4(0.06)
Bentazone	2-amino-N-isopropylbenzamide	0	2(0.03)	0	1(0.06)	1(0.06)
	Bentazone	1(0.01)	39(1.6)	45(6.4)	161(20)	20(43)
Bifenox	Bifenox		2(0.04)	1(0.03)	3(0.15)	6(0.09)
	Bifenox acid		1(0.1)	12(4.2)	12(1.9)	17(8.6)
	Nitrofen		0	1(0.02)	0	6(0.16)
Ethofumesate	Ethofumesate			20(0.23)	35(3.36)	14(12)
Fluazifop-P-butyl	Fluazifop-P	0	0	0		9(3.8)
	TFMP	0	0	21(0.52)		0
Glyphosate	AMPA		1(0.01)	122(0.35)	367(1.6)	15(0.11)
	Glyphosate		0	67(4.7)	254(31)	5(0.09)
Metalaxyl-M	CGA 108906	13(0.52)	18(2.3)			
	CGA 62826	7(0.04)	17(1.2)			
	Metalaxyl-M	4(0.03)	7(0.04)			
Metamitron	Desamino-metamitron			58(0.67)	49(5.55)	16(2.5)
	Metamitron			46(1)	42(26.37)	12(1.7)
Metribuzin	Desamino-diketo-metribuzin	67(2.1)				
	Diketo-metribuzin	185(0.62)	3(0.09)			
Picolinafen	CL153815		0		31(0.5)	
	Picolinafen		1(0.02)		17(0.07)	
Pirimicarb	Pirimicarb	0	0	14(0.05)	40(0.08)	7(0.06)
	Pirimicarb-desmethyl	0	1(0.01)	1(0.05)	0	6(0.05)
	Pirimicarb-desmethyl-formamido	0	0	0	26(0.38)	3(0.04)
Propyzamide	Propyzamide	0		23(1.6)		4(0.51)
	RH-24580	0		2(0.02)		0
	RH-24644	0		15(0.05)		4(0.02)
	RH-24655	0		0		1(0.02)
Rimsulfuron	PPU	119(0.09)	168(0.29)			
	PPU-desamino	27(0.03)	98(0.13)			
Tebuconazole	Tebuconazole	0	0		41(2)	4(0.05)
Terbuthylazine	2-hydroxy-desethyl-terbuthylazine	5(0.02)	0	28(0.11)	87(6.3)	8(1)
	Desethyl-terbuthylazine	2(0.01)	20(0.06)	108(1.08)	146(8.2)	89(8.3)
	Desisopropylatrazine	17(0.04)	0	43(0.04)	71(0.44)	25(0.36)
	Hydroxy-terbuthylazine	1(0.04)	0	26(0.04)	88(0.99)	21(0.58)
	Terbuthylazine	0	0	60(1.55)	112(11)	41(10)
Amidosulfuron	Amidosulfuron		3(0.11)		0	
Bromoxynil	Bromoxynil	0	0		3(0.6)	0
Clomazone	Clomazone	0				1(0.28)
	FMC 65317	0				1(0.3)
Dimethoate	Dimethoate	0	0	1(1.42)	0	0
Epoxiconazole	Epoxiconazole	0	0	0	14(0.39)	0
Flamprop-M-isopropyl	Flamprop	0		7(0.1)	13(0.03)	1(0.09)
	Flamprop-M-isopropyl	0		12(0.11)	20(0.07)	1(0.04)
Fluroxypyr	Fluroxypyr	0	0	0	3(1.4)	1(0.19)
Ioxynil	Ioxynil	0	0		20(0.25)	1(0.01)
MCPA	2-methyl-4-chlorophenol		0	0	1(0.05)	1(0.24)
	MCPA		0	0	12(3.89)	2(0.28)
Mancozeb	ETU	6(0.04)				
Mesosulfuron-methyl	Mesosulfuron-methyl		0		13(0.06)	
Pendimethalin	Pendimethalin	0	0	14(0.06)	4(0.04)	2(0.04)
Phenmedipham	MHPC			0		2(0.19)
Propiconazole	Propiconazole	0	0	6(0.03)	26(0.86)	0
Prosulfocarb	Prosulfocarb			5(0.18)		0
Pyridate	PHCP		0	4(2.69)		
Triflusulfuron-methyl	IN-E7710			5(0.01)		0

Table 17. Detections of pesticides and their degradation products in water samples from **the groundwater monitoring screen**s at the five PLAP sites (see Table 20 for details Pesticides applied in spring 2011 are not included in the table.

	Tylstrup	Jyndevad	Silstrup	Estrup	Faardrup
Azoxystrobin	▨	▨	🟥	🟦	▨
Bentazone	▨	▨	🟥	🟦	🟥
Bifenox		🟦	🟥	▨	🟥
Ethofumesate			🟦	▨	🟥
Fluazifop-P-butyl	▨ 2)	▨ 2)	🟥		🟥 2)
Glyphosate		🟦	🟦	🟥	🟦
Metalaxyl-M	🟥	🟥			
Metamitron			🟥	▨	🟥
Metribuzin	🟥	🟥 1)			
Picolinafen		▨		▨	
Pirimicarb	▨	▨	🟦	🟦	🟦
Propyzamide	▨		🟥		🟦
Pyridate		▨	🟥		
Rimsulfuron	🟦	🟥			
Tebuconazole	🟦	🟦		🟥	🟦
Terbuthylazine	🟦	🟦	🟥	🟦	🟥
Amidosulfuron		▨ 2)		▨ 2)	
Bromoxynil	▨	▨		▨	▨
Clomazone	▨				▨
Dimethoate	▨	▨	🟦	▨	▨
Epoxiconazole	▨	🟦	▨	▨	▨
Flamprop-M-isopropyl	▨		🟦	▨	▨
Fluroxypyr	▨	▨	▨	🟦	🟦
Ioxynil	▨	▨		▨	🟦
MCPA		▨	▨	🟦	▨
Mancozeb	🟦				
Mesosulfuron-methyl		▨		▨	
Pendimethalin	▨	▨	▨		▨
Phenmedipham			▨		🟦
Propiconazole	▨	▨	▨	🟦	🟦
Prosulfocarb			🟦		▨
Triflusulfuron-methyl			🟦		▨
Chlormequat		▨	▨	▨	
Clopyralid	▨		▨		
Desmedipham			🟦		▨
Fenpropimorph	▨	🟦	▨	▨	▨
Florasulam		▨		▨	
Iodosulfuron-methyl			▨		
Linuron	▨				
Metsulfuron-methyl			▨	🟦	
Thiamethoxam	▨				▨
Triasulfuron	▨				
Tribenuron-methyl	▨	▨	▨		▨

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 18. 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 (see Appendix 5 for further details). The parent pesticide and metabolites are mentioned if analyzed under compound. Only pesticides with more than 3 detections at one site are included. Pesticides applied in spring 2011 are not included.

Parent	Compound	Tylstrup	Jyndevad	Silstrup	Estrup	Faardrup
Azoxystrobin	Azoxystrobin	0	0		1(0.01)	0
	CyPM	0	0	28(0.1)	11(0.09)	0
Bentazone	2-amino-N-isopropylbenzamide	0	0	0	1(0.03)	0
	Bentazone	0	0	29(0.44)	16(0.02)	13(0.6)
Bifenox	Bifenox		2(0.05)	5(0.1)	0	0
	Bifenox acid		0	13(3.1)	0	1(0.19)
Ethofumesate	Ethofumesate			5(0.04)	0	31(1.4)
Fluazifop-P-butyl	Fluazifop-P	0	0	1(0.07)		6(0.17)
	TFMP	0	0	48(0.29)		0
Fluroxypyr	Fluroxypyr	0	0	0	1(0.06)	1(0.07)
Glyphosate	AMPA		2(0.02)	15(0.08)	8(0.07)	2(0.03)
	Glyphosate		0	4(0.03)	42(0.67)	3(0.02)
Metalaxyl-M	CGA 108906	63(0.26)	65(1)			
	CGA 62826	2(0.02)	21(0.02)			
	Metalaxyl-M	6(0.08)	8(0.54)			
Metamitron	Desamino-metamitron			30(0.19)	0	48(1.3)
	Metamitron			29(0.17)	0	24(0.63)
Metribuzin	Desamino-diketo-metribuzin	239(0.2)	20(1.83)			
	Diketo-metribuzin	456(0.55)	26(1.37)			
	Metribuzin	1(0.01)	0			
Pirimicarb	Pirimicarb	0	0	3(0.01)	1(0.02)	2(0.04)
	Pirimicarb-desmethyl	0	0	0	0	3(0.04)
	Pirimicarb-desmethyl-formamido	0	0	0	0	2(0.08)
Propyzamide	Propyzamide	0		9(0.14)		1(0.03)
	RH-24644	0		2(0.03)		0
Pyridat	PHCP		0	14(0.309)		
Rimsulfuron	PPU	19(0.05)	319(0.11)			
	PPU-desamino	0	76(0.03)			
Tebuconazole	Tebuconazole	1(0.01)	1(0.01)		5(0.12)	1(0.01)
Terbuthylazine	2-hydroxy-desethyl-terbuthylazine	1(0.03)	0	1(0.02)	0	7(0.09)
	Desethyl-terbuthylazine	0	27(0.02)	161(0.14)	7(0.05)	66(0.94)
	Desisopropylatrazine	1(0.01)	0	4(0.05)	27(0.03)	60(0.04)
	Hydroxy-terbuthylazine	0	0	0	0	34(0.07)
	Terbuthylazine	0	0	36(0.12)	1(0.02)	51(1.9)

- Bentazone leached through the root zone (1 m b.g.s.) in average concentrations exceeding 0.1 µg/l in the drainage system at the loamy sites of Silstrup, Estrup, and Faardrup. Moreover, bentazone was frequently detected in the monitoring screens situated beneath the drainage system at Silstrup and Faardrup (Table 17 and 18). Apart from eight samples, however, concentrations detected were all below 0.1 µg/l. At Estrup leaching was mostly confined to the depth of the drainage system and rarely detected in deeper monitoring screens (Appendix 5). On the sandy soils, bentazone leached at Jyndevad, but was only detected once 1 m b.g.s. at Tylstrup. At Jyndevad high concentrations (exceeding 0.1 µg/l) were detected in the soil water samples from suction cups 1 m b.g.s. four months after application. Thereafter, leaching diminished and bentazone was not subsequently detected in the monitoring wells. Although leached in high average concentrations (>0.1 µg/l) at four sites, bentazone was generally leached within a short period of time. Initial concentrations of bentazone were usually very high, but then decreased rapidly. In general, concentrations exceeding 0.1µg/l were only found within a period of one to four months following the application. The degradation product 2-amino-N-isopropylbenzamide was detected twice in the vadose zone at Jyndevad, once in drainage water at Estrup and Faardrup (Table 16), and once in water from a horizontal well at Estrup (Table 20).

- Bifenox acid (degradation product of bifenox) leached through the root zone and entered the drainage water system in average concentrations exceeding 0.1 µg/l at the loamy sites of both Silstrup, Estrup and Faardrup. While leaching at Estrup seems to be confined to the depth of the drainage system, leaching to groundwater monitoring wells situated beneath the drainage system was observed at Silstrup, where concentrations exceeding 0.1 µg/l were observed up to six months after application. As in Silstrup and Estrup the metabolite bifenox acid was found in very high concentrations in drain water from Faardrup. in a yearly average concentrations 2,54 µg/l (Table 11). Another unwanted metabolite from bifenox, nitrofen, was found in drain water form Faardrup, but in rater low concentrations. Similar evidence of pronounced leaching was **not** observed on the coarse sandy soil as there was only a single detection of bifenox acid in soil water, whereas bifenox was detected very sporadically in soil and groundwater, concentrations always less than 0.1 µg/l.

- In the loamy soil of Estrup, ethofumesate, metamitron, and its degradation product Desamino-metamitron leached through the root zone (1 m b.g.s.) into the drainage water in average concentrations exceeding 0.1 µg/l (Table 15). 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 15 and 16) and groundwater monitoring screens (Table 17 and 18). Average concentrations in drainage water were not as high as at Estrup, although concentrations exceeding 0.1 µg/l were observed in both drainage water and groundwater monitoring screens during a 1–6-month period at both Silstrup and Faardrup (see Kjær *et al.,* 2002 and Kjær *et al.,* 2004 for details). The above leaching was observed following an application of 345 g/ha of ethofumesate and 2,100 g/ha of metamitron in 2000 and 2003. Since then, ethofumesate has been regulated and the leaching risk related to the new admissible dose of 70 g/ha was evaluated with the two recent applications (2008 at Silstrup and 2009 at Faardrup). Although metamitron has not been regulated, a reduced dose of 1400 g/ha was applied at one of the two recent applications, namely that at Silstrup in 2008. The leaching following these recent applications (2008 at Silstrup and 2009 at Faardrup) was minor. Apart from a few samples from the drainage system and groundwater monitoring wells containing less than 0.1 µg/l, neither ethofumesate nor metamitron was found in any of the analysed water samples (see section 4.2.3 and 6.2.3).

- Fluazifop-P-butyl has several times been included in the monitoring programme at Jyndevad, Tylstrup, Silstrup, and Faardrup. As fluazifop-P-butyl rapidly degrades, until July 2008 monitoring has focused only on its degradation product fluazifop-P (free acid). Except for one detection below 0.1 µg/l in groundwater at Silstrup and 17 detections with eight exceeding 0.1 µg/l (four drains, three vadose zone, one groundwater, Table 16 and 18) at Faardrup, leaching was not evident. TFMP, the degradation product of fluazifop-P-butyl, was included in the monitoring programme at Silstrup in July 2008 following an application of fluazifop-P-butyl. After approximately one month, TFMP was detected in the groundwater monitoring wells, where concentrations at or above 0.1 µg/l were detected within a ten-month period following application (Figure 25, Table 17 and 18). 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 25). The average TFMP concentration in drain water was 0,24 µg/l in 2008/09. The leaching pattern of TFMP indicates pronounced preferential flow also in periods with a relatively dry vadose zone. After use in low doses at Silstrup no leaching was observed.

- Glyphosate and AMPA was found to leach through the root zone at high average concentrations on loamy soils. At the loamy sites Silstrup and Estrup, glyphosate has been applied two (in 2001 and 2003) and four (in 2000, 2002, 2005 and 2007) times within the monitoring period, respectively. All six autumn applications have resulted in detectable leaching of glyphosate and AMPA from the upper meter into the drainage water, often at concentrations exceeding 0.1 µg/l several months after application. Higher leaching levels of glyphosate and AMPA have mainly been confined to the depth of the drainage system and have rarely been detected in monitoring screens located below the depth of the drainage systems, although it should be noted that detections of particularly glyphosate in groundwater monitoring wells at Estrup seem to increase over the years (Figure 35D).This increase may be underestimated for the period June 2007 to July 2010 as external quality assurance of analytical methods in this period indicates that the true concentration of glyphosate may be underestimated (see section 7.2.2). On two occasions heavy rain events and snowmelt triggered leaching to the groundwater monitoring wells in concentrations exceeding 0.1 µg/l more than two year after the application (Figure 35D). Numbers of detections exceeding 0.1 µg/l in groundwater monitoring wells are, however, very limited (only few samples). Glyphosate and AMPA were also detected in drainage water at the loamy site of Faardrup (as well as at the now discontinued Slaeggerup site), but in low concentrations (Kjær *et al.,* 2004). Evidence of glyphosate leaching was only seen on loamy soils, whereas the leaching risk was negligible on the coarse sandy soil of Jyndevad. Here, infiltrating water passed through a matrix rich in aluminium and iron, thereby providing good conditions for sorption and degradation (see Kjær *et al.,* 2005a for details).

