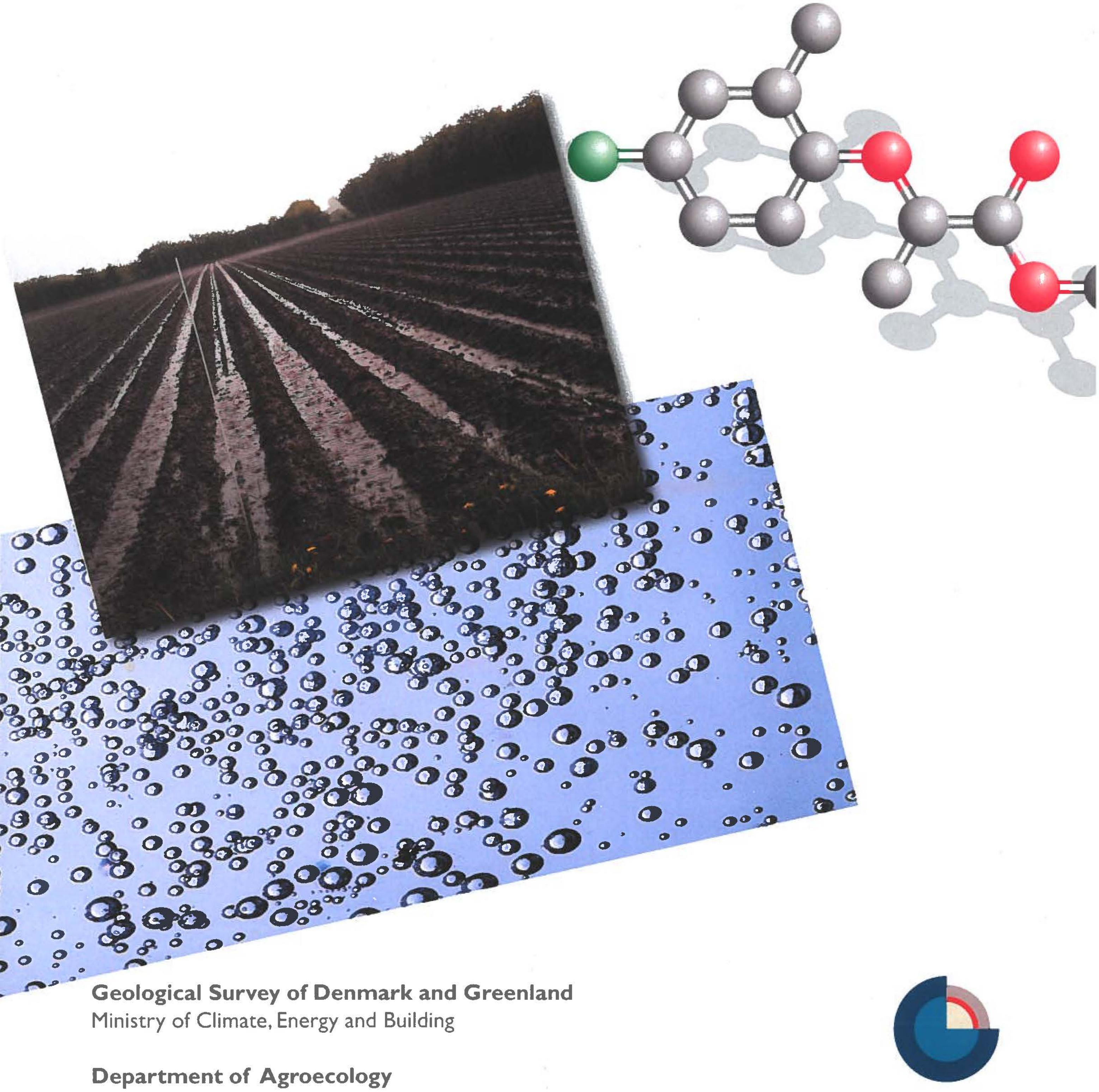
The Danish Pesticide Leaching Assessment Programme

Monitoring results

May 1999 - June 2013



Geological Survey of Denmark and Greenland
Ministry of Climate, Energy and Building

Department of Agroecology
University of Aarhus

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GEUS

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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 (EPA) 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 Walter Brüsch (GEUS), Annette E. Rosenbom (GEUS), Lis Wollesen de Jonge (AGRO), Preben Olsen (AGRO), Carsten B. Nielsen (BIOS), Steen Marcher (Danish EPA) and Anne Louise Gimsing (Danish EPA).

Lea Frimann Hansen (Danish EPA) is chairman of the steering group, and the members are Steen Marcher, Anne Louise Gimsing (Danish EPA), Flemming Larsen, Walter Brüsch (GEUS), Erik Steen Kristensen (AGRO) and Christian Kjær (BIOS).

This report presents the results for the period May 1999–June 2013. Results including part of the periode May 1999–June 2012 have been reported previously (Kjær *et al.*, 2002, Kjær *et al.*, 2003, Kjær *et al.*, 2004, Kjær *et al.*, 2005c, Kjær *et al.*, 2006, Kjær *et al.*, 2007, Kjær *et al.*, 2008, Kjær *et al.*, 2009, Rosenbom *et al.*, 2010b, Kjær *et al.*, 2011, Brüsch *et al.*, 2013a, and Brüsch *et al.*, 2013b). 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 the monitoring period 2011-2013.

The report was prepared jointly by Walter Brüsch (GEUS), Annette E. Rosenbom (GEUS), Nora Badawi (GEUS), Frants von Platten-Hallermund (GEUS), Lasse Gudmundsson (GEUS), Troels Laier (GEUS), Preben Olsen (AGRO), Finn Plauborg (AGRO) 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, Annette E. Rosenbom and Walter Brüsch.
- Soil water dynamics and water balances: Annette E. Rosenbom, Finn Plauborg and Carsten B. Nielsen.
- Pesticide analysis quality assurance: Nora Badawi.
- Appendix 9: Troels Laier.

Walter Brüsch
February 2015

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 analyze whether pesticides applied in accordance with current regulations will result in leaching of the pesticide and/or its degradation products to groundwater in unacceptable concentrations.

Throughout the monitoring period (1999-2013) 101 pesticides and/or degradation products have been analyzed in PLAP comprising five agricultural fields (1.2 to 2.4 ha) grow with different crops. The 15 most frequently analyzed pesticides and/or degradation products includes analyzes of 2.300–4.000 water samples collected from groundwater, drainage, and suction cups, including quality analysis samples (Table 0.1).

Evaluation of pesticides is based upon detections in 1 meters depth (water collected via drains and suction cups) and detections in groundwater monitoring screens (1.5-4.5 meter below ground surface, hereafter m b.g.s.).

This report presents the results of the monitoring period July 2011–June 2013 comprising 9.090 single analyzes conducted on water samples collected at the five PLAP-fields: two sandy fields (Tylstrup and Jyndevad) and three clayey till fields (Silstrup, Estrup and Faardrup). In this period, PLAP has evaluated the leaching risk of 19 pesticides and 22 degradation products (Table 0.2) after applying the maximum allowed dose of the specific pesticide to the specific crop (Table 0.3).

Table 0.1. The 15 most frequently analyzed pesticides and/or degradation product in the period 1999-June 2013. The water samples being analyzed include quality analysis (QA) samples, samples from groundwater, and samples from the vaiably-saturatede zone (drainage and suction cups).

Pesticide or degradation products		Parent	All samples incl. QA	Ground-water	Drainage + suction cups
Bentazone	P	Bentazone	3.926	2.433	983
AMPA	M	Glyphosat	3.571	2.108	1.044
Glyphosate	P	Glyphosat	3.568	2.106	1.043
Pirimicarb	P	Pirimicarb	3.432	2.120	887
Propiconazole	P	Propiconazol	3.421	2.084	899
Pirimicarb-desmethyl	M	Pirimicarb	3.078	1.911	780
Pendimethalin	P	Pendimethalin	2.881	1.811	694
CyPM	M	Azoxystrobin	2.854	1.801	691
Azoxystrobin	P	Azoxystrobin	2.701	1.689	668
Pirimicarb-desmethyl-formamido	M	Pirimicarb	2.678	1.638	707
Desethyl-terbuthylazine	M	Terbuthylazin	2.619	1.664	612
Fenpropimorph	P	Fenpropimorph	2.494	1.531	657
Triazinamin-methyl	M	Tribenuron-methyl	2.386	1.523	569
Fenpropimorph acid	M	Fenpropimorph	2.341	1.435	636
PPU	M	Rimsulfuron	2.311	1.519	502
PPU-desamino	M	Rimsulfuron	2.311	1.519	502

P: Parent pesticide. M: Degradation product.

Results covering the period May 1999–June 2011 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, Kjær *et al.*, 2011, and Brüsch *et al.*, 2013a+b). 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 June 2011- June 2013.

Table 0.2. 19 pesticides and 22 degradation products have been analyzed in PLAP in the period June 2011-June 2013. The number of water samples analyzed, detections, and detections ≥ 0.1µg/L in water samples from the variably-saturated zone (drainage and suction cups) and groundwater (groundwater wells).

Analyte	Parent pesticide	Samples analyzed	Drain+suction cups Detections	Drain+suction cups ≥ 0.1µg/L	Groundwater wells Detections	Groundwater wells ≥ 0.1µg/L	Max. conc.
Aclonifen	**Aclonifen**	216					**ND**
Aminopyralid	**Aminopyralid**	216					**ND**
Azoxystrobin	**Azoxystrobin**	264	19	1	1		0.13
CyPM	Azoxystrobin	264	64	29	7	1	0.4
Bentazone	**Bentazone**	289	17	6	1		1.9
Bifenox	**Bifenox**	485	5	2			0.38
Bifenox acid	Bifenox	490	13	8	15	11	4.8
Nitrofen	Bifenox	485	4	3			0.34
Boscalid	**Boscalid**	142					**ND**
Bromoxynil	**Bromoxynil**	36					**ND**
Clomazone	**Clomazone**	20					**ND**
FMC 65317	Clomazone	21					ND
Cyazofamid	**Cyazofamid**	170					**ND**
Diflufenican	**Diflufenican**	265	9	1	1	1	0.47
AE-B107137	Diflufenican	273	5	1			0.13
AE-05422291	Diflufenican	265					ND
TFMP	Fluazifop-P-buthyl	326	30	7	39	7	0.64
Fluazifop-P	Fluazifop-P-buthyl	68					ND
Glyphosate	**Glyphosat**	327	53	18	20	2	10
AMPA	Glyphosat	327	63	16	5		0.58
Ioxynil	**Ioxynil**	36					**ND**
Mesotrione	**Mesotrione**	113					**ND**
AMBA	Mesotrione	113					ND
MNBA	Mesotrione	113					ND
Metalaxyl-M	**Metalaxyl-M**	392	3		42	18	1.3
CGA 62826	Metalaxyl-M	403	55	11	75	8	0.68
CGA 108906	Metalaxyl-M	403	100	41	230	65	4.8
Metrafenone	**Metrafenone**	258	20		1		0.072
Propyzamide	**Propyzamid**	58					**ND**
RH-24655	Propyzamid	58					ND
RH-24644	Propyzamid	58					ND
RH-24580	Propyzamid	58					ND
Prosulfocarb	**Prosulfocarb**	58					**ND**
PPU	Rimsulfuron	264	72	11	94	11	0.23
PPU-desamino	Rimsulfuron	264	48	2	31		0.18
Tebuconazole	**Tebuconazole**	57	2				0.084
Thiacloprid	**Thiacloprid**	74					ND
M34	Thiacloprid	79					ND
Thiacloprid sulfonic acid	Thiacloprid	79					ND
Thiacloprid-amide	Thiacloprid	74	1				0.012
Triazinamin-methyl	Tribenuron-methyl	95					**ND**

ND - Pesticide not detected in monitoring period 2011-2013.Bold - parent pesticide analyzed.