- Two degradation products of metribuzin – Diketo-metribuzin and Desamino-diketo-metribuzin – 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).

- Metalaxyl-M was applied found in low concentrations in few samples from the unsaturated zone at Tylstrup. Two degradation products (CGA 62829 and CGA 108906) however, were leached from the root zone (1 m b.g.s.), and CGA 108906 in average concentrations exceeding 0.1 µg/l (Table 3, Figure 7, Table 15-18. CGA 108906 was found in 95% of the analysed groundwater samples and in 27% of the analysed samples the concentration exceeded 0.1 µg/l. Similar to the other compounds GCA 108906 was detected in samples from the upstream well of M1 and present in the groundwater before metalaxyl-M was applied. The background concentration makes it difficult to determine whether the elevated concentrations observed in downstream monitoring wells are due to the metalaxyl-M applied in 2010 or to previous applications "upstream". Evaluating these results it should be noted that the precipitation following the application amounted to 140 mm in July 2004 (97% higher than normal) and 111 mm in June 2004 (50% higher than normal) (see Appendix 4 and Table 3). Both metabolites were found at Jyndevad in concentrations exceeding 0,1µg/l and in increasing concentrations.

- At Estrup, CL153815 (degradation product of picolinafen) leached through the root zone upper meter into the drainage water in average concentrations exceeding 0.1 µg/l (Appendix 5). CL153815 has not been detected in deeper monitoring screens (Table 17). Leaching of CL153815 has not been observed on the sandy soil at Jyndevad after application in October 2007, (Table 15, Table 17 and Appendix 5).

- Pirimicarb together with its two degradation products pirimicarb-desmethyl and pirimicarb-desmethyl-formamido has been included in the monitoring programme for all five sites. All of the three compounds have been detected, but only pirimicarb-desmethyl-formamido leached through the root zone (1 m b.g.s.) entering the drainage system in average concentrations exceeding 0.1 µg/l (Table 15) at Estrup. Comparable high levels of leaching of pirimicarb-desmethyl-formamido have not been observed with any of the previous applications of pirimicarb at the other PLAP sites (Table 15 and Kjær *et al.*, 2004). Both degradation products (pirimicarb-desmethyl and pirimicarb-desmethyl-formamido) have been detected in deeper monitoring screens at Faardrup (Table 17 and 18).

- Propyzamide leached through the root zone (1 m b.g.s.) at the loamy Silstrup and Faardrup sites, entering the drainage system at average concentrations exceeding 0.1 µg/l (Table 15 and 16). 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 17 and 18).

- One degradation product of rimsulfuron – PPU – leached from the root zone (1 m b.g.s.) in average concentrations reaching 0.10–0.13 µg/l at the sandy soil site at Jyndevad. Minor leaching of PPU was also seen at the sandy site Tylstrup, where low concentrations (0.021-0.11 µg/l) were detected in the soil water sampled 1 and 2 m b.g.s (Table 15 and 16). 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 17 and 18). At both sites, PPU was relatively stable and persisted in the soil water for several years, with relatively little further degradation into PPU-desamino. E.g. average leaching concentrations reaching 0.1 µg/l were seen as much as three years after application at Jyndevad. With an overall transport time of about four years, PPU reached the downstream monitoring screens. Thus, the concentration of PPU-desamino was much lower and apart from four samples at Jyndevad, never exceeded 0.1 µg/l. It should be noted that the concentration of PPU is likely to be underestimated by up to 22-47%. Results from the field-spiked samples thus indicate that PPU is unstable and may have further degraded to PPU-desamino during analysis (Rosenbom *et al.*, 2010a).

- Terbuthylazine as well as its degradation products leached through the root zone (1 m b.g.s.) at high average concentrations on loamy soils. At the three loamy soil sites Silstrup, Estrup, and Faardrup, desethyl-terbuthylazine leached from the upper meter entering the drainage water in average concentrations exceeding 0.1 µg/l (Table 15 and 16). Four years after application in 2005 at Estrup, both terbuthylazine and desethyl-terbuthylazine were detected in drainage water, but not exceeding 0.1 µg/l. At Silstrup (Kjær *et al.,* 2007) and Faardrup (Kjær *et al.*, 2009), desethyl-terbuthylazine was frequently detected in the monitoring screens situated beneath the drainage system (Table 17 and 18) at concentrations exceeding 0.1 µg/l during a 2- and 24-month period, respectively. Leaching at Estrup (Kjær *et al.,* 2007) was confined to the drainage depth, however. Minor leaching of desethyl-terbuthylazine was also seen at the two sandy sites Jyndevad and Tylstrup, where desethyl-terbuthylazine was detected in low concentrations (<0.1 µg/l) in the soil water sampled 1 m b.g.s. While desethyl-terbuthylazine was not detected in the groundwater monitoring screens at Tylstrup, it was frequently detected in low concentration (< 0.1 µg/l) at Jyndevad (Table 18, Kjær *et al.,* 2004). Marked leaching of terbuthylazine was also seen at two of the three loamy sites (Estrup and Faardrup), the leaching pattern being similar to that of desethyl-terbuthylazine. 2-hydroxy-desethyl-terbuthylazine and Hydroxy-terbuthylazine leached at both Faardrup and Estrup and at the latter site the average drainage concentration exceeded 0.1 µg/l. Leaching of these two degradation products was at both sites confined to the drainage system. None of the two degradation products were detected in groundwater monitoring screen at Estrup, whereas at Faardrup both were found, but at low frequencies of detection and concentrations.

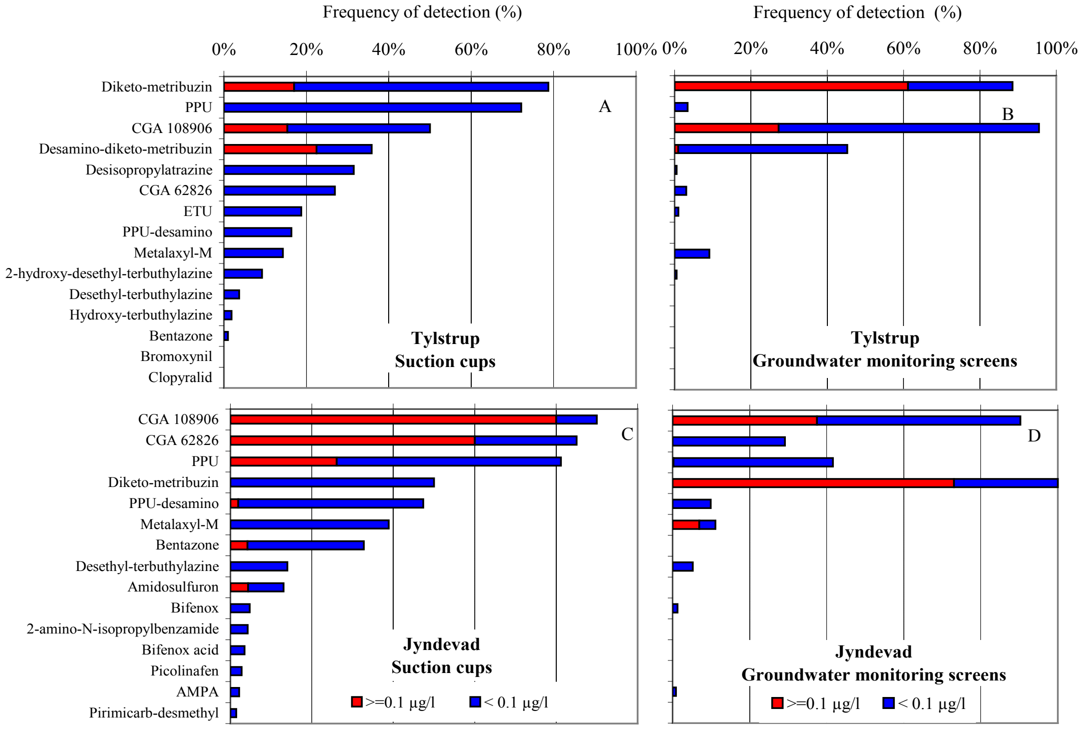


Figure 43. Frequency of detection in samples from the suction cups (left) and groundwater monitoring screens located deeper than the suction cups (right) at the sandy soil sites: **Tylstrup** (A, B) and **Jyndevad** (C, D). Frequency is estimated for the entire monitoring period and the length of time that the different pesticides have been included in the programme and the number of analysed samples thus varies considerably among the different pesticides. The figure only includes the fifteen most frequently detected pesticides. Pesticides monitored for less than one year are not included.

- Tebuconazole has been applied in autumn 2007 at Tylstrup, Jyndevad, Estrup and Faardrup. Only on the loamy soil of Estrup did it leach through the root zone (1 m b.g.s.) and into the drainage water in average concentrations exceeding 0.1 µg/l in an average yearly concentration of 0,44 µg/l (Table 15 and 16). Leaching was mainly confined to the depth of the drainage system, although the snow melt occurring in March 2011 (more than two years after application) induced leaching of tebuconazole to the groundwater monitoring well in concentrations exceeding 0.1 µg/l (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 a few samples from the groundwater monitoring screens (Table 17 and 18).

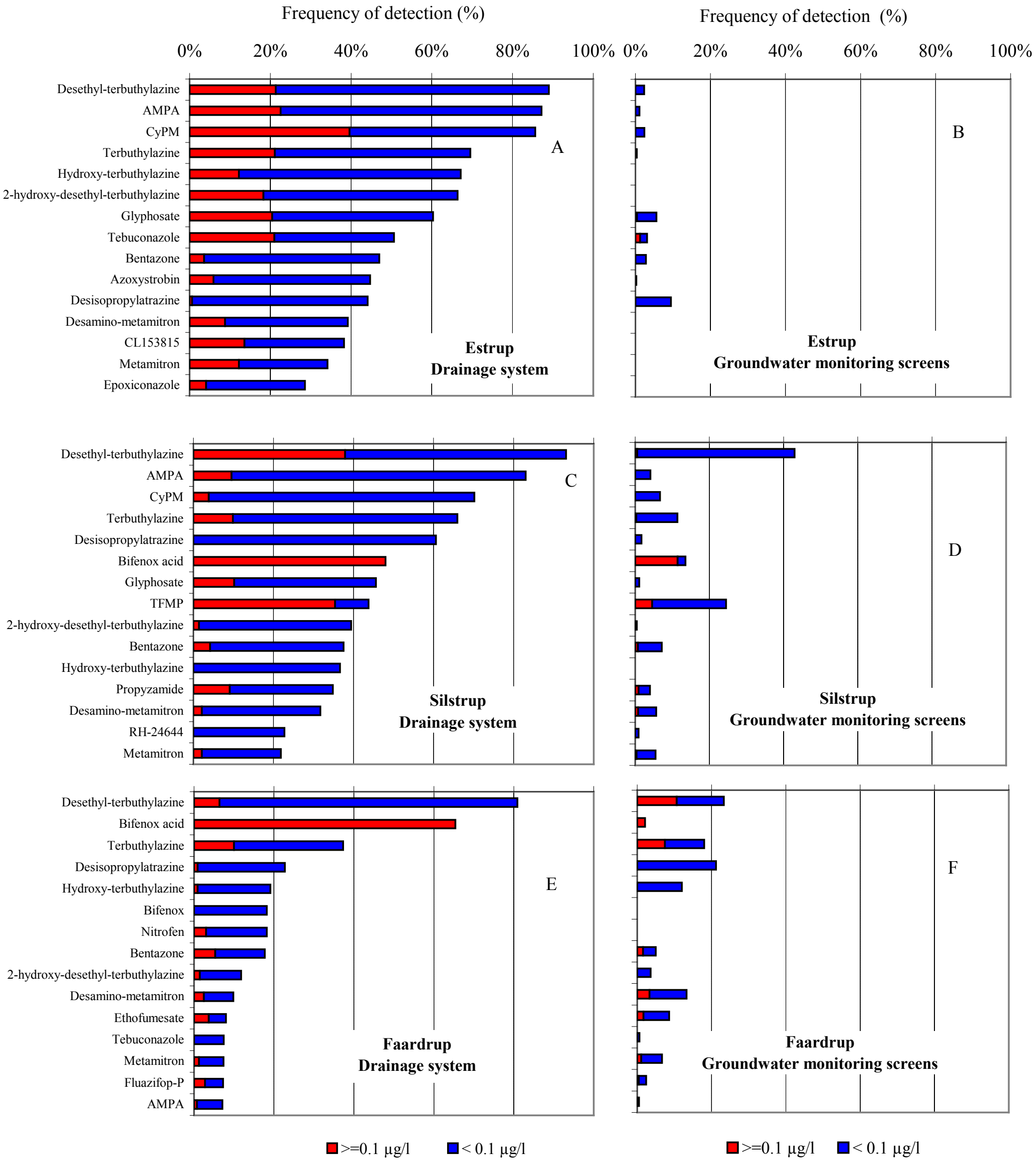


Figure 44. Frequency of detection in samples from the drainage system (left) and groundwater monitoring screens located deeper than the drainage system (right) at the loamy soil sites: **Estrup** (A, B), **Silstrup** (C, D) and **Faardrup** (E, F). Frequency is estimated for the entire monitoring period and the time that the different pesticides have been included in the programme and the number of analysed samples thus varies considerably among the different pesticides. The figure only includes the fifteen most frequently detected pesticides. Pesticides monitored for less than one year are not included.

The monitoring data also indicate leaching 1 m b.g.s. of a further 17 pesticides (or their degradation products), but often in low concentrations. Although the concentrations detected 1 m b.g.s. exceeded 0.1 µg/l in several samples, the average leaching concentration (1 m b.g.s.) did not. This is summarized in Table 15.

Table 16 show 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 17 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.

11 of the 43 pesticides applied – about 26% – did not leach at all from 1 m b.g.s. during the monitoring period (Table 15). 3 of the 11 were, however, detected in the groundwater monitoring screens (Table 17). The group of 11 includes the three different sulfonylureas – metsulfuron-methyl, triasulfuron, iodosulfuron-methyl-sodium and tribenuron-methyl applied at several sites. For example, tribenuron-methyl was applied at four different sites under different hydrological conditions, with percolation (1 m b.g.s.) during the first month after application ranging from 0 to 114 mm. The monitoring results give no indication of leaching for any of the compounds or their degradation products.

It should, however, be noted, that the leaching risk associated with an autumn application of tribenuron-methyl, where preferential transport is likely to occur, has not yet been evaluated for the loamy soils.

The leaching patterns of the sandy and loamy sites are further illustrated in Figure 43 and 44, 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 43 and 44), 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, which provide 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 macro pore 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 drainage system (Figure 44). Several pesticides were often detected in the drainage system, whereas the frequency of detection in the monitoring screens situated beneath the drainage system was lower and varied considerably between the three sites (Figure 44). 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 49, 91 and 64 samples containing glyphosate, desisopropyl-atrazine, and bentazone respectively, pesticides have only occasionally been detected in the screens beneath the drainage system (Appendix 5).

The differences are, however, largely attributable to the hydrological conditions. Compared to the Silstrup and Faardrup sites, the C horizon (situated beneath the drainage depth) at the Estrup site is less permeable with less preferential flow through macro pores (see Kjær *et al.* 2005c for details). The movement of water and solute may therefore be slower at Estrup, allowing for dispersion, dilution, sorption and degradation and thereby reducing the risk of transport to deeper soil layers. An indication thereof are the long periods with groundwater table beyond drainage depth in which an increasing lateral transport to the drainage system and decreased leaching to the deeper groundwater will occur.

Comparing the loamy sites, the number of drainage water samples containing pesticides/degradation products was 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 7, Table 9 and Table 11).