Table 0.3. Crops grown on the five PLAP-fields in 2011, 2012 and 2013.

	Tylstrup	Jyndevad	Silstrup	Estrup	Faardrup
2011	Spring barley	Spring barley	Red fescue	Winter wheat	Red fescue
2012	Spring barley	Maize	Red fescue and winter wheat	Spring barley	Spring barley and white clover
2013	Winter rye	Peas	Winter wheat/spring barley*	Peas	White clover

**Spring barley replacing frost affected winter wheat.*

Highlights from the **monitoring period June 2011-June 2013**:

- Bentazone was applied to peas at Jyndevad and Estrup in 2013, white clower at Faardrup in 2012 and 2013, and maize at Jyndevad in 2012. At the sandy field Jyndevad bentazone was found to leaching through the variably-saturated zone (suction cups) after application on peas in 2013. It was, however, only detected once (0.01 µg/L) in a mixed groundwater sample from the horizontal well at 2.5 m b.g.s. This confirmes the leaching pattern detected after the bentazon application on maize in 2012, where it was frequently detected in the variably-saturated zone (suction cups) in concentrations up to 1.9 µg/L, but not in the groundwater. After use on clower, at the clayey till field Faardrup in 2012 and 2013, bentazone was detected in one drainage sample (0.02 µg/L). Bentazone did not leach after use on peas at the clayey till field Estrup in 2013. In total, bentazone has until 15 May 2013 been applied 17 times to the five fields in PLAP and on different crops. In the period May 2001-June 2013 bentazone has been detected in 66 groundwater samples, where eight groundwater samples had concentration above 0.1 µg/L. A total of 3.728 groundwater samples has been analyzed for bentazone.

- Metalaxyl-M, and especially its two degradation products CGA 108906 and CGA 62826, have been detected in high frequency and concentrations both in the variably-saturated zone and in the groundwater at the two sandy PLAP-fields, why the compounds still will be under evaluation in PLAP. Metalaxyl-M was detected a few times in low concentrations in watersamples from the variably-saturated zone (suction cups). The degradation products CGA 108906 and CGA 62826, however, leached to 1 m depth in concentrations often exceeding 0.1 µg/L up to 3 years after application. The highest concentrations for both compounds were detected 1 m depth in concentrations up to 3.7 µg/L (January 2012). In the period June 2011-June 2013 both degradation products were found in 83-100% of the water samles from the variably-saturated zone (suction cups) and especially CGA 108906 was detected frequently in groundwater samples (75-83%) from Tylstrup and Jyndevad, where 20-30% of the analyzed groundwater samples exceeded 0.1 µg/L. Concentration measured in water samples from the variably-saturated zone and from a horisontal well collecting groundwater just beneath the fluctuating groundwater table at Jyndevad, clearly indicate leaching of the compounds after metalaxyl-M was applied to potatoes in 2010 at the PLAP-fields. As a consequence of these monitoring results, the Danish EPA has withdrawn the approval of metalaxyl-M per August 1st, 2013.

- Fluazifop-P-butyl was used in a new dose (50% lower than in past applications) in the spring 2011 at the clayey till field Silstrup, and leaching of the degradation product TFMP was negligible in 2011. Before the regulation, TFMP leached to both drainage and groundwater in concentrations above 0.1 µg/L at Silstrup. Fluazifop-P-butyl was also applied at Faardrup in May 2011, and TFMP did not leach. In April

2012 Fluazifop-P-butyl was applied on red fescue at Silstrup (50% reduced dose), and TFMP-concentrations exceeding 0.1 µg/L was measured in drainage and groundwater. In the monitoring year 2013, TFMP was found in both drainage and groundwater, but in concentrations below 0.1 µ/L. Given these different TFMP-leaching scenarios, the leaching risk of the compound will still be evaluated in PLAP in the years to come. Fluazifop-P-butyl has been applied 10 times in PLAP at four of the fields.

- After application on red fescue at the clayey till field Silstrup September 2012, glyphosate and AMPA were found in drainage in concentrations up to 0.66 µg/L. The compounds were however not exceeding 0.1 µg/L in groundwater. Here glyphosate was only detected in 10 groundwater samples from vertical wells and in three groundwater samples from a horizontal well. At the clayey till field Estrup, concentrations of glyphosate and AMPA in drainage both exceeded 0.1 µg/L frequently after glyphosate application on winter wheat in October 2011. In the groundwater AMPA was never detected, only glyphosate was occasionally detected in two groundwater samples with concentrations ≥ 0.1 µg/L (0.21 and 0.13 µg/L). At the clayey till field Faardrup, glyphosate was found in low concentrations (0.025 and 0.019 µg/L) in two samples from two levels in a vertical monitoring well after application after harvest of spring barley and white clover in October 2011. Monitoring at Faardrup stopped in August 2012.

- Azoxystrobine was applied at the clayey till field Estrup in June 2012, and both azoxystrobine and CyPM leached to drainage in concentrations above 0.1µg/L. CyPM was detected in seven groundwater samples from both the new and old horizontal wells, and one sample was exceeding 0.1 µg/L. There was no detections in groundwater samples collected from the vertical monitoring wells.

- The fungicide metrafenone was applied twice, 9 May and 7 June 2011, at the clayey till field Estrup. 20 water samples of drainage and one of groundwater contained metrafenone in concentrations <0.1 µg/L.

- Diflufenican was applied in April 2012 and in November 2012 (red fescue and winter wheat) at the clayey till field Silstrup. Diflufenican was detected in 9 water samples of the drainage and in one groundwater sample. One drainage and one groundwater sample exceeded 0.1 µg/L. The degradation product of diflufenican AE-B107137 was detected in 5 water samples of the drainage, while the other degradation product AE-05422291 was not detected (Table 0.2). Diflufenican and the two degradation products were not detected in groundwater nor drainage after application at spring barley in April 2011 at the sandy field Jyndevad.

- Aclonifen, aminopyralid, boscalid, bromoxynil, clomazon, cyazofamid, ioxynil, mesotrione, propyzamid, prosulfocarb, tribenuron-methyl and degradation products were not detected in drainage and groundwater during the monitoring period. The degradation product thiacloprid amid of thiacloprid was detected in one sample from the drainage, while thiacloprid was not detected. Tebuconazole was detected in two water samples collected in the drainage in August and September 2012 (Table 0.2).

The results of the **entire monitoring period 1999-2013** covering **50** pesticides and **51** degradation products show that:

- Of the 50 pesticides applied, 16 pesticides and/or their degradation product(s) (aclonifen, aminopyralid, boscalid, clopyralid, chlormequat, cyazofamid, desmedipham, fenpropimorph, florasulam, iodosulfuron-methyl-natrium, linuron, mesotrione, thiacloprid, thiamethoxam, tribenuron-methyl and triasulfuron) were not detected in either drainage or groundwater during the entire monitoring period.

- The monitoring data indicate pronounced leaching of 16 of the applied pesticides and/or their degradation product(s). The following compounds leached through the soil entering tile drains or suction cups (placed 1 m depth) in average concentrations exceeding 0.1 µg/L:

    - *azoxystrobin* and its degradation product *CyPM*
    - *bentazone*
    - *CL153815* (degradation product of picolinafen)
    - *AE-B107103* (degradation product of diflufenican)
    - *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 pesticides and/or their degradation products *marked in italics*, pronounced leaching is mainly confined to the depth of 1 m b.g.s., where pesticides were frequently detected in water samples collected from tile drains and suction cups, while a limited number of detections (fewer than five samples per field) exceeding 0.1 µg/L were detected in water samples collected from groundwater monitoring wells.

  For the pesticides and/or their degradation products **marked in bold**, pronounced leaching below the depth of 1 m b.g.s. was observed. Apart from PPU, these were all frequently detected in groundwater in concentrations exceeding 0.1µg/L more than six months after application.

- **The monitoring data also indicate leaching of an additional 18 pesticides, but in low** concentrations. Although concentrations exceeded 0.1 µg/L in several water samples collected from suction cups and tile drains (1 m b.g.s.), average leaching concentrations on a yearly basis did not exceed 0.1 µg/L. None of the compounds were detected in water samples from the groundwater monitoring wells in concentrations exceeding 0.1 µg/L.

In order to describe the water flow through the variably-saturated zone and into the groundwater zone, a bromide tracer has been applied at least twice to each of the five PLAP-fields. Bromide and pesticide concentrations are measured monthly in both the variably-saturated zones and in the saturated zones, and weekly in the drainage.

Dansk sammendrag

I 1998 vedtog Folketinget at iværksætte projektet ”Varslingssystem for udvaskning af Pesticider til grundvand” (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 101 pesticider og nedbrydningsprodukter er med udgangen af juni 2013 (1999-2013) undersøgt på en til fem marker, og ofte på forskellige afgrøder på samme mark. Disse fem marker har en størrelse på mellem 1,2 og 2,4 ha. De 15 mest analyserede pesticider og nedbrydningsprodukter er analyseret i ca. 2.300 til 4.000 vandprøver fra sugeceller i den umættede zone (den variabelt mættede zone), dræn- og grundvand fra marker med forskellige jordbundsforhold og på forskellige afgrøder, se tabel 0.1. Undersøgelse af pesticider bygger på moniteringsresultater, som henholdsvis repræsenterer 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 analyser for 19 pesticider og 22 nedbrydningsprodukter, i alt 41 stoffer, der har indgået i moniteringsprogrammet for de fem VAP marker i perioden fra juli 2011 til juni 2013 (se tabel 0.2), efter anvendelse af pesticider på de afgrøder, der er dyrket på de fem marker, (se tabel 0.3). I denne periode er der foretaget 9.090 enkeltstof analyser på vandprøver indsamlet på de fem VAP marker: to sandede marker (Tylstrup og Jyndevad) og tre morænelers marker (Silstrup, Estrup og Fårdrup). Analyseresultater fra foregående år (maj 1999 til juni 2011) er tidligere afrapporteret.