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

Parameter	Systematic chemical nomenclature
Aclonifen	2-chloro-6-nitro-3-phenoxyaniline
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
- *CyPM*	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
- *2-amino-N-isopropyl-benzamide*	2-amino-N-isopropyl-benzamide
Bromoxynil	3,5-dibromo-4-hydroxybenzonitrile
Bifenox	methyl 5-(2,4-dichlorophenoxy)-2-nitrobenzoate
- *Bifenox acid*	5-(2,4-dichlorophenoxy)-2-nitrobenzoic acid
- *Nitrofen*	2,4-dichlorophenyl 4'-nitrophenyl ether
Chlormequat	2-chloroethyltrimethylammonium chloride
Clomazone	2-[(2-chlorphenyl)methyl]-4,4-dimethyl-3-isoxazolidione
- *FMC65317*	(N-[2- chlorophenol)methyl] -3-hydroxy-2,2- dimethyl propanamide*(Propanamide-clomazone)*
Clopyralid	3,6-Dichloropyridine-2-carboxylic acid
Cyafamid	4-chloro-2-cyano-N,N-dimethyl-5-p-tolylimidazole-1-sulfonamide
Desmedipham	Ethyl 3-(phenylcarbamoyloxy)phenylcarbamate
- *EHPC*	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
- *Fluazifop-P*[2)]	(R)-2-(4-((5-(trifluoromethyl)-2-pyridinyl)oxy)phenoxy-propanoic acid
- *TFMP*[2)]	5-trifluoromethyl-pyridin-2-ol
Epoxiconazole	(2RS, 3SR)-1-(2-(2-chlorophenyl)-2,3-epoxy-2-(4-fluorophenyl)propyl)-1H-1,2,4-triazol
- *ETU*[1)]	Ethylenethiourea
Fenpropimorph	Cis-4-[3-[4-(1,1-dimethylethyl)-phenyl]-2-methylpropyl]-2,6-imethylmorpholine
- *Fenpropimorph acid*	Cis-4-[3-[4-(2-carboxypropyl)-phenyl]-2-methylpropyl]-2,6-dimethylmorpholine
Flamprop-M-isopropyl	Isopropyl N-benzoyl-N-(3-chloro-4-flourophenyl)-D-alaninate
- *Flamprop*	N-benzoyl-N-(3-chloro-4-flourophenyl)-D-alanine
Florasulam	2’,6’,8-Trifluoro-5-methoxy-s-triazolo [1,5-c]pyrimidine-2-sulfonanilide
- *Florasulam-desmethyl*	N-(2,6-difluorophenyl)-8-fluro-5-hydroxy[1,2,4]triazolo[1,5-c]pyrimidine-2-sulfonamide
Fluroxypyr	(4-amino-3,5-dichloro-6-fluro-2-pyridinyl)oxy]acetic acid
Glyphosate	N-(phosphonomethyl)glycine
- *AMPA*	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
- *Triazinamin*	2-amino-4-methoxy-6-methyl-1,3,5-triazine
- *Metsulfuron-methyl*	Methyl2-[[[[(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
- *2-methyl-4-chlorophenol*	2-methyl-4-chlorophenol
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
- *Desamino-metamitron*	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
- *Desamino-metribuzin*	6-(1,1-dimethylethyl)-3-(methylthio)- 1,2,4-triazin-5-(4H)-one
- *Desamino-diketo-metribuzin*	6-tert-butyl-4,5-dihydro-3-methylthio-1,2,4-triazine-3,5-dione
- *Diketo-metribuzin*	4-amino-6-tert-butyl-4,5-dihydro-1,2,4-triazine-3,5-dione
Metalaxyl-M	methyl N-(methoxyacetyl)-N-(2,6-xylyl)-D-alaninate
-*CGA 62826*	2-[(2,6-dimethylphenyl)(methoxyacetyl)amino]propanoic acid
- *CGA 108906*	2-[(1-carboxyethyl)(methoxyacetyl)amino]-3-methylbenzoic acid
Metsulfuron-methyl	Methyl2-[[[[(4-methoxy-6-methyl-1,3,5-triazine-2-yl)amino]=carbonyl]amino]-sulfonyl]benzoic acid
- *Mesosulfuron*	2-[[[[(4,6-dimethoxy-2-pyrimidinyl)amino]carbonyl]amino]sulfonyl]-4-[[(methylsulfonyl)amino]methyl]benzoic acid

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

Parameter	Systematic chemical nomenclature
Pendimethalin	N-(1-ethyl)-2,6-dinitro-3,4-xynile
Phenmedipham	3-[(methoxycarbonyl)amino]phenyl (3-methylphenyl)carbamate
- *MHPC*	Methyl-N-(3-hydoxyphenyl)-carbamate
- *3-aminophenol*	1-amino-3-hydroxybenzene
- *PHCP*3)	3-phenyl-4-hydroxy-6-chloropyridazine
Picolinafen	4'-fluoro-6-(α,α,α-trifluoro-m-tolyloxy)pyridine-2-carboxanilide
- *CL153815*	6-(3-trifluoromethylphenoxy)-2-pyridine carboxylic acid
Pirimicarb	2-(dimethylamino)-5,6-dimethyl-4-pyrimidinyldimethylcarbamate
- *Pirimicarb-desmethyl*	2-(dimethylamino)-5,6-dimethyl-4-pyrimidinylmethylcarbamate
- *Pirimicarb-desmethyl-formamido*	2-methylformamido-5,6-dimethylpyrimidine-4-yl dimethylcarbamate
Propiconazole	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
- *RH-24644*	2-(3,5-dichlorophenyl)-4,4-dimethyl-5-methylene-oxalzoline
- *RH-24580*	N-(1,1-dimethylacetonyl)-3,5-dichlorobenzamide
- *RH-24655*	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,-trifluro=propyl)phenylsulfonyl]urea
Rimsulfuron	N-[[(4,6-dimethoxy-2-pyrimidinyl)amino]carbonyl]-3-(ethylsulfonyl)-2-pyridinesulfonamide
- *PPU*	N-(4,6-dimethoxy-2-pyrimidinyl-N-((3-ethylsulfonyl)-2-pyridinyl)urea (IN70941)
- *PPU-desamino*	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
- *Desethyl-terbuthylazine*	6-chloro-N-(1,1-dimethylethyl)-1,3,5,triazine-2,4-diamine
- *Desisopropyl-atrazine*	6-chloro-N-ethyl-1,3,5,triazine-2,4-diamine
- *2-hydroxy-desethyl-terbuthylazine*	6-hydroxy-N-(1,1-dimethylethyl)-1,3,5,triazine-2,4-diamine
- *Hydroxy-terbuthylazine*	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-cholro-thiazol-5-ylmethyl)-5-methyl[1,3,5]oxadiazinan-4ylidene-N-nitroamine
- CGA 322704	[C(E)]-N-[(2-chloro-5-thiazolyl)methyl]-N'-methyl-N'-nitroguanidine
- *Triazinamin-methyl*4)	*4-methoxy-6-methyl-1,3,5-triazin-methylamine*
Thiacloprid	*(Z)-3-(6-chloro-3-pyridylmethyl)-1,3-thiazolidin-2-ylidenecyanamide*
-Thiacloprid sulfonic acid	*sodium 2-[[[(aminocarbonyl)amino]-carbonyl][(6-chloro-3-pyridinyl)-methyl]amino]ethanesulfonate*
-Thiacloprid-amide	*(3-[(6-chloro-3-pyridinyl)methyl]-2-thiazolidinylidene) urea*
-M34	*2-{carbamoyl[(6-chloropyridin-3-yl)methyl]amino}etanesulfonic acid*
Triflusulfuron-methyl	methyl 2-[4-dimethylamino-6-(2,2,2-trifluoroethoxy)-1,3,5-triazin-2-ylcarbamoylsulfamoyl]-m-toluate
- *IN-E7710*	N-methyl-6-(2,2,2-trifluoroethoxy)-1,3,5-triazine-2,4-diamine
- *IN-D8526*	N,N-dimethyl-6-(2,2,2-trifluoroethoxy)-1,3,5-triazine-2,4-diamine
- *IN-M7222*	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 fluazifop-P-butyl.*

3) *Degradation product of pyridate.*

4) *Degradation product of tribenuron-methyl.*

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

Until March 2002, pesticide analysis was performed monthly on water samples from the suction cups located both 1 m b.g.s. and 2 m b.g.s., from two screens of the horizontal monitoring wells and from two of the downstream vertical monitoring wells. In addition, more intensive monitoring encompassing all four groups of suction cups, six screens of the horizontal monitoring wells and five monitoring wells was performed every four months (Kjær *et al.*, 2002). At the loamy sites, the pesticide analysis was also performed on drainage water samples.

The monitoring programme was revised in March 2002 and the number of pesticide analyses was reduced. At the loamy sites, pesticide analysis of water sampled from the suction cups was ceased, and the monthly monitoring was restricted to just one monitoring well. At Jyndevad, pesticide analysis of the suction cups located 2 m b.g.s. was ceased and the interval for the intensive monitoring encompassing the larger number of monitoring screens was extended to six months, except for the suction cups 2 m b.g.s. at Tylstrup, where the four-month interval was retained (Kjær *et al.*, 2003).

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

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

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

Site	Monthly monitoring (Intensive)	Half-yearly monitoring (Extensive)	Not monitored
Tylstrup	M4, M5, S1a, S2a	M1, M3, M4, M5, S1a, S2a, S1b*, S2b*	M2, **M6**, M7
Jyndevad	M1, M4, S1a, S2a	M1, M2, M4, M5, M7, S1a, S2a	M3, **M6**, S1b, S2b
Silstrup	M5, H1.2	M5, M9, M10, M12, H1.1, H1.2, H1.3	M1, M2, M4,**M6**, M8, M7,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, M5, 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.

**At Tylstrup suctions cups installed 2 m b.g.s are monitored four times a year (see text).*

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

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

$$M_i = C_i \cdot V_i$$

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

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

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

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

where:
n = Number of weeks within the period of continuous drainage runoff.
V_i= Weekly accumulated drainage runoff (mm/week).
Vf_i = Drainage runoff accumulated during a “flow event” (mm/storm event).
Cf_i = Pesticide concentration in the “event samples” collected by means of the flow-proportional sampler (µg/l).
Ct_i = Pesticide concentration in the weekly samples collected by means of the time-proportional sampler (µg/l).

Table 3, 5, 7, 9 and 11 report the weighted average leachate concentration in the drainage water within the first drainage season after application. In these tables this calculation period is defined as the period from application until 1 July the following year, as pesticides are usually present in the first drainage runoff occurring after application of pesticide.

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

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

where
t = sampling date; $t_1 = 0.5(t_{i-1}+t_i)$; $t_2=0.5(t_i+t_{i+1})$
P_t = daily percolation at 1 m b.g.s. as estimated by the MACRO model (mm)

The average concentration was estimated according to the equation:

$$C = \frac{\sum C_i \cdot P_i}{\sum P_i}$$

where
C_i = measured pesticide concentration in the suction cups located 1 m b.g.s.

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

Table A3.1. Management practice at **Tylstrup** during the 2008 to 2010 growing seasons. The active ingredients of the various pesticides are indicated in parentheses.

Date	Management pratice
14.10.08	Stubbleharrowed - depth 7.0 cm
10.04.09	Ploughed - depth 24 cm.
10.04.09	Rolled with concrete roller
14.04.09	Spring barley sown, cv. Keops, seeding rate 170 kg/ha, sowing depth 2.5 cm, row distance 13 cm. Using combine driller with a tubular packer roller, Finalplant number 392 /m2
15.05.09	Basagran M75 (bentazone+MCPA) - weeds - 1.5 l/ha
23.06.09	Amistar (azoxystrobin) - fungi - 1.0 l/ha
08.07.09	Insecticide - 0.1 l/ha Mavrik (tau-fluvalinat) (not analyzed)
08.07.09	Irrigation - 27mm
20.08.09	Harvest of spring barley. Grain yield 53.4 hkg/ha, 85% DM
28.08.09	Straw remowed, yield 17.4 hkg/ha 100% DM
04.04.10	Ploughed - 24 cm depth
26.04.10	Rolled with concrete roller
04.05.10	Seed bed preparation - 10 cm depth
06.05.10	Planting of potatoes - cv. Kuras
17.05.10	Ridging
26.05.10	Herbicides - 1.0 l/ha Fenix (aclonifen) + 10 g/ha Titus WSB (rimsulfuron)
08.06.10	Herbicide - 20 g/ha Titus WSB (rimsulfuron)
15.06.10	Fungicide - 0.2 l/ha Ranman (cyazofamid)
24.06.10	Fungicide - 0.2 l/ha Ranman (cyazofamid)
01.07.10	Fungicide - 0.2 l/ha Ranman (cyazofamid)
06.07.10	Irrigation - 29 mm
09.07.10	Fungicide - 2.0 kg/ha Ridomil Gold MZ Pepite (mancozeb - metalaxyl) (mancozeb not analyzed)
16.07.10	Fungicide - 0.2 l/ha Ranman (cyazofamid)
23.07.10	Fungicide - 0.2 l/ha Ranman (cyazofamid)
27.07.10	Irrigation - 28 mm
02.08.10	Fungicide - 0.2 l/ha Ranman (cyazofamid)
09.08.10	Fungicide - 2.0 kg/ha Dithane NT (mancozeb) (not analyzed)
17.08.10	Fungicide - 2.0 kg/ha Dithane NT (mancozeb) (not analyzed)
23.08.10	Fungicide - 2.0 kg/ha Dithane NT (mancozeb) (not analyzed)
20.10.10	Harvest of potatoes. Tuber yield 128.0 hkg/ha, 100% DM
17.04.11	Ploughed - 24 cm depth
18.04.11	Rolled with concrete roller
19.04.11	Seed bed preparation - 8 cm depth
19.04.11	Spring barley sown, cv.TamTam
10.05.11	Herbicides - 0.4 l/ha Oxitril CM (ioxynil + bromoxynil) (not analyzed)
20.06.11	Fungicide - 1.5 L/ha Bell (boscalid + epoxiconazol) (epoxiconazol not analyzed)

Table A3.2. Management practice at **Jyndevad** during the 2008 to 2011 growing seasons. The active ingredients of the various pesticides are indicated in parentheses.