Resultater fra den seneste **moniteringsperiode juni 2011-juni 2013** viser følgende:

- Bentazon blev anvendt på ærter i Jyndevad og Estrup i 2013, på hvidkløver i Fårdrup i 2012 og 2013, samt på majs i Jyndevad i juni 2012. Bentazon blev fundet som begyndende udvaskning i sugeceller i den umættede zone på den sandede mark i Jyndevad, efter stoffet blev anvendt på ærter i 2013. Bentazon blev fundet i en enkelt grundvandsprøve fra en horisontal boring (0,01µg/l). Bentazon blev fundet hyppigt i vandprøver fra den umættede zone efter anvendelse på majs i 2012 i Jyndevad, hvor den højeste koncentration var 1,9 µg/L, mens bentazon ikke blev fundet i grundvandet. Efter anvendelse på hvidkløver på morænelersmarken i Fårdrup i 2012 og 2013, blev bentazon fundet i en enkelt drænprøve (0,02 µg/l) men ikke i grundvand, og efter anvendelse på ærter på morænelersmarken i Estrup i 2013 blev bentazon ikke fundet i hverken dræn eller grundvand. Bentazon har frem til den 15. maj 2013 været anvendt 17 gange på de fem marker på forskellige afgrøder. Bentazon er i hele moniteringsperioden fundet i 66 grundvandsprøver, og i otte af disse i koncentrationer ≥ 0,1 µg/l (hhv. 2003 og 2005). 3.728 grundvandsprøver er i alt analyseret for bentazon.

- Moniteringen af metalaxyl-M og nedbrydningsprodukter er fortsat i 2011-2013 på grund af mange fund af nedbrydningsprodukterne i grundvand. Metalaxyl-M blev fundet få gange i små koncentrationer i den umættede zone, hvorimod to af dets nedbrydningsprodukter CGA62826 og CGA108906 blev fundet i høje koncentrationer i grundvand, der ofte overskred grænseværdien for grundvand på de to sandede marker Tylstrup og Jyndevad. Begge nedbrydningsprodukter blev fundet i vand fra sugeceller placeret 1 m u.t. med stigende koncentration indtil januar 2012 (maksimum koncentration 3,7 µg/l). Metalaxyl-M blev fundet i grundvandet opstrøms sandmarkerne før sprøjtningen med metalaxyl-M i 2010, og disse fund stammer fra tidligere sprøjtninger på nabomarker beliggende opstrøms. I moniteringsperioden fra juni 2011 til juni 2013 blev begge nedbrydningsprodukter fundet i 83-100% af vandprøverne fra den umættede zone (sugeceller), mens særligt CGA 108906 blev fundet hyppigt i vandprøver udtaget fra grundvand (75-83%) fra de to sandede marker. Disse fund i vand fra den umættede zone og fra en horisontal boring placeret under grundvandsspejlet i Jyndevad, viser at sprøjtningen på kartofler med metalaxyl-M i 2010 medførte udvaskning af moderstof og nedbrydningsprodukter fra markerne og at udvaskningen ikke stammer fra anvendelse på marker opstrøms marken. Som følge af fund i grundvandet blev anvendelsen af metalaxyl-M forbudt i 2013.

- Fluazifop-P-butyl blev i 2008 pålagt restriktioner bl.a. i form af en nedsat dosering for at beskytte grundvandet. Ved test af den nye lave dosering i foråret 2011 var udvaskningen af nedbrydningsproduktet TFMP ubetydelig. Dette var ikke tilfældet i 2008, hvor TFMP blev fundet i høje koncentrationer i grundvandet efter anvendelse af fluazifop-P-butyl. I 2012 blev fluazifop-P-butyl igen udbragt i den nye reducerede dosis, hvilket resulterede i mange TFMP fund, også i 2013, i lave koncentrationer. Dette indikerer, at TFMP ved anvendelse af moderstoffet i den nye dosering, i nogle tilfælde kan overskride grænseværdien for grundvand. Udvaskningen af TFMP følges stadigvæk i VAP. Fluazifop-P-butyl har frem til juli 2013 været anvendt ti gange på fire VAP marker. Fluazifop-P-butyl er ikke længere godkendt i Danmark. Såfremt der ansøges om godkendelse igen, vil resultaterne fra VAP blive inddraget i Miljøstyrelsens vurdering af, hvorvidt der kan gives godkendelse til svampemidler med dette aktivstof.

- Efter udbringning på rødsvingel i september 2012 på den lerede mark i Silstrup blev glyphosat og nedbrydningsproduktet AMPA fundet i koncentrationer op til 0,66 µg/l i drænvand, men ikke i koncentrationer over grænseværdien i grundvand, hvor glyphosat blev fundet i ti vandprøver fra moniteringsboringer og i tre vandprøver fra en horisontal boring. Begge stoffer er fundet i koncentrationer over 0,1 µg/l i drænvand fra morænelersmarken i Estrup efter anvendelse i oktober 2011, hvor der var dyrket vinterhvede. Glyphosat blev fundet i to grundvandsprøver på samme mark i koncentrationer over 0,1 µg/l (0,21 og 0,13 µg/l), mens AMPA ikke blev detekteret. På den lerede mark i Fårdrup blev moderstoffet fundet i små koncentrationer under grænseværdien i to vandprøver fra de øverste to indtag i en vertikal grundvandsboring efter anvendelse i oktober 2011. Moniteringen i Fårdrup stoppede i august 2012.

- Azoxystrobin blev anvendt på Estrup i 2012 hvilket resulterende i, at både azoxystrobin og nedbrydningsproduktet CyPM blev udvasket til dræn i koncentrationer over 0,1 µg/l. CyPM blev fundet i syv ud af 37 grundvandsprøver fra horisontale boringer, hvoraf en prøve havde en koncentration over 0,1 µg/l. Der var ikke fund i vertikale grundvandsboringer.

- Metrafenone blev anvendt to gange i maj og juni 2011 på den lerede mark i Estrup, og stoffet blev fundet i 20 drænvandsprøver og i en grundvandsprøve i koncentrationer under 0,1 µg/l.