Date	Management practice
07.05.08	Irrigation - 42 mm
14.05.08	Irrigation - 27 mm
21.05.08	Irrigation - 27 mm
30.05.08	Irrigation - 30 mm
05.06.08	Irrigation - 35 mm
11.06.08	Fungicide - 1.0 l/ha Amistar (azoxystrobin)
25.06.08	Irrigation - 35 mm
08.07.08	Irrigation - 30 mm
30.08.08	Winter wheat harvested (seed yield 68.1 hkg/ha 85% DM, straw yield 28.1 hkg/ha 100% DM)
17.03.09	Ploughed - 22 cm depth
18.03.09	Rolled with a concrete roller
18.03.09	Spring barley sown cv. Simba
27.04.09	Herbicide - 1.2 l/ha Fox 480 SC (bifenox)
11.05.09	Herbicide - 1.5 l/ha Basagran M75 (bentazone+ MCPA)
26.05.09	Fungicide - 1.5 l/ha Bell (boscalide + epoxiconazole)
27.05.09	Irrigation - 30 mm
05.06.09	Irrigation - 27 mm
29.06.09	Irrigation - 27 mm
07.08.09	Harvest of spring barley. Grain yield 64.0 hkg/ha 85% DM, straw yield 19.5 hkg/ha 100% DM
14.04.10	Ploughed. Depth 24 cm
15.04.10	Rolled with concrete roller
22.04.10	Seedbed preparation - 9 cm depth
04.05.10	Planting of potatoes - cv. Kuras
04.05.10	Ridging
27.05.10	Herbicides - 1.0 l/ha Fenix (aclonifen) + 10 g/ha Titus WSB (rimsulfuron)
08.06.10	Herbicide - 20 g/ha Titus WSB (rimsulfuron)
24.06.10	Irrigation - 25 mm
28.06.10	Fungicide - 0.2 l/ha Ranman (cyazofamid)
30.06.10	Irrigation - 25 mm
06.07.10	Fungicide - 0.5 l/ha Amistar (azoxystrobin) (not analyzed)
07.07.10	Fungicide - 0.2 l/ha Ranman (cyazofamid)
08.07.10	Irrigation - 30 mm
14.07.10	Fungicide - 0.2 l/ha Ranman (cyazofamid)
16.07.10	Pesticide - 0.3 kg/ha Karate 2,5 WG (Lambda-cyhalothrin) (not analyzed)
25.07.10	Fungicide - 2.0 kg/ha Ridomil Gold MZ Pepite (metalaxyl + mancozeb) (mancozeb not analyzed)
01.08.10	Fungicide - 0.2 l/ha Ranman (cyazofamid)
09.08.10	Fungicide - 0.2 l/ha Ranman (cyazofamid)
16.08.10	Fungicide - 0.2 l/ha Ranman (cyazofamid)
23.08.10	Fungicide - 2.0 l/ha Tyfon (propamocarb + fenamidon) (not analyzed)
31.08.10	Fungicide - 2.0 kg/ha Dithane NT (mancozeb) (not analyzed)
10.09.10	Fungicide - 2.0 kg/ha Dithane NT (mancozeb) (not analyzed)
23.09.10	Fungicide - 0.4 l /ha Shirlan (fluazinam) (not analyzed)
19.10.10	Harvest of potatoes Tuber yield 120.6 hkg/ha, 100% DM
22.03.11	Ploughed - 24 cm depth
23.03.11	Spring barley sown - cv. Quench
24.03.11	Rolled with concrete roller
26.04.11	Herbicides - 0.5 l/ha Oxitril CM (bromoxynil + ioxynil) (not analyzed) + 0.25 l/ha DFF (diflufenican)
02.05.11	Irrigation - 30 mm
23.05.11	Irrigation - 32 mm

Table A3.3. Management practice at **Silstrup** during the 2008 to 2011 growing seasons. The active ingredients of the various pesticides are indicated in parentheses.

Date	Management practice
07.05.08	Fodder beet sown - cv. Kyros
22.05.08	Herbicide - 30 g/ha Safari (triflusulfuron) + 0.5 l/ha Goliath (metamitron) + 1.5 l/ha Betanal (phenmedipham)
30.05.08	Herbicide - 30 g/ha Safari (Triflusulfuron-methyl) + 0.5 l/ha Goliath (metamitron) + 1.5 l/ha Betanal (phenmedipham) + 0.07 l/ha Tramat 500 SC (ethofumesate)
17.06.08	Herbicide - 30 g/ha Safari (Triflusulfuron-methyl) + 0.5 l/ha Goliath (metamitron) + 1.5 l/ha Betanal (phenmedipham) + 0.07 l/ha Tramat 500 SC (ethofumesate)
26.06.08	Insecticide - 0.30kg/ha Pirimor G (pirimicarb)
01.07.08	Herbicide - 3.0 l/ha Fusilade Max (fluazifop-P-butyl)
04.07.08	Herbicide - 30 g/ha Safari (Triflusulfuron-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)
16.07.09	Wholecrop harvest of spring barley - 94.6 hkg/ha 100% DM
24.08.09	Herbicide - 0.020 l/ha Hussar OD (iodosulfuron)
09.09.09	Herbicide - 1.5 l/ha Fox 480 SC (bifenox)
02.05.10	Herbicide - 1.5 l/ha Fusilade Max (fluazifop-P-butyl)
05.05.10	Herbicides - 0.1 l/ha Hussar OD (iodosulfuron) + 0.7 l/ha SweDane MCPA 750 (not analyzed)
20.07.10	Harvest of grass. Seed yield 16.5 hkg/ha, 87% DM
21.07.10	Straw burned, 69.3 hkg/ha, 100% DM
15.04.11	Herbicide - 0.05 l/ha Hussat OD (iodosulfuron) (not analyzed)
26.04.11	Herbicide - 1.5 l/ha Fusilade Max (fluazifop-P-butyl)

Table A3.4. Management practice at **Estrup** during the 2008 to 2011 growing seasons. The active ingredients of the various pesticides are indicated in parentheses.

Date	Management practice
13.06.08	Fungicide - 1.0 Amistar (azoxystrobin)
16.08.08	Winter wheat harvested (seed yield 83.8 hkg/ha 85% DM)
16.08.08	Straw shredded - 40.7 hkg/ha 100% DM
12.03.09	Ploughed - depth 18 cm - packed with a ring roller
06.04.09	Tracer - 30 kg/ha potassium bromide
08.04.09	Spring barley sown - cv. Keops
08.04.09	Rolled with a cambridge roller
01.05.09	Herbicide - 1.2 l/ha Fox 480 SC (bifenox)
14.05.09	Herbicide - 1.5 l/ha Basagran M75 (bentazone/MCPA)
04.06.09	Fungicide - 1.0 l/ha Amistar (azoxystrobin)
07.08.09	Spring barley harvested. Grain yield 71.4 hkg/ha, 85% DM,
07.08.09	Straw shredded. 39.9 hkg/ha, 100% DM
24.08.09	Ploughed - 20 cm depth - packed with a ring roller
24.08.09	Rotor harrowed - 4 cm depth
24.08.09	Winter rape sown - cv.Cabernet
25.08.09	Herbicide - 0.33 l/ha Command CS (clomazone)
30.09.09	Herbicide - 0.75 l/ha Fox 480 SC (bifenox)
09.10.09	Insecticide - 0.15 l/ha Cyperb (cypermethrin) (not analyzed)
20.04.10	Field partially resown with spring rape - cv. Pluto
10.05.10	Insecticide - 0.3 l/ha Biscay OD 240 (thiacloprid)
20.08.10	Winter rape harvested. Seed yield 38.3 hkg/ha, 91% DM
06.09.10	Rotor harrowed - 5 cm depth
14.09.10	Ploughed - 20 cm depth - packed with a ring roller
14.09.10	Seedbed preparation - 5 cm depth
14.09.10	Winter wheat sown cv. Frument
30.09.10	Herbicide - 1 tablet/ha Express ST (tribenuron-methyl)
26.04.11	Herbicide - 1.2 l/ha Fox 480 SC (bifenox)
09.05.11	Fungicide - 0.5 l/ha Flexity (metrafenon)
07.06.11	Fungicide - 0.5 l/ha Flexity (metrafenon)

Table A3.5. Management practice at **Faardrup** during the 2008 to 2011 growing seasons. The active ingredients of the various pesticides are indicated in parentheses.

Date	Management practice
10.08.07	Stubble cultivation - 15 cm depth
22.08.07	Stubble cultivation - 15 cm depth
18.09.07	Ploughed and packed - 25 cm depth
18.09.07	Winter wheat sown – cv. Ambition
09.10.07	Herbicide - 5.0 l/ha Stomp (pendimethalin)
20.11.07	Fungicide - 1.0 l/ha Folicur 250 (tebuconazole)
20.08.08	Winter wheat harvested (seed yield 89.6 hkg 85% DM, straw yield 65.2 hkg/ha 100% DM)
26.08.08	Tracer - 30 kg/ha potassium bromide
01.12.08	Ploughing - 23 cm depth
05.04.09	Sugar beet sown - cv. Palace
24.04.09	Herbicide - 1.5 l/ha Betanal (phenmedipham) + 1.0 l/ha Goliath (metamitron)
30.04.09	Herbicide - 10 g/ha Safari (Triflusulfuron-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 (Triflusulfuron-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)
06.10.09	Sugar beet harvested. Root yield 147.9 hkg/ha 100% DM, top yield 40.1 hkg/ha, 100% DM
01.11.09	Ploughing - 20 cm depth
07.04.10	Seed bed preparation - 6 cm depth
22.04.10	Spring barley sown - mixture of varieties. Undersown red fescue - cv Maximum
01.06.10	Herbicide - 1.25 l/ha Fighter 480 (bentazon)
02.07.10	Fungicide - 1.0 l/ha Amistar (azoxystrobin) (not analyzed)
21.08.10	Spring barley harvested. Grain yield 58.5 hkg/ha, 85% DM
21.08.10	Straw removed. Straw yield 27.5 hkg/ha
25.10.10	Herbicide - 1.5 l/ha Fox 480 SC (bifenox)
21.05.11	Herbicide - 1.5 l/ha Fusilade Max (fluazifop-P-butyl)

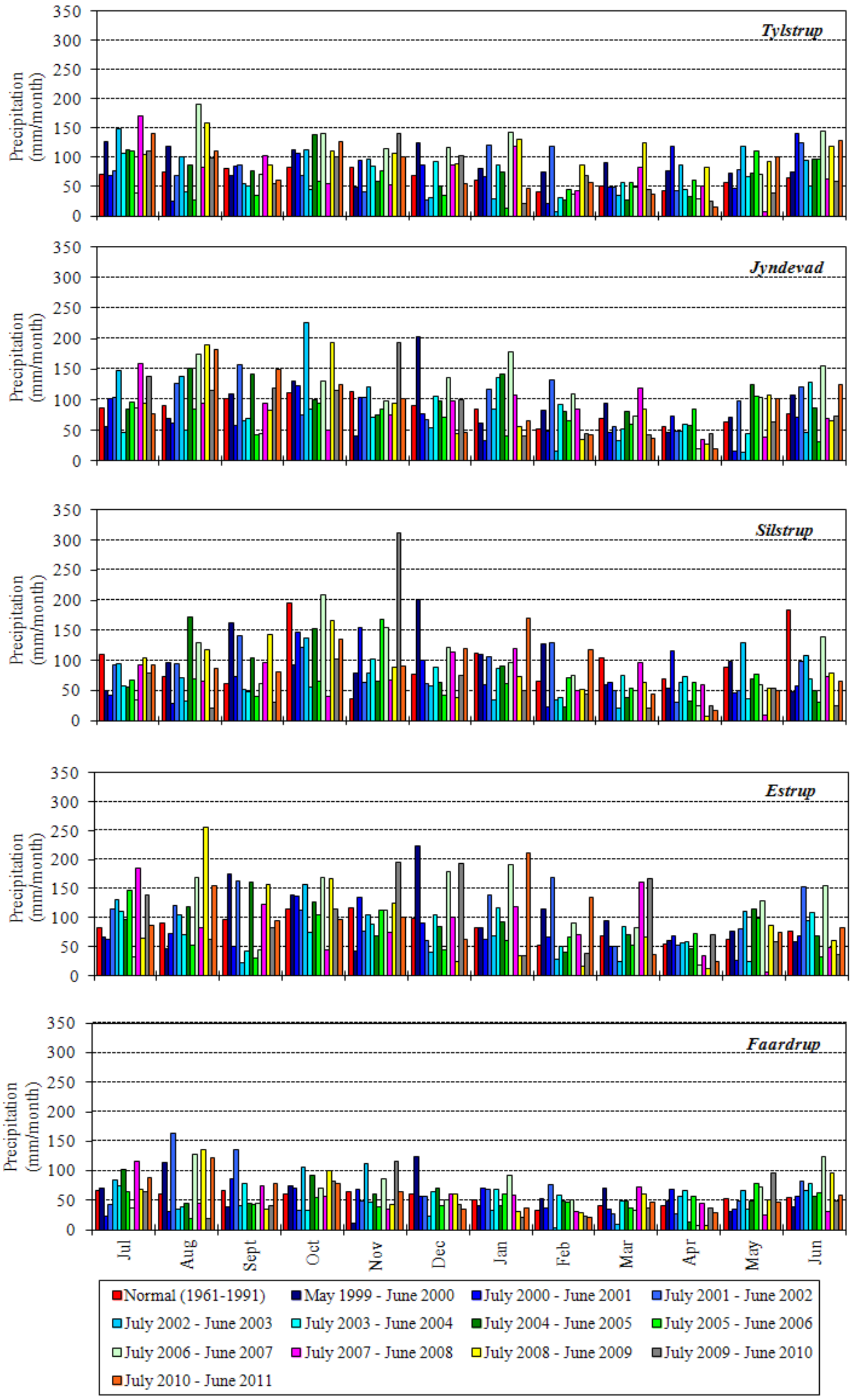

Figure A4.1. Monthly precipitation at all localities for the monitoring period July 2000–June 2010. Normal values (1961–1990) are included for comparison.

Table A5.1. Number of samples where pesticides were either not detected (nd), detected in concentrations below 0.1 µg/l (<0.1 µg/l) or detected in concentrations above 0.1 µg/l (>=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			Suction cups		
Parent	Compound	nd	<0.1 µg/l	>= 0.1µg/l	nd	<0.1 µg/	>= 0.1µg/l
Aclonifen	Aclonifen	66	.	.	36	.	.
Azoxystrobin	Azoxystrobin	216	.	.	95	.	.
	CyPM	216	.	.	95	.	.
Bentazone	2-amino-N-isopropylbenzamide	191	.	.	72	.	.
	Bentazone	330	.	.	136	1	.
Bromoxynil	Bromoxynil	192	.	.	72	.	.
Clomazone	Clomazone	224	.	.	82	.	.
	FMC 65317	208	.	.	76	.	.
Clopyralid	Clopyralid	77	.	.	78	.	.
Cyazofamid	Cyazofamid	66	.	.	36	.	.
Dimethoate	Dimethoate	176	.	.	63	.	.
Epoxiconazole	Epoxiconazole	199	.	.	74	.	.
Fenpropimorph	Fenpropimorph	307	.	.	89	.	.
	Fenpropimorph acid	276	.	.	73	.	.
Flamprop-M-isopropyl	Flamprop	176	.	.	63	.	.
	Flamprop-M-isopropyl	176	.	.	63	.	.
Fluazifop-P-butyl	Fluazifop-P	178	.	.	63	.	.
	TFMP	3	.	.			
Fluroxypyr	Fluroxypyr	194	.	.	69	.	.
Ioxynil	Ioxynil	198	.	.	72	.	.
Linuron	Linuron	270	.	.	67	.	.
Mancozeb	ETU	198	2	.	37	7	.
Metalaxyl-M	CGA 108906	3	45	18	16	12	6
	CGA 62826	64	2	.	27	7	.
	Metalaxyl-M	60	6	.	32	4	.
Metribuzin	Desamino-diketo-metribuzin	289	234	5	167	35	51
	Desamino-metribuzin	365	.	.	85	.	.
	Diketo-metribuzin	59	141	315	65	194	61
	Metribuzin	386	1	.	89	2	.
Pendimethalin	Pendimethalin	430	.	.	144	.	.
Pirimicarb	Pirimicarb	295	.	.	82	.	.
	Pirimicarb-desmethyl	295	.	.	81	.	.
	Pirimicarb-desmethyl-formamido	167	.	.	52	.	.
Propiconazole	Propiconazole	307	.	.	89	.	.
Propyzamide	Propyzamide	221	.	.	82	.	.
	RH-24580	221	.	.	82	.	.
	RH-24644	221	.	.	82	.	.
	RH-24655	157	.	.	58	.	.
Rimsulfuron	PPU	543	19	.	72	145	3
	PPU-desamino	562	.	.	180	40	.
	Rimsulfuron	178	.	.	65	.	.
Tebuconazole	Tebuconazole	195	1	.	77	.	.
Terbuthylazine	2-hydroxy-desethyl-terbuthylazine	190	1	.	67	5	.
	Desethyl-terbuthylazine	191	.	.	70	2	.
	Desisopropylatrazine	190	1	.	55	17	.
	Hydroxy-terbuthylazine	191	.	.	71	1	.
	Terbuthylazine	179	.	.	72	.	.
Thiamethoxam	CGA 322704	175	.	.	64	.	.
	Thiamethoxam	175	.	.	64	.	.
Triasulfuron	Triasulfuron	295	.	.	82	.	.
Tribenuron-methyl	Triazinamin-methyl	440	.	.	137	.	.

Table A5.2. Number of samples where pesticides were either not detected (nd), detected in concentrations below 0.1 µg/l (<0.1 µg/l) or detected in concentrations above 0.1 µg/l (>=0.1µg/l) at **Jyndevad**. Numbers are accumulated for the entire monitoring period, and pesticides monitored for less than one year are not included.

		Vertical			Suction cups		
Parent	Compound	nd	<0.1 µg/l	>= 0.1µg/l	nd	<0.1 µg/l	>= 0.1µg/l
Aclonifen	Aclonifen	72	.	.	18	.	.
Amidosulfuron	Amidosulfuron	88	.	.	20	2	1
	Desmethyl-amidosulfuron	88	.	.	23	.	.
Azoxystrobin	Azoxystrobin	233	.	.	65	.	.
	CyPM	233	.	.	65	.	.
Bentazone	2-amino-N-isopropylbenzamide	178	.	.	45	2	.
	Bentazone	436	.	.	80	34	5
Bifenox	Bifenox	157	2	.	40	2	.
	Bifenox acid*	107	.	.	28	1	.
	Nitrofen	159	.	.	42	.	.
Bromoxynil	Bromoxynil	218	.	.	61	.	.
Chlormequat	Chlormequat	14	.	.	28	.	.
Cyazofamid	Cyazofamid	72	.	.	18	.	.
Dimethoate	Dimethoate	190	.	.	52	.	.
Epoxiconazole	Epoxiconazole	323	1	.	90	.	.
Fenpropimorph	Fenpropimorph	253	1	.	78	1	.
	Fenpropimorph acid	260	.	.	79	.	.
Florasulam	Florasulam	191	.	.	54	.	.
	Florasulam-desmethyl				28	.	.
Fluazifop-P-butyl	Fluazifop-P	190	.	.	51	.	.
	TFMP	3	.	.			
Fluroxypyr	Fluroxypyr	193	.	.	55	.	.
Glyphosate	AMPA	221	2	.	68	1	.
	Glyphosate	223	.	.	69	.	.
Ioxynil	Ioxynil	218	.	.	61	.	.
MCPA	2-methyl-4-chlorophenol	210	.	.	56	.	.
	MCPA	210	.	.	56	.	.
Mesosulfuron-methyl	Mesosulfuron	12	.	.	45	.	.
	Mesosulfuron-methyl	285	.	.	78	.	.
Metalaxyl-M	CGA 108906	7	38	27	2	2	16
	CGA 62826	51	21	.	3	5	12
	Metalaxyl-M	64	3	5	11	7	.
Metribuzin	Desamino-diketo-metribuzin	6	7	13	6	.	.
	Desamino-metribuzin	26	.	.	4	.	.
	Diketo-metribuzin	.	7	19	3	3	.
	Metribuzin	26	.	.	6	.	.
Pendimethalin	Pendimethalin	257	.	.	71	.	.
Picolinafen	CL153815	35	.	.	36	.	.
	Picolinafen	35	.	.	35	1	.
Pirimicarb	Pirimicarb	251	.	.	69	.	.
	Pirimicarb-desmethyl	251	.	.	68	1	.
	Pirimicarb-desmethyl-formamido	251	.	.	69	.	.
Propiconazole	Propiconazole	293	.	.	89	.	.
Pyridate	PHCP	184	.	.	59	.	.
	Pyridate	116	.	.	39	.	.
Rimsulfuron	PPU	448	317	2	39	114	54
	PPU-desamino	691	76	.	109	94	4
	Rimsulfuron	189	.	.	52	.	.
Tebuconazole	Tebuconazole	213	1	.	58	.	.
Terbuthylazine	Desethyl-terbuthylazine	490	27	.	130	20	.
	Terbuthylazine	260	.	.	79	.	.
Tribenuron-methyl	Triazinamin-methyl	248	.	.	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 (nd), detected in concentrations below 0.1 µg/l (<0.1 µg/l) or detected in concentrations above 0.1 µg/l (>=0.1µg/l) at **Silstrup**. Numbers are accumulated for the entire monitoring period, and pesticides monitored for less than one year are not included.

		Drainage			**Horizontal**			**Vertical**			**Suction cups**		
Parent	Compound	nd	<0,1 µg/l	>= 0.1µg/l	nd	<0,1 µg/l	>= 0.1µg/l	nd	<0,1 µg/l	>= 0.1µg/l	nd	<0,1 µg/l	>= 0.1µg/l
Amidosulfuron	Amidosulfuron	1											
	Desmethyl-amidosulfuron	1	.	.									
Azoxystrobin	Azoxystrobin	71	10	.	106	.	.	202	.	.			
	CyPM	31	69	4	135	8	.	257	20	.			
Bentazone	2-amino-N-isopropylbenzamide	65	.	.	74	.	.	131	.	.			
	Bentazone	75	40	5	133	8	1	244	18	2			
Bifenox	Bifenox	30	1	.	31	.	.	61	5	.			
	Bifenox acid	13	.	12	26	1	4	57	1	7			
	Nitrofen	30	1	.	31	.	.	66	.	.			
Bromoxynil	Bromoxynil	1	.	.									
Chlormequat	Chlormequat	20	1	.	36	.	.	66	.	.			
Clopyralid	Clopyralid	44	.	.	67	.	.	124	.	.			
Desmedipham	Desmedipham	101	.	.	107	1	.	240	.	.	58	.	.
	EHPC	68	.	.	62	.	.	118	.	.	20	.	.
Dimethoate	Dimethoate	81	.	1	73	1	.	148	.	.	27	.	.
Epoxiconazole	Epoxiconazole	36	.	.	62	.	.	117	.	.			
Ethofumesate	Ethofumesate	127	14	1	169	2	.	355	3	.	54	3	2
Fenpropimorph	Fenpropimorph	82	.	.	74	.	.	148	.	.	27	.	.
	Fenpropimorph acid	81	1	.	74	.	.	147	.	.	27	.	.
Flamprop-M-isopropyl	Flamprop	73	7	.	74	.	.	148	.	.	26	.	.
	Flamprop-M-isopropyl	70	11	1	73	1	.	148	.	.	27	.	.
Fluazifop-P-butyl	Fluazifop-P	115	.	.	140	1	.	299	.	.	56	.	.
	TFMP	27	4	17	57	10	.	91	29	9			
Fluroxypyr	Fluroxypyr	50	.	.	74	.	.	142	.	.			
Glyphosate	AMPA	25	108	14	123	5	.	226	10	.	8	.	.
	Glyphosate	80	52	15	128	.	.	232	4	.	8	.	.
Iodosulfuron-methyl-sodium	Iodosulfuron-methyl-sodium	60	.	.	85	.	.	165	.	.			
	Metsulfuron-methyl	60	.	.	85	.	.	165	.	.			
Ioxynil	Ioxynil	1	.	.									
MCPA	2-methyl-4-chlorophenol	51	.	.	67	.	.	124	.	.			
	MCPA	51	.	.	67	.	.	123	.	.			
Metamitron	Desamino-metamitron	97	42	3	165	3	3	334	23	1	40	15	4
	Metamitron	111	28	3	161	10	.	339	17	2	40	10	9
Pendimethalin	Pendimethalin	91	14	.	122	.	.	223	.	.			
Phenmedipham	3-aminophenol	53	.	.	70	.	.	170	.	.	36	.	.
	MHPC	100	.	.	106	.	.	234	.	.	55	.	.
	Phenmedipham	101	.	.	108	.	.	240	.	.	59	.	.
Pirimicarb	Pirimicarb	160	14	.	210	.	.	433	3	.	59	.	.
	Pirimicarb-desmethyl	173	1	.	210	.	.	436	.	.	59	.	.
	Pirimicarb-desmethyl-formamido	141	.	.	160	.	.	308	.	.	20	.	.
Propiconazole	Propiconazole	76	6	.	74	.	.	148	.	.	27	.	.
Propyzamide	Propyzamide	43	17	6	75	2	1	143	5	1			
	RH-24580	64	2	.	78	.	.	149	.	.			
	RH-24644	51	15	.	77	1	.	148	1	.			
	RH-24655	66	.	.	78	.	.	149	.	.			
Prosulfocarb	Prosulfocarb	69	4	1	78	1	.	147	.	.			
Pyridate	PHCP	62	.	4	66	2	.	109	8	4			
Rimsulfuron	PPU	1	.	.									
	PPU-desamino	1	.	.									

Table A5.3 (continued). Number of samples where pesticides were either not detected (nd), detected in concentrations below 0.1 µg/l (<0.1 µg/l) or detected in concentrations above 0.1 µg/l (>=0.1µg/l) at **Silstrup**. Numbers are accumulated for the entire monitoring period, and pesticides monitored for less than one year are not included.

		Drainage			**Horizontal**			**Vertical**			**Suction cups**		
Parent	Compound	nd	<0,1 µg/l	>= 0.1µg/l	nd	<0,1 µg/l	>= 0.1µg/l	nd	<0,1 µg/l	>= 0.1µg/l	nd	<0,1 µg/l	>= 0.1µg/l
Terbuthylazine	2-hydroxy-desethyl-terbuthylazine	43	27	1	84	.	.	151	1	.			
	Desethyl-terbuthylazine	8	64	44	101	32	.	113	127	2			
	Desisopropylatrazine	28	43	.	84	.	.	148	4	.			
	Hydroxy-terbuthylazine	45	26	.	84	.	.	152	.	.			
	Terbuthylazine	31	51	9	107	5	.	173	30	1			
Tribenuron-methyl	Triazinamin-methyl	82	.	.	74	.	.	148	.	.	27	.	.
Triflusulfuron-methyl	IN-D8526	32	.	.	56	.	.	102	.	.			
	IN-E7710	27	5	.	56	.	.	102	.	.			
	IN-M7222	32	.	.	55	1	.	102	.	.			
	Triflusulfuron-methyl	32	.	.	56	.	.	102	.	.			

Table A5.4. Number of samples where pesticides were either not detected (nd), detected in concentrations below 0.1 µg/l (<0.1 µg/l) or detected in concentrations above 0.1 µg/l (>=0.1µg/l) at **Estrup**. Numbers are accumulated for the entire monitoring period, and pesticides monitored for less than one year are not included.

		Drainage			Horizontal			Vertical			Suction cups		
Parent	Compound	nd	<0,1 µg/l	>= 0.1µg/l	nd	<0,1 µg/l	>= 0.1µg/l	nd	<0,1 µg/l	>= 0.1µg/l	nd	<0,1 µg/l	>= 0.1µg/l
Amidosulfuron	Amidosulfuron	99	.	.		.	.	10 9	.	.			
Azoxystrobin	Azoxystrobin	131	92	14	111	.	.	354	1	.			
	CyPM	34	109	94	105	6	.	350	5	.			
Bentazone	2-amino-N-isopropylbenzamide	237	1	.	79	1	.	271	.	.	5	.	.
	Bentazone	177	145	12	122	15	.	439	1	.	3	2	2
Bifenox	Bifenox	41	2	1	34	.	.	81	.	.			
	Bifenox acid	35	4	8	33	.	.	81	.	.			
	Nitrofen	44	.	.	34	.	.	81	.	.			
Bromoxynil	Bromoxynil	136	1	2	41	.	.	125	.	.	3	.	.
Chlormequat	Chlormequat	45	1	.	18	.	.	56	.	.			
Clopyralid	Clopyralid	1	.	.									
Dimethoate	Dimethoate	88	.	.	42	.	.	159	.	.	23	.	.
Epoxiconazole	Epoxiconazole	35	12	2	19	.	.	69	.	.			
Ethofumesate	Ethofumesate	91	27	8	46	.	.	158	.	.			
Fenpropimorph	Fenpropimorph	82	1	.	39	.	.	151	.	.	23	.	.
	Fenpropimorph acid	82	.	.	34	.	.	124	.	.	17	.	.
Flamprop-M-isopropyl	Flamprop	119	13	.	55	.	.	209	.	.	23	.	.
	Flamprop-M-isopropyl	112	20	.	55	.	.	209	.	.	23	.	.
Florasulam	Florasulam	92	.	.	35	.	.	125	.	.			
	Florasulam-desmethyl	81	.	.	30	.	.	100	.	.			
Fluroxypyr	Fluroxypyr	87	1	2	34	.	.	120	1	.			
Glyphosate	AMPA	54	272	95	173	1	.	577	7	.	23	.	.
	Glyphosate	167	168	86	170	3	.	543	36	3	23	.	.
Iodosulfuron-methyl-sodium	Metsulfuron-methyl	131	.	.	55	.	.	209	.	.	22	1	.
Ioxynil	Ioxynil	119	15	5	41	.	.	125	.	.	3	.	.
MCPA	2-methyl-4-chlorophenol	102	1	.	34	.	.	112	.	.			
	MCPA	91	10	2	34	.	.	111	1	.			
Mesosulfuron-methyl	Mesosulfuron	74	.	.	24	.	.	83	.	.			
	Mesosulfuron-methyl	62	13	.	27	.	.	99	.	.			
Metamitron	Desamino-metamitron	76	38	11	46	.	.	158	.	.			
	Metamitron	81	27	15	46	.	.	158	.	.			
Pendimethalin	Pendimethalin	119	4	.	41	.	.	147	.	.	7	.	.
Picolinafen	CL153815	50	20	11	40	.	.	118	.	.			
	Picolinafen	64	17	.	40	.	.	118	.	.			
Pirimicarb	Pirimicarb	159	40	.	67	.	.	225	1	.	6	.	.
	Pirimicarb-desmethyl	199	.	.	67	.	.	226	.	.	6	.	.
	Pirimicarb-desmethyl-formamido	206	13	13	78	.	.	266	.	.	5	.	.
Propiconazole	Propiconazole	192	23	3	86	.	.	310	2	.	23	.	.
Tebuconazole	Tebuconazole	40	24	17	39	.	.	118	3	2			
Terbuthylazine	2-hydroxy-desethyl-terbuthylazine	44	63	24	50	.	.	180	.	.			
	Desethyl-terbuthylazine	18	111	35	59	7	.	232	.	.			
	Desisopropylatrazine	90	70	1	62	1	.	197	26	.			
	Hydroxy-terbuthylazine	43	72	16	50	.	.	180	.	.			
	Terbuthylazine	49	78	34	63	.	.	222	1	.			

Table A5.4 (continued). Number of samples where pesticides were either not detected (nd), detected in concentrations below 0.1 µg/l (<0.1 µg/l) or detected in concentrations above 0.1 µg/l (>=0.1µg/l) at **Estrup**. Numbers are accumulated for the entire monitoring period, and pesticides monitored for less than one year are not included.

		Drainage			**Horizontal**			**Vertical**			**Suction cups**		
Parent	Compound	nd	<0,1 µg/l	>= 0.1µg/l	nd	<0,1 µg/l	>= 0.1µg/l	nd	<0,1 µg/l	>= 0.1µg/l	nd	<0,1 µg/l	>= 0.1µg/l
Thiacloprid	M34	24	.	.	18	.	.	36	.	.			
	Thiacloprid	18	.	.	18	.	.	37	.	.			
	Thiacloprid sulfonic acid	23	.	.	18	.	.	36	.	.			
	Thiacloprid-amide	18	.	.	18	.	.	37	.	.			
Tribenuron-methyl	Triazinamin-methyl	16	2	.	14	.	.	31	.	.			