- Diflufenican blev fundet i ni drænvandsprøver fra morænelersmarken i Silstrup efter stoffet blev anvendt på rødsvingel og vinterhvede i april og november 2012. Diflufenican blev fundet i koncentrationer større end 0,1 µg/l i en grundvandsprøve og i en drænvandprøve. Nedbrydningsproduktet AE-B107137 blev fundet i fem drænvandsprøver, mens det andet nedbrydningsprodukt AE-05422291 ikke blev detekteret. Ingen af de tre stoffer blev fundet i vandprøver fra den sandede mark i Jyndevad, efter diflufenican blev udsprøjtet på forårsbyg i april 2011.

- Aclonifen, aminopyralid, boscalid, bromoxynil, clomazon, cyazofamid, ioxynil, mesotrione, propyzamid, prosulfocarb, tribenuron-methyl og deres nedbrydningsprodukter blev ikke udvasket i moniteringsperioden fra juni 2011 til juni 2013. Nedbrydningsproduktet thiacloprid-amid fra thiacloprid blev fundet i en enkelt drænvandsprøve, mens moderstoffet og thiacloprid-sulfonsyre ikke blev påvist. Tebuconazole blev fundet i to drænprøver (se tabel 0.2, der viser alle stoffer analyseret i perioden).

Resultater for **hele moniteringsperioden 1999-2013**, som omfatter 50 pesticider viser følgende:

- Af de 50 pesticider, der er blevet udbragt, blev 16 pesticider eller nedbrydningsprodukter heraf (aclonifen, aminopyralid, boscalid, clopyralid, chlormequat, cyazofamid, desmedipham, fenpropimorph, florasulam, iodosulfuron-methyl-natrium, linuron, mesotrion, thiacloprid, thiamethoxam, tribenuron-methyl og triasulfuron) ikke fundet udvasket til hverken dræn-, jord- eller grundvand i løbet af den samlede moniteringsperiode.

- 16 udbragte stoffer, eller nedbrydningsprodukter fra disse, gav anledning til en udvaskning gennem rodzonen til dræn og til sugeceller i den umættede zone beliggende i ca. 1 m u.t. i gennemsnitskoncentrationer over 0,1 µg/l:
    - *azoxystrobin* og dets nedbrydningsprodukt *CyPM*
    - *bentazon*
    - *CL153815* (nedbrydningsprodukt af picolinafen)
    - *diflufenican og AE-B107103*
    - *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 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 fem pr. mark), og der var ikke tale om, at udvaskningen som årsgennemsnit var højere end 0,1 µg/l.

Pesticider **markeret med fed** blev udvasket til grundvandsfiltrene i en grad, så Miljøstyrelsen har foretaget nye vurderinger med forbud eller anden regulering af anvendelsen til følge.

- Andre 18 stoffer gav anledning til mindre udvaskning. Selv om flere af disse stoffer i 1 m u.t. ofte blev fundet i koncentrationer over 0,1 µg/l, var der ikke tale om, at udvaskningen som årsgennemsnit var højere end 0,1 µg/l i dræn eller sugeceller. Stofferne blev heller ikke fundet i grundvandsfiltrene i koncentrationer over 0,1 µg/l.

Bromid er anvendt som sporstof for at beskrive den nedadrettede vandtransport gennem den variabelt mættede zone mod grundvandet, og der er mindst to gange tilført bromid til de fem VAP marker. Bromid- og pesticidkoncentrationer bliver analyseret månedligt i vandprøver udtaget i den variabelt-mættede zone og i den mættede zone, samt ugentligt i prøver af drænvand.

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 52% of all screens monitored and in 62% of the screens placed in the upper shallow groundwater (Thorling, L. (ed.), 2013).

The detection of pesticides in groundwater over the past 20 years has caused 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, Jacobsen & Kjær, 2007).

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 since 1987 included field-scale studies in its risk assessments. 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 analyze whether pesticides applied in accordance with current regulations leach at levels exceeding the maximum allowable concentration of 0.1µg/L.

1.2 Structure of the PLAP

The pesticides included in the PLAP were selected by the Danish EPA on the basis of expert judgement. At present, 50 pesticides and 51 degradation products have been included in the PLAP. All the compounds analyzed since 1999 are listed in Appendix 1.

Figure 1.1. Location of the PLAP field 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 1.1).

Monitoring at the Slaeggerup site was terminated on 1 July 2003, and the monitoring results are reported in Kjær *et al.* (2003). The groundwater table is shallow at all the field sites, thereby enabling pesticide leaching to groundwater to be rapidly detected (Table 1.1). 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 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 1.1).

Table 1.1. 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
Width (m) x Lenght (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 surface.*
[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 2013, but the main focus of this report is on the leaching risk of pesticides applied during 2011-2013. For a detailed description of the earlier part of the monitoring periods (May 1999–June 2011), 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 PLAP 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 variably-saturated zone at each PLAP site supports the monitoring data. The MACRO model (version 5.2), 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 2013. The five site models have been calibrated for the monitoring period May 1999–June 2004 and validated for the monitoring period July 2004–June 2013.

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 analyzes 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 1.1). The test field covers a cultivated area of 1.2 ha (70 m 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 1.1). 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 2.1). During the monitoring period the groundwater table was 2.6–4.5 m b.g.s. (Figure 2.2). A brief description of the sampling procedure is provided in Appendix 2 and the analysis methods in Kjær *et al.* (2002). The monitoring design and test site are described in detail in Lindhardt *et al.* (2001). In September 2011, the monitoring system was extended with three horizontal screens (H1) 4.5 m b.g.s. in the South-Eastern corner of the field (Figure 2.1). A brief description of the drilling and design of H1 is given in Appendix 8.