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

		Drainage			Horizontal			Vertical			Suction cups		
Parent	Compound	nd	<0,1 µg/l	>= 0.1µg/l	nd	<0,1 µg/l	>= 0.1µg/l	nd	<0,1 µg/l	>= 0.1µg/l	nd	<0,1 µg/l	>= 0.1µg/l
Azoxystrobin	Azoxystrobin	106	.	.	92	.	.	194	.	.			
	CyPM	102	4	.	92	.	.	194	.	.			
Bentazone	2-amino-N-isopropylbenzamide	67	1	.	61	.	.	132	.	.			
	Bentazone	93	14	6	74	5	1	174	4	3			
Bifenox	Bifenox	27	6	.	13	.	.	35	.	.			
	Bifenox acid	9	.	17	12	.	1	34	.	.			
	Nitrofen	27	5	1	13	.	.	35	.	.			
Bromoxynil	Bromoxynil	101	.	.	81	.	.	225	.	.	73	.	.
Clomazone	Clomazone	84	.	1	69	.	.	166	.	.			
	FMC 65317	84	.	1	69	.	.	166	.	.			
Desmedipham	Desmedipham	99	.	.	66	.	.	165	.	.	29	.	.
	EHPC	83	.	.	52	.	.	123	.	.	16	.	.
Dimethoate	Dimethoate	77	.	.	58	.	.	148	.	.			
Epoxiconazole	Epoxiconazole	81	.	.	66	.	.	143	.	.			
Ethofumesate	Ethofumesate	150	7	6	104	.	.	226	25	6	27	2	.
Fenpropimorph	Fenpropimorph	101	.	.	80	1	.	225	.	.	73	.	.
	Fenpropimorph acid	101	.	.	81	.	.	225	.	.	73	.	.
Flamprop-M-isopropyl	Flamprop	76	1	.	58	.	.	148	.	.			
	Flamprop-M-isopropyl	70	1	.	56	.	.	142	.	.			
Fluazifop-P-butyl	Fluazifop-P	102	5	3	72	.	.	173	5	1	26	3	.
	Fluazifop-P-butyl	99	.	.	66	.	.	165	.	.	29	.	.
	TFMP				7	.	.	16	.	.			
Fluroxypyr	Fluroxypyr	182	.	1	146	1	.	368	.	.	73	.	.
Glyphosate	AMPA	131	9	1	110	.	.	282	2	.	57	5	.
	Glyphosate	137	4	.	109	1	.	282	2	.	61	1	.
Ioxynil	Ioxynil	99	1	.	81	.	.	224	1	.	73	.	.
MCPA	2-methyl-4-chlorophenol	142	.	1	109	.	.	254	.	.			
	MCPA	141	1	1	109	.	.	255	.	.			
Metamitron	Desamino-metamitron	147	12	4	104	.	.	209	36	12	29	.	.
	Metamitron	151	10	2	104	.	.	233	20	4	29	.	.
Pendimethalin	Pendimethalin	55	2	.	55	.	.	125	.	.			
Phenmedipham	MHPC	97	1	1	66	.	.	164	1	.	29	.	.
	Phenmedipham	99	.	.	66	.	.	163	2	.	29	.	.
Pirimicarb	Pirimicarb	148	7	.	116	.	.	318	2	.	73	.	.
	Pirimicarb-desmethyl	94	6	.	66	.	.	162	3	.	29	.	.
	Pirimicarb-desmethyl-formamido	97	3	.	66	.	.	163	2	.	29	.	.
Propiconazole	Propiconazole	178	.	.	138	.	.	372	1	.	73	.	.
Propyzamide	Propyzamide	70	2	2	68	1	.	155	.	.			
	RH-24580	74	.	.	69	.	.	155	.	.			
	RH-24644	70	4	.	69	.	.	155	.	.			
	RH-24655	73	1	.	69	.	.	155	.	.			
Prosulfocarb	Prosulfocarb	78	.	.	61	.	.	126	.	.			
Tebuconazole	Tebuconazole	50	4	.	53	.	.	120	1	.			
Terbuthylazine	2-hydroxy-desethyl-terbuthylazine	60	7	1	60	1	.	126	6	.			
	Desethyl-terbuthylazine	21	82	7	68	21	.	149	15	30			
	Desisopropylatrazine	85	24	1	57	32	.	166	28	.			
	Hydroxy-terbuthylazine	89	20	1	85	4	.	164	30	.			
	Terbuthylazine	69	30	11	83	5	1	149	25	20			
Thiamethoxam	CGA 322704	68	.	.	58	.	.	126	.	.			
	Thiamethoxam	68	.	.	58	.	.	126	.	.			

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

		Drainage			**Horizontal**			**Vertical**			**Suction cups**		
Parent	Compound	nd	<0,1 µg/l	>= 0.1µg/l	nd	<0,1 µg/l	>= 0.1µg/l	nd	<0,1 µg/l	>= 0.1µg/l	nd	<0,1 µg/l	>= 0.1µg/l
Tribenuron-methyl	Triazinamin-methyl	77	.	.	57	.	.	147	.	.			
Triflusulfuron-methyl	IN-D8526	63	.	.	38	.	.	92	.	.			
	IN-E7710	63	.	.	38	.	.	92	.	.			
	IN-M7222	63	.	.	38	.	.	92	.	.			
	Triflusulfuron-methyl	63	.	.	38	.	.	92	.	.			

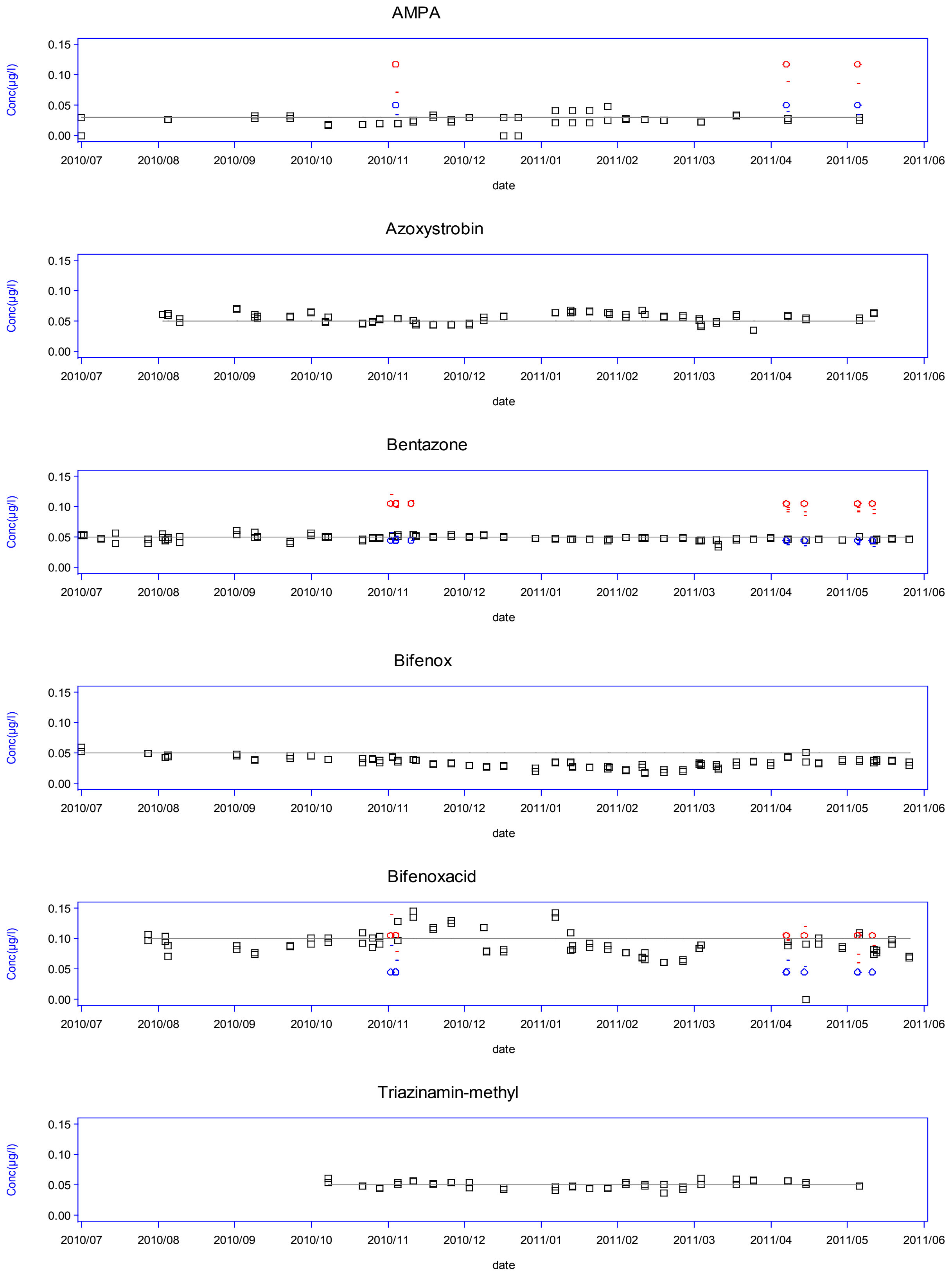

Figure A6.1. Quality control data for pesticide analysis by laboratory 1. Internal laboratory control samples are indicated by square symbols and the nominal level is indicated by the solid grey line (■ IQ measured, — IQ nominal concentration). External control samples are indicated by circles. Open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

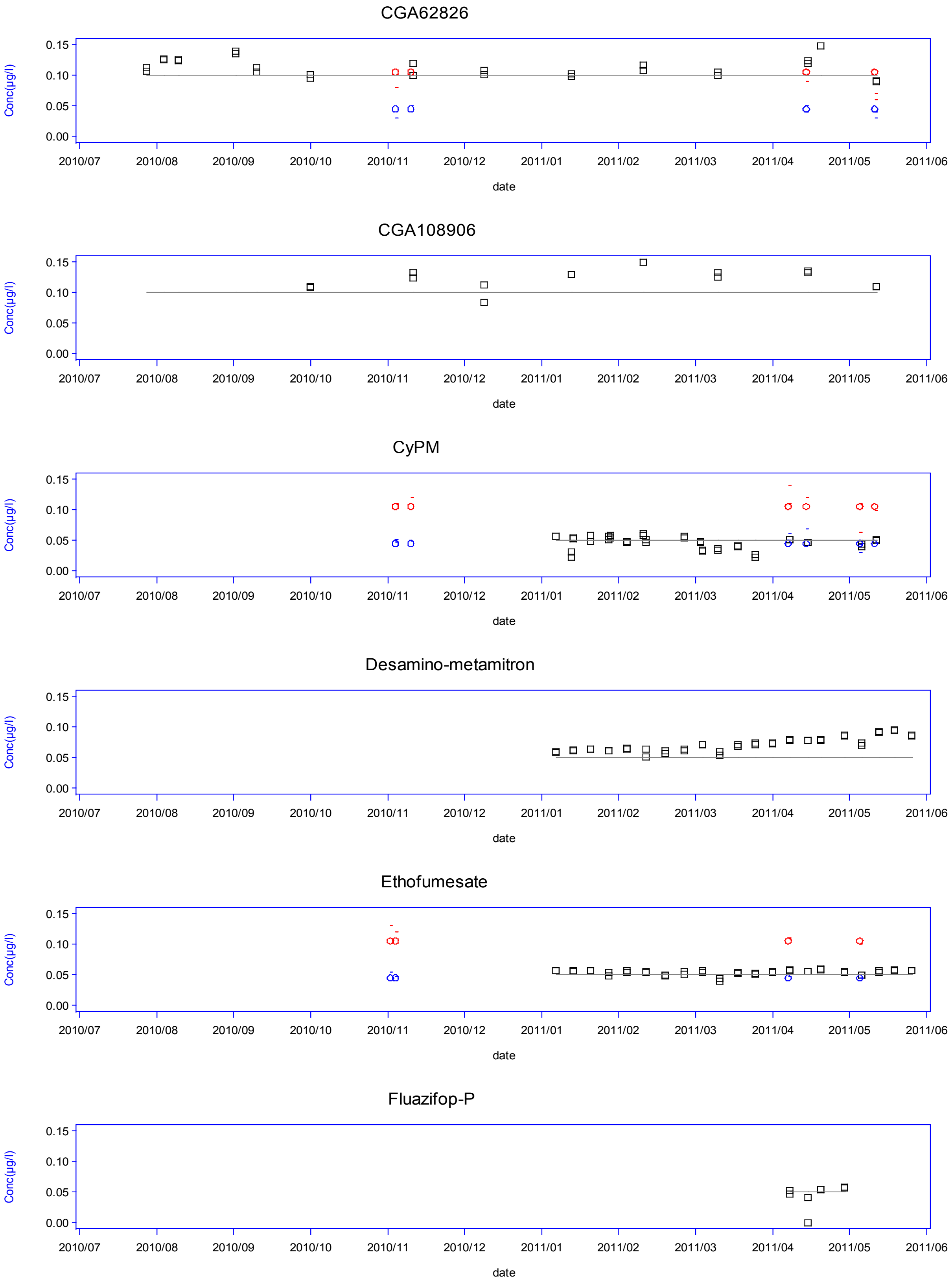

Figure A6.1 continued. Quality control data for pesticide analysis by laboratory 1. Internal laboratory control samples are indicated by square symbols and the nominal level is indicated by the solid grey line (■IQ measured, — IQ nominal concentration). External control samples are indicated by circles.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

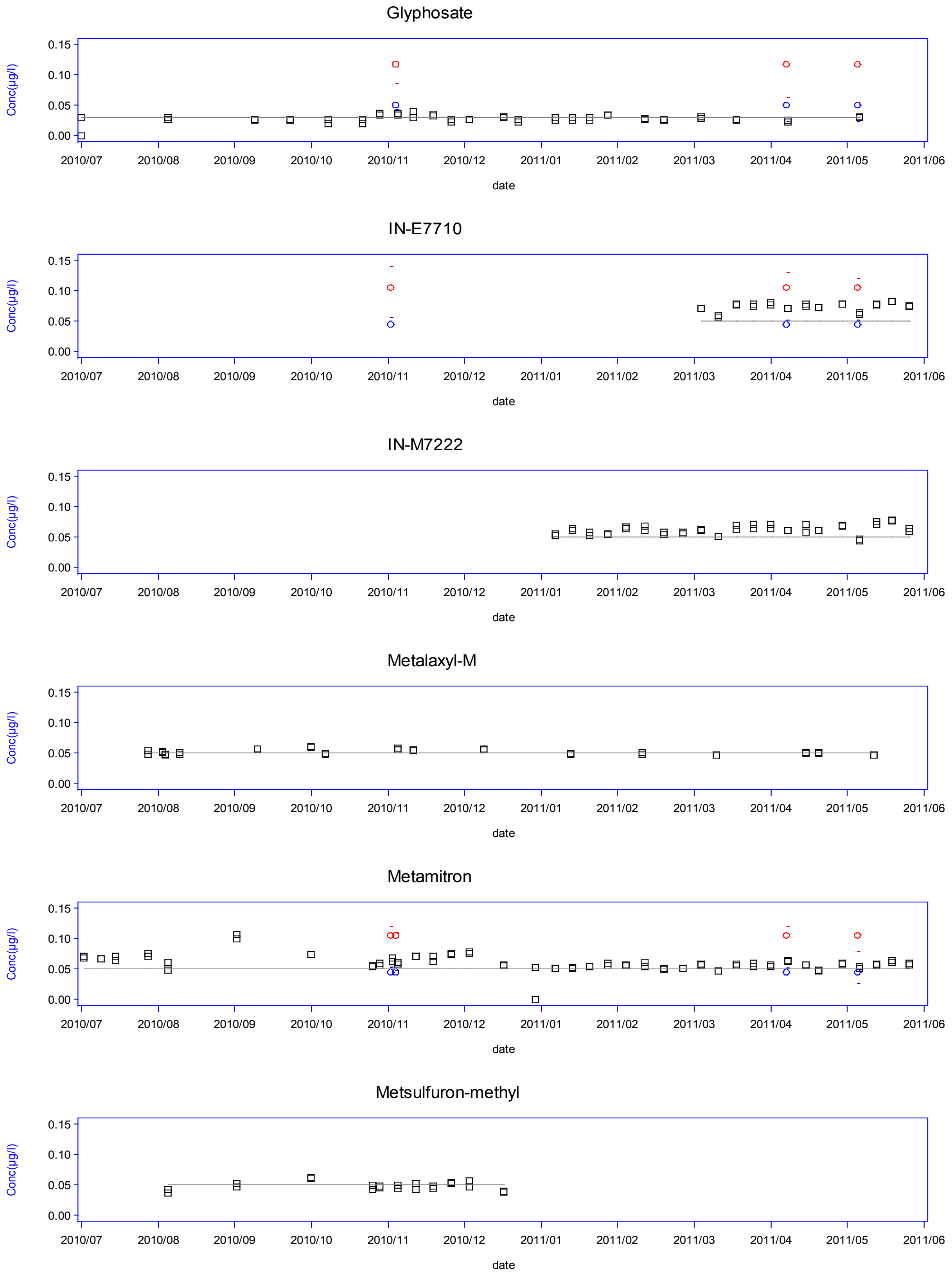

Figure A6.1 continued. Quality control data for pesticide analysis by laboratory 1. Internal laboratory control samples are indicated by square symbols and the nominal level is indicated by the solid grey line (■IQ measured, — IQ nominal concentration). External control samples are indicated by circles.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

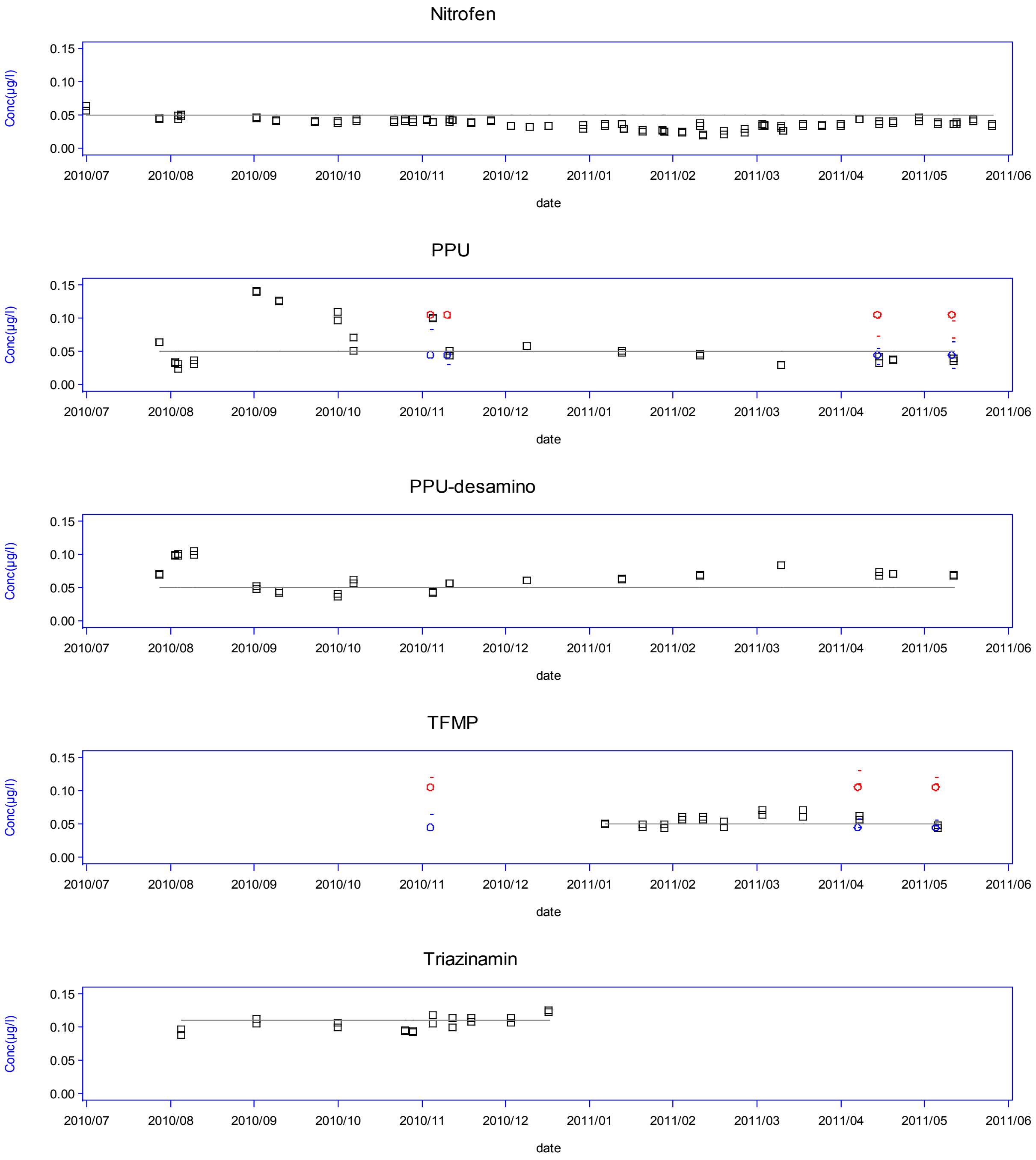

Figure A6.1 continued. Quality control data for pesticide analysis by laboratory 1. <u>Internal laboratory control</u> samples are indicated by square symbols and the nominal level is indicated by the solid grey line (■IQ measured, — IQ nominal concentration). <u>External control</u> samples are indicated 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).

Metalaxyl was on the Danish market from 1980-1995, reported maximum allowed dosage from 1984-1995 being 375 gr. a.i./ha. It re-entered the Danish marked in 2007 as Metalaxyl-M with a maximum allowed dosage of 77.6 g/ha. Available usage data is gathered in Table A7.2 and Appendix 8.

At Tylstrup exacts information on usage available from 2006 (upstream neighboring field) and 1989 (Tylstrup and field 1) and are listed in Table A7.1 At the upstream neighboring fields data covering the initial period of metalaxyl usage 1980-19995 were not available, but the following information have been obtained from local farmers in the area: From 1980-1995 field 3, 4 and 5 received metalaxyl once every four years when potatoes were grown. Potatoes were never grown on field 2 and 6 and metalaxyl have thus not been applied on these fields. Usage data from the Tylstrup field site and site 1 were available from 1989 respectively. From 1980-1989 potatoes were grown approximately every four year at these two fields but information on the applied fungicide is not available.

Table A7.1. Ridomil application at the **Tylstrup** PLAP test site (marked in red) and neighboring upstream fields, since metalxyl reentered the Danish marked in 2007. The positions of the various fields are indicated in the figure below, those upstream field receiving metalaxyl-M being marked with yellow filling. The direction of groundwater flow is indicated by a blue arrow.

Field-ID	Year of application	Dosage (g a.i./ha)[1]
5	2011	77.6
1	2010	77.6
Tylstrup PLAP site	2010	77.6
3	2009	77.6
Tylstrup PLAP site (left half of the field)	1990	187.5
1 (right half of the field)	1989	187.5

[1] *The active ingredient was metalaxyl from 1980-1995 and metalaxyl-M from 2006–2011.*

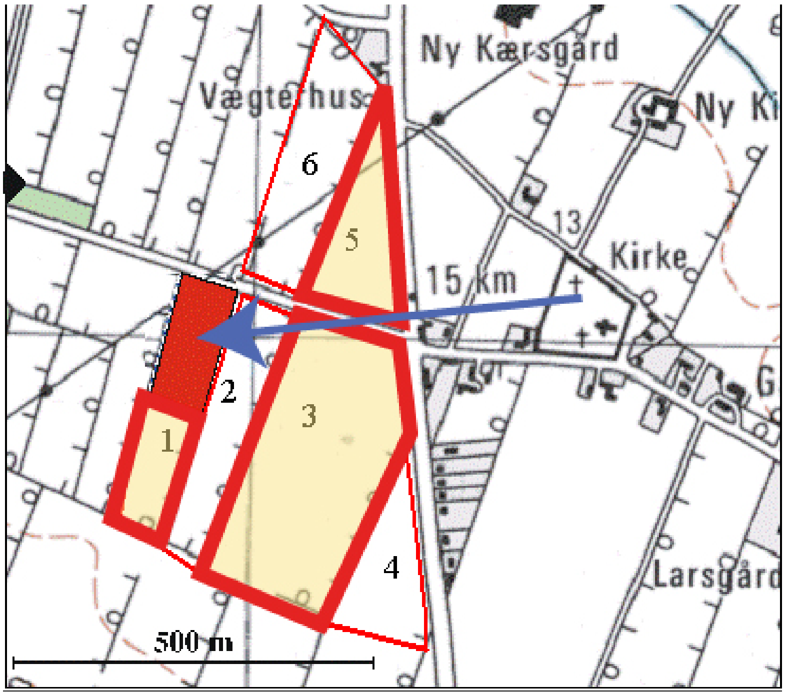

Table A7.2. Ridomil application at the **Jyndevad** PLAP test site (marked in red) and neighboring upstream fields. The positions of the various fields are indicated in the figure below, those upstream field receiving metalaxyl-M being marked with yellow fillling. The direction of groundwater flow is indicated by a blue arrow. Usage data from the Jyndevad field site and the upstream neighboring field were available from 1999 and 1988 respectively.

Field-ID	Year of application	Applied product (kg/ha)	Applied pesticide[1] (g a.i /ha)
K	2010	2 kg/ha - Ridomil Gold MZ Pepite	77.6
F-2	2010	2 kg/ha - Ridomil Gold MZ Pepite	77.6
Jyndevad PLAP-test site	2010	2 kg/ha - Ridomil Gold MZ Pepite	77.6
F5	2009	2 kg/ha - Ridomil Gold MZ Pepite	77.6
M4	2009	2 kg/ha - Ridomil Gold MZ Pepite	77.6
N-øst	2009	2 kg/ha - Ridomil Gold MZ Pepite	77.6
S1	2009	2 kg/ha - Ridomil Gold MZ Pepite	77.6
D-3(less than 0,2 ha.)	2009	2 kg/ha - Ridomil Gold MZ Pepite	77.6
S-4	2008	2 kg/ha - Ridomil Gold MZ Pepite	77.6
D2	2008	2 kg/ha - Ridomil Gold MZ Pepite	77.6
N-vest	2008	2 kg/ha - Ridomil Gold MZ Pepite	77.6
S3	2007	2 kg/ha - Ridomil Gold MZ Pepite	77.6
K	2007	2 kg/ha - Ridomil Gold MZ Pepite	77.6
D-3	1993	3*2,5 kg/ha - Ridomil MZ	3·187.5[2]
S-2	1990	1*2,5 kg/ha - Ridomil MZ	187.5
F-1	1989	2*2,5 kg/ha - Ridomil MZ	375
M-4	1988	1,0+2+2.5 kg/ha - Ridomil MZ	412.5

[1] *The active ingredient was metalaxylfrom 1980-1995 and metalaxyl-M from 2006-2010.*

[2] *The field is subdivided into parcel and three of these received 187.5 g/ha metalaxyl each.*

Table A8.1. 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 (See Appendix 2 for calculation method).

Crop and analysed pesticides	Application date	End of monitoring	Prec. (mm)	Perc. (mm)	1st month perc. (mm)	C_{mean} (µg/L)
Potatoes 1999						
Linuron (Afalon)	May 99	Jul 01	2550	1253	87	<0.01
- *ETU*1) (Dithane DG)	Jun 99	Oct 01	2381	1169	73	<0.01
Metribuzine (Sencor WG)	Jun 99	Jul 03	4223	2097	85	<0.01
- *metribuzine-diketo*		Jul 10†	11142	5387	85	0.05–0.36
- *metribuzine-desamino*		Jul 03	4223	2097	85	<0.02
- *metribuzine-desamino-diketo*		Apr 08	8689	4192	85	0.14–0.97
Spring barley 2000						
Triasulfuron (Logran 20 WG)	May 00	Apr 03	2740	1283	13	<0.02
- *triazinamin*						<0.02
Propiconazole (Tilt Top)	Jun 00	Jul 03	2948	1341	11	<0.01
Fenpropimorph (Tilt Top)	Jun 00	Jul 03	2948	1341	11	<0.01
- *fenpropimorphic acid*						<0.02
Pirimicarb (Pirimor G)	Jun 00	Apr 03	2622	1263	17	<0.01
- *pirimicarb-desmethyl*						<0.02
- *pirimicarb-desmethyl-formamido*						<0.02
Winter rye 2001						
Pendimethalin (Stomp SC)	Nov 00	Apr 03	2271	1219	109	<0.01
Triazinamin-methyl 2) (Express)	Nov 00	Apr 03	2271	1219	109	<0.02
Propiconazole (Tilt Top)	May 01	Jul 03	2948	1341	11	<0.01
Fenpropimorph (Tilt Top)	May 01	Jul 03	2948	1341	11	<0.01
- *fenpropimorphic acid*						<0.01
Winter rape 2002						
Clomazone (Command CS)	Sep 01	Jul 04	2534	1194	9	<0.01
- *FMC65317 (propanamide-clomazone)*						<0.02
Winter wheat 2003						
Bromoxynil (Oxitril CM)	Oct 02	Apr 05	2082	995	53	<0.01
Ioxynil (Oxitril CM)	Oct 02	Apr 05	2082	995	53	<0.01
Fluroxypyr (Starane 180)	May 03	Jul 05	1867	787	50	<0.02
Flamprop-M-isopropyl (Barnon Plus 3)	May 03	Jul 05	2635	1031	42	<0.01
- *Flamprop-M (free acid)*						
Dimethoate (Perfekthion 500 S)	Jul 03	Jul 05	1629	722	14	<0.01
Potatoes 2004						
-*Fluazifop-P (free acid)*3) (Fusilade X-tra)	May 04	Jul 06	1754	704	16	<0.01
- *PPU*4) (Titus)	Jun 04	Jul 10†	6211	3008	13	<0.01 5)
- *PPU-desamino*4) (Titus)	Jun 04	Jul 10†	6211	3008	13	<0.01 5)
Maize 2005						
Terbuthylazine (Inter-Terbutylazine)	May 05	Jul 07	2145	933	16	<0.01
-*desethyl-terbuthylazine*						<0.01
-*2-hydroxy-terbuthylazine*						<0.01
-*desisopropyl-atrazine*						<0.01 6)
-*2-hydroxy-desethyl-terbuthylazine*						<0.01
Bentazone (Laddok TE)	Jun 05	Jul 07	2061	927	33	<0.01
-*AIBA*						<0.01
Spring barley 2006						
-*triazinamin-methyl*7) (Express ST)	Jun 06	Jul 08	2349	1184	43	<0.02
Epoxiconazole (Opus)	Jul 06	Jul 08	2233	1148	24	<0.01

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.*

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

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

5) *Leaching increased the second and third year after application*

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

7) *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.

Table A8.2. Pesticides analysed at **Jyndevad** with the product used shown in parentheses. Degradation products are in italics. Precipitation (prec.) and percolation (perc.) are accumulated from date of first application until end of monitoring. 1st month perc. refers to accumulated percolation within the first month after application. C_{mean} refers to average leachate concentration 1 m b.g.s the first year after application (See Appendix 2 for calculation method).