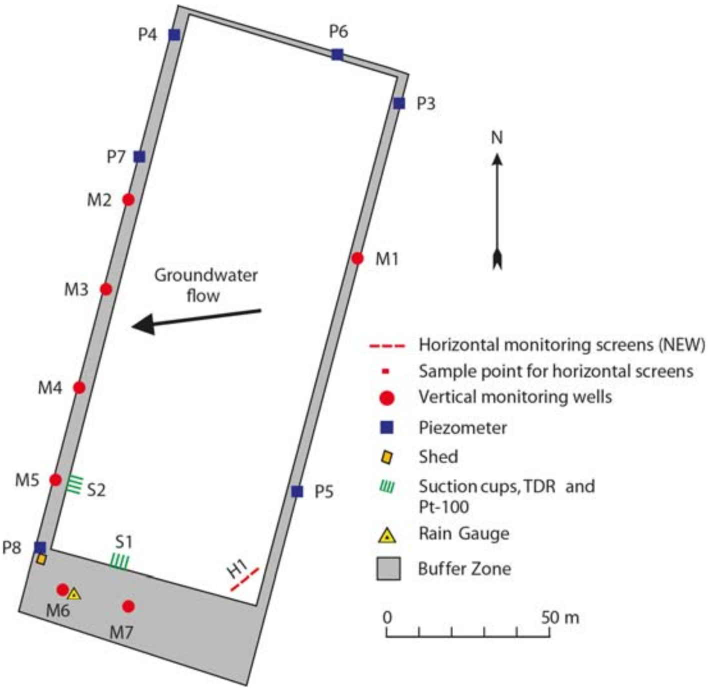

Figure 2.1. Overview of the **Tylstrup** site. The innermost white area indicates the cultivated land, while the grey area indicates the surrounding buffer zone. The positions of the various installations are indicated, as is the direction of groundwater flow (by an arrow). Pesticide monitoring is conducted monthly and half-yearly from suction cups and selected both vertical and horizontal monitoring screens as described in Table A2.1 in Appendix 2.

2.1.2 Agricultural management

Management practice during the 2012-2013 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.

Ploughing of the field was done on 22 March 2012 and 2 days later the field was sown with spring barley (cv. TamTam), which emerged on 10 April. Spraying of weeds was done twice: Bifenox was used on 21 May whereafter aminopyralid, florasulam and 2,4-D were applied on 25 May. sAminopyralid was subsequently included in the monitoring. Monitoring of bifenox and it's degradation products ended in December 2012. Irrigation was done once using 24 mm on 31 May.

Spraying of fungi was done on 28 June 2012, using epoxiconazole and boscalid of which only the later was monitored. Monitoring of boscalid ended on 11 December 2012. On 13 August 2012 the barley was sprayed with glyphosate due to problems with couch-grass (Agropyrum repens, L.). The glyphosate was not monitored. At harvest on 27 August 2012, 62.0 hkg/ha of grain (85% dry matter) and 37.3 hkg/ha of straw (100% dry matter) was removed from the field.

After ploughing on 20 September 2012 the field was sown with winter rye (cv. Magnifico) on 23 September, which emerged on 5 October. The herbicides prosulfocarb was applied on 12 October 2012 and fluroxypyr on 8 May 2013. Only prosulfocarb is monitored.

2.1.3 Model setup and calibration

The numerical model MACRO (version 5.2 Larsbo *et al.,* 2005) 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 variably-saturated zone during the full monitoring period May 1999–June 2013 and to establish an annual water balance.

Compared to Brüsch *et al.* (2013b), one additional 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 2013. 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 2.1) 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 2.1. 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	506	501
1.7.11–30.6.12	773	923	24	501	446
1.7.12–30.6.13	773	803	0	528	275

[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 variably-saturated zone (Figure 2.2). The overall trends in soil water saturation were modelled successfully, with the model capturing soil water dynamics at all depths (Figure 2.2 C-E). During the last six hydraulic years excluding the latest spring period, the level in water saturation at 25 cm b.g.s. has been overestimated and the initial decrease in water saturation observed during the summer periods at 25, 60 and 110 cm b.g.s. has been less well captured.

The dynamics of the groundwater table were well captured whereas the amplitude of the fluctuations was not (Figure 2.2B).

The resulting annual water balance is shown for each hydraulic year of the monitoring period (July–June) in Table 2.1. In the recent hydraulic year, July 2012–June 2013, precipitation were in the low end of the range observed since monitoring began at the site and the actual evapotranspiration in the high end, leaving the groundwater recharge/percolation being the lowest compared to the other hydraulic years (Figure 2.2B). The monthly precipitation pattern for this year was low to medium compared with earlier years. March 2013 was the driest month ever monitored with only 3 mm of precipitation (Appendix 4). No artificial irrigation was however needed on the winter rye.