Crop and analysed pesticides	Application date	End of monitoring	Prec. (mm)	Perc. (mm)	1st month perc. (mm)	C_{mean} (µg/l)
Winter rye 2000						
Glyphosate (Roundup 2000)	Sep 99	Apr 02	2759	1607	139	<0.01
- *AMPA*						<0.01
Triazinamin-methyl[1] (Express)	Nov 99	Apr 02	2534	1451	86	<0.02
Propiconazole (Tilt Top)	Apr 00	Jul 02	2301	1061	3	<0.01
Fenpropimorph (Tilt Top)	Apr 00	Apr 02	2015	1029	3	<0.01
- *fenpropimorphic acid*						<0.01
Maize 2001						
Terbuthylazine (Lido 410 SC)	May 01	Apr 04	3118	1809	4	<0.01
- *desethyl-terbuthylazine*	May 01	Apr 07	6742	3826	4	<0.01-0.02
PHCP[2] (Lido 410 SC)	May 01	Jul 03	2413	1366	4	<0.02
Potatoes 2002						
- *PPU* (Titus)[3]	May 02	Jul 10†	9389	5126	11	0.06[4]-0.13
- *PPU-desamino* (Titus)[3]		Jul 10†	9389	5126	11	0.01-0.03
Spring barley 2003						
MCPA (Metaxon)	Jun 03	Jul 05	2340	1233	0	<0.01
- *4-chlor,2-methylphenol*						<0.01
Dimethoate (Perfekthion 500 S)	Jun 03	Jul 05	2278	1232	1	<0.01
Pea 2004						
Bentazone (Basagran 480)	May 04	Jul 07	3888	2044	4	0.02-0.13
- *AIBA*						<0.01
Pendimethalin (Stomp SC)	May 04	Apr 07	3557	1996	4	<0.01
Pirimicarb (Pirimor G)	Jun 04	Apr 07	3493	1993	27	<0.01
- *Pirimicarb-desmethyl*						<0.01
-*Pirimicarb-desmethyl-formamido*						<0.02
- *fluazifop-P(free acid)*[5] (Fusilade X-tra)	Jun 04	Jul 06	2395	1233	27	<0.01
Winter wheat 2005						
Ioxynil (Oxitril CM)	Oct 04	Apr 07	2955	1791	81	<0.01
Bromoxynil (Oxitril CM)	Oct 04	Apr 07	2955	1791	81	<0.01
Amidosulfuron (Gratil 75 WG)	Apr 05	Jul 07	1070	515	33	<0.01
Fluroxypyr (Starane 180 S)	May 05	Jul 07	2683	1360	37	<0.02
Azoxystrobin (Amistar)	May 05	Apr 07	2274	1283	49	<0.01
- *CyPM*						<0.02
Spring barley 2006						
Florasulam (Primus)	May 06	Jul 08	2779	1487	34	<0.01
- *florasulam-desmethyl*						<0.03
Epoxiconazole (Opus)	Jun 06	Dec 09	4698	2592	31	<0.01

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.*

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

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

Table A8.3. 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).

Crop and analysed pesticides	Application date	End of monitoring	Prec. (mm)	Perc. (mm)	1st month perc. (mm)	C_{mean} (µg/l)
Fodder beet 2000						
Metamitron (Goltix WG)	May 00	Apr 03	2634	1328	53	0.05
- *metamitron-desamino*						0.06
Ethofumesate (Betanal Optima)	May 00	Apr 03	2634	1328	53	0.03
Desmedipham (Betanal Optima)	May 00	Apr 03	2634	1328	53	<0.01
- *EHPC*						<0.02
Phenmedipham (Betanal Optima)	May 00	Apr 03	2634	1328	53	<0.01
- *MHPC*						<0.02
- *3-aminophenol*						<0.02
Fluazifop-P-butyl (Fusilade X-tra)	Jun 00	Jul 02	1953	1019	5	<0.01
- *fluazifop (free acid)*						<0.02
Pirimicarb (Pirimor G)	Jul 00	Jul 07	6452	2825	1	<0.01
- *pirimicarb-desmethyl*						<0.01
- *pirimicarb-desmethyl-formamido*						<0.02
Spring barley 2001						
*Triazinamin-methyl*1) (Express)	May 01	Jul 03	1941	951	10	<0.02
Flamprop-M-isopropyl (Barnon Plus 3)	Jun 01	Jul 03	1928	944	3	<0.01
- *flamprop (free acid)*						<0.01
Propiconazole (Tilt Top)	Jun 01	Jul 03	1928	944	3	<0.01
Fenpropimorph (Tilt Top)	Jun 01	Jul 03	1928	944	3	<0.01
- *fenpropimorphic acid*						<0.01
Dimethoate (Perfekthion 500 S)	Jul 01	Jul 03	1882	937	3	0.02
Maize 2002						
Glyphosate (Roundup Bio)	Oct 01	Apr 06	3802	1694	44	0.13
- *AMPA*						0.06
*PHCP*2) (Lido 410 SC)	May 02	Jul 04	1764	738	6	0.06
Terbuthylazine (Lido 410 SC)	May 02	Apr 06	3320	1327	6	0.07
- *desethyl-terbuthylazine*		Apr 05				0.15
- *2- hydroxy-terbuthylazine*		Apr 05				3)
- *2-hydroxy-desethyl-terbuthylazine*		Apr 05				3)
- *desisopropyl-atrazine*		Apr 05				3)
Peas 2003						
Bentazone (Basagran 480)	May 03	Jul 06	2634	1055	44	0.26
- *AIBA*						<0.01
Pendimethalin (Storm SC)	May 03	Apr 06	2634	1055	44	<0.01
Glyphosate (Roundup Bio)	Sep 03	Apr 06	2207	971	0	<0.01
- *AMBA*						0.02
Winter wheat 2004						
Prosulfocarb (Boxer EC)	Oct 03	Apr 06	2125	974	37	0.01
MCPA (Metaxon)	May 04	Jul 06	1797	710	4	<0.01
- *4-chlor,2-methylphenol*						<0.01
Azoxystrobin (Amistar)	Jun 04	Jul 06	1781	706	0	0.01
- *CyPM*		Jul 07	2931	1202	0	0.09
Pirimicarb (Pirimor G)	Jul 04	Jul 07	2818	1205	0	<0.01
- *Pirimicarb-desmethyl*						<0.01
- *Pirimicarb-desmethyl-formamido*						<0.02
Spring barley 2005						
Fluroxypyr (Starane 180 S)	May 05	Jul 07	2012	830	11	<0.02
Azoxystrobin (Amistar)	Jun 05	Jul 06	862	332	10	0.01
- *CyPM*	Jun 05	Jul 07	2012	828	10	0.02
Pirimicarb (Pirimor G)	Jul 05	Jul 07	1933	818	0	<0.01
- *Pirimicarb-desmethyl*						<0.01
- *Pirimicarb-desmethyl-formamido*						<0.01

Table A8.3 (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).

Crop and analysed pesticides	Application date	End of monitoring	Prec. (mm)	Perc. (mm)	1st month perc. (mm)	C_{mean} (µg/l)
Winter rape 2006						
Propyzamide (Kerb 500 SC)	Nov 05	Apr 08	2345	1115	75	0.22⁴⁾
- *RH-24644*						0.01⁴⁾
- *RH-24580*						<0.01⁴⁾
- *RH-24655*						<0.01⁴⁾
Clopyralid (Matrigon)	Apr 06	Apr 08	2009	859	8	<0.01

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 months after application). See Kjær et al.(2007) for further information.*

4) *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.*

Table A8.4. 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).

Crop and analysed pesticides	Application date	End of monitoring	Prec. (mm)	Perc. (mm)	1st month perc. (mm)	C_{mean} (µg/l)
Spring barley 2000						
Metsulfuron-methyl (Ally)	May 00	Apr 03	2990	1456	29	<0.01
- *triazinamin*						<0.02
Flamprop-M-isopropyl (Barnon Plus 3)	May 00	Apr 03	2914	1434	2	0.02
- *flamprop (free acid)*						0.01
Propiconazole (Tilt Top)	Jun 00	Apr 05	4938	2294	0	0.01
Fenpropimorph (Tilt Top)	Jun 00	Jul 02	2211	1048	0	<0.01
- *fenpropimorphic acid*						<0.02
Dimethoate (Perfekthion 500 S)	Jun 00	Jul 02	2211	1048	0	<0.01
Pea 2001						
Glyphosate (Roundup Bio)	Oct 00	Jul 10†	10484	4977	123	0.54
- *AMPA*						0.17
Bentazone (Basagran 480)	May 01	Jul 08	7629	3621	9	0.03
- *AIBA*						<0.01
Pendimethalin (Stomp SC)	May 01	Jul 03	2208	1096	9	<0.01
Pirimicarb (Pirimor G)	Jun 01	Jul 05	4251	1995	10	0.01
- *pirimicarb-desmethyl*						<0.02
- *pirimicarb-desmethyl-formamido*						<0.02
Winter wheat 2002						
Ioxynil (Oxitril CM)	Nov 01	Jul 03	1580	860	52	0.04[1]
Bromoxynil (Oxitril CM)	Nov 01	Jul 03	1580	860	52	0.01[1]
Amidosulfuron (Gratil 75 WG)	Apr 02	Jul 04	2148	928	8	<0.01
MCPA (Metaxon)	May 02	Jul 04	2091	928	0	<0.01
- *4-chlor,2-methylphenol*						<0.01
Propiconazole (Tilt 250 EC)	May 02	Apr 05	2920	1336	39	0.02
Pirimicarb (Pirimor G)	Jun 02	Jul 05	2982	1403	58	0.01
- *pirimicarb-desmethyl*						<0.02
- *pirimicarb-desmethyl-formamido*		Apr 06				<0.02
Fodder beet 2003						
Glyphosate (Roundup Bio)	Sep 02	Jul 10†	8289	3900	0	0.43
- *AMPA*						0.19
Ethofumesate (Betanal Optima)	May 03	Apr 06	2901	1371	50	0.11
Metamitron (Goltix WG)	May 03	Apr 06	2901	1371	50	1.1
- *metamitron-desamino*						0.21
Pirimicarb (Pirimor G)	Jul 03	Jul 05	2071	939	0	<0.01
- *pirimicarb-desmethyl*		Jul 05				<0.01
- *pirimicarb-desmethyl-formamido*		Apr 06				0.12
Spring barley 2004						
Fluroxypyr (Starane 180)	May 04	Jul 06	2073	1030	0	<0.02
Azoxystrobin (Amistar)	Jun 04	Jul 08	4452	2209	38	0.12
- *CyPM*						0.23
Maize 2005						
Terbuthylazine (Inter-Terbuthylazin)	May 05	Apr 09	4247	2042	32	0.48
- *desethyl-terbuthylazine*		Jul 09	4406	2051	32	0.31
- *2-hydroxy-terbuthylazine*		Jul 08	3338	1628	32	0.11
- *desisopropyl-atrazine*		Apr 09	4247	2042	32	0.02
- *2-hydroxy-desethyl-terbuthylazine*		Jul 08	3338	1628	32	0.24
Bentazone (Laddok TE)	Jun 05	Jul 08	3338	1628	10	0.18
- *AIBA*						<0.01
Glyphosate (Roundup Bio)	Nov 05	Jul 10†	5191	2460	68	4.04[1]
- *AMPA*						0.42[1]
Spring barley 2006						
Florasulam (Primus)	Jun 06	Jul 08	2442	1163	0	<0.01
- *florasulam-desmethyl*						<0.03
Azoxystrobin (Amistar)	Jun 06	Jul 08	2414	1170	0	0.03
- *CyPM*						0.13

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

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

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

Table A8.5. 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).

Crop and analysed pesticides	Application date	End of monitoring	Prec. (mm)	Perc. (mm)	1st month perc. (mm)	C_{mean} (µg/l)
Winter wheat 1999						
Glyphosate (Roundup 2000)	Aug 99	Apr 03	2526	947	0	<0.01
- *AMPA*						<0.01
Bromoxynil (Briotril)	Oct 99	Apr 02	1738	751	35	<0.01
Ioxynil (Briotril)	Oct 99	Apr 02	1738	751	35	<0.01
Fluroxypyr (Starane 180)	Apr 00	Apr 02	1408	494	7	<0.01
Propiconazole (Tilt Top)	May 00	Jul 03	2151	669	0	<0.01
Fenpropimorph (Tilt Top)	May 00	Jul 02	1518	491	0	<0.01
- *fenpropimorphic acid*						<0.01
Pirimicarb (Pirimor G)	Jun 00	Jul 03	2066	684	0	<0.01
- *pirimicarb-desmethyl*						<0.01
- *pirimicarb-desmethyl-formamido*						<0.02
Sugar beet 2001						
Glyphosate (Roundup 2000)	Oct 00	Jul 03	1747	709	0	<0.01
- *AMPA*						0.01
Metamitron (Goltix WG)	May 01	Jul 03	1512	507	4	0.01
- *metamitron-desamino*						0.01
Ethofumesate (Betanal Optima)	May 01	Jul 03	1512	507	4	0.06
Desmedipham (Betanal Optima)	May 01	Jul 03	1512	507	4	<0.01
- *EHPC*						<0.02
Phenmedipham (Betanal Optima)	May 01	Jul 03	1512	507	4	<0.01
- *MHPC*						<0.02
Fluazifop-P-butyl (Fusilade X-tra)	Jun 01	Jul 03	1460	503	0	<0.01
- *fluazifop-P (free acid)*						0.02
Pirimicarb (Pirimor G)	Jul 01	Jul 03	1460	503	1	<0.01
- *pirimicarb-desmethyl*						<0.01
- *pirimicarb-desmethyl-formamido*						<0.02
Spring barley 2002						
Flamprop-M-isopropyl (Barnon Plus 3)	May 02	Jul 04	1337	333	0	<0.01
- *flamprop-M (free acid)*						<0.01
MCPA (Metaxon)	May 02	Jul 04	1358	337	4	<0.01
- *4-chlor-2-methylphenol*						<0.02
- *triazinamin-methyl*1) (Express)	May 02	Jul 04	1358	337	4	<0.02
Dimethoate (Perfekthion 500 S)	Jun 02	Jul 04	1328	333	0	<0.01
Propiconazole (Tilt 250 EC)	Jun 02	Jul 04	1328	333	0	<0.01
Winter rape 2003						
Clomazone (Command CS)	Aug 02	Apr 05	1761	509	4	<0.02
- *FMC65317 (propanamide-clomazon)*						<0.02
Winter wheat 2004						
Prosulfocarb (Boxer EC)	Oct 03	Apr 06	1542	454	0	<0.01
MCPA (Metaxon)	Jun 04	Jul 06	1307	331	0	<0.01
- *4-chlor,2-methylphenol*						<0.01
Azoxystrobin (Amistar)	Jun 04	Jul 07	2098	636	0	<0.01
- *CyPM*						<0.01
Maize 2005						
Terbuthylazine (Inter-Terbutylazin)	May 05	Jul 08	2078	666	4	0.67
- *desethyl-terbuthylazine*	May 05	Jul 08	2078	666		0.59
- *2-hydroxy-terbuthylazine*	May 05	Jul 08	2078	666		0.04
- *desisopropyl-atrazine*	May 05	Jul 08	2078	666		0.03
- *2- hydroxy-desethyl-terbuthylazine*	May 05	Jul 07	1428	465	4	0.07
Bentazone (Laddok TE)	May 05	Jul 07	1408	464	6	2.82
- *AIBA*						<0.01
Spring barley 2006						
Fluroxypyr (Starane 180 S)	May 06	Jul 08	1496	524	17	<0.02
Epoxiconazole (Opus)	Jun 06	Jul 08	1441	507	3	<0.01

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.*

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