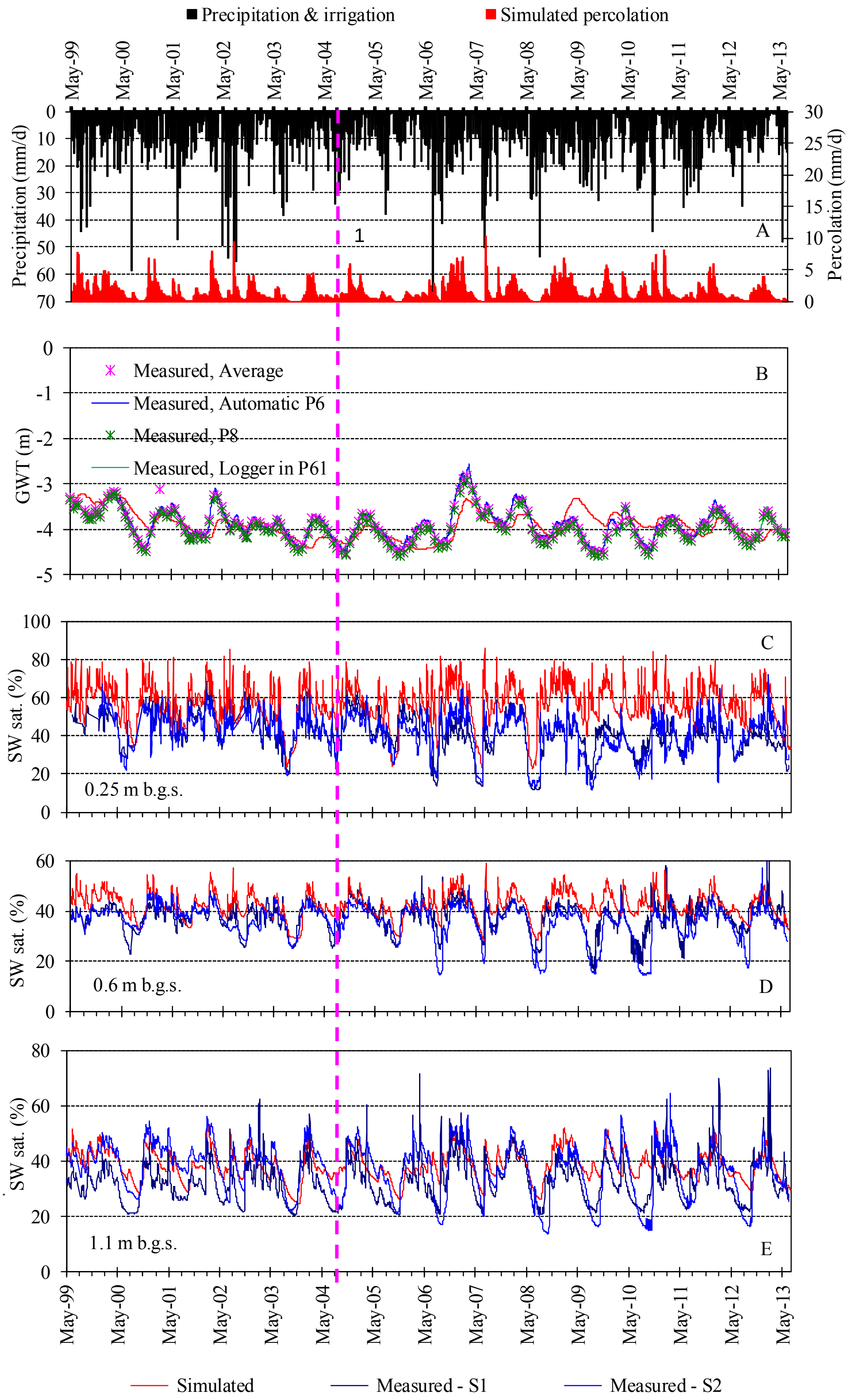

Figure 2.2. Soil water dynamics at **Tylstrup**: Measured precipitation, irrigation and simulated percolation 1 m b.g.s. (A), simulated and measured groundwater level GWT (B), and simulated and measured soil water saturation (SW sat.) at three different soil depths (C, D, and E). The measured data in 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 2.1). The broken vertical line indicates the beginning of the validation period (July 2004-June 2013).

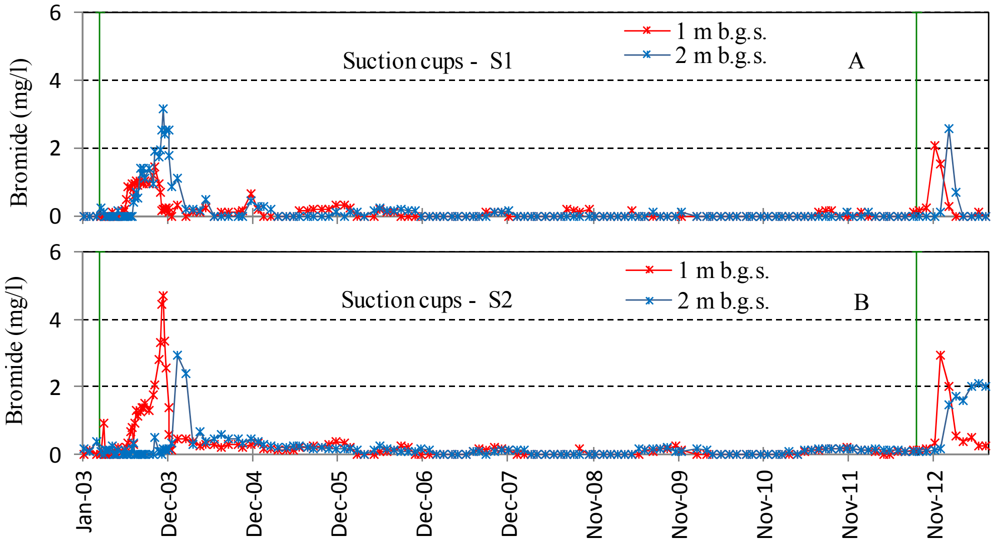

Figure 2.3. Measured bromide concentration in the variably-saturated zone at **Tylstrup**. The measured data derive from suction cups installed 1 m b.g.s. and 2 m b.g.s. at locations S1 (A) and S2 (B) indicated in Figure 2.1. The green vertical lines indicate the dates of bromide applications.

2.2.2 Bromide leaching

Bromide has now been applied three times (1999, 2003 and 2012) at Tylstrup. The bromide concentrations measured until April 2003 (Figure 2.3, Figure 2.4 and Figure 2.5) 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).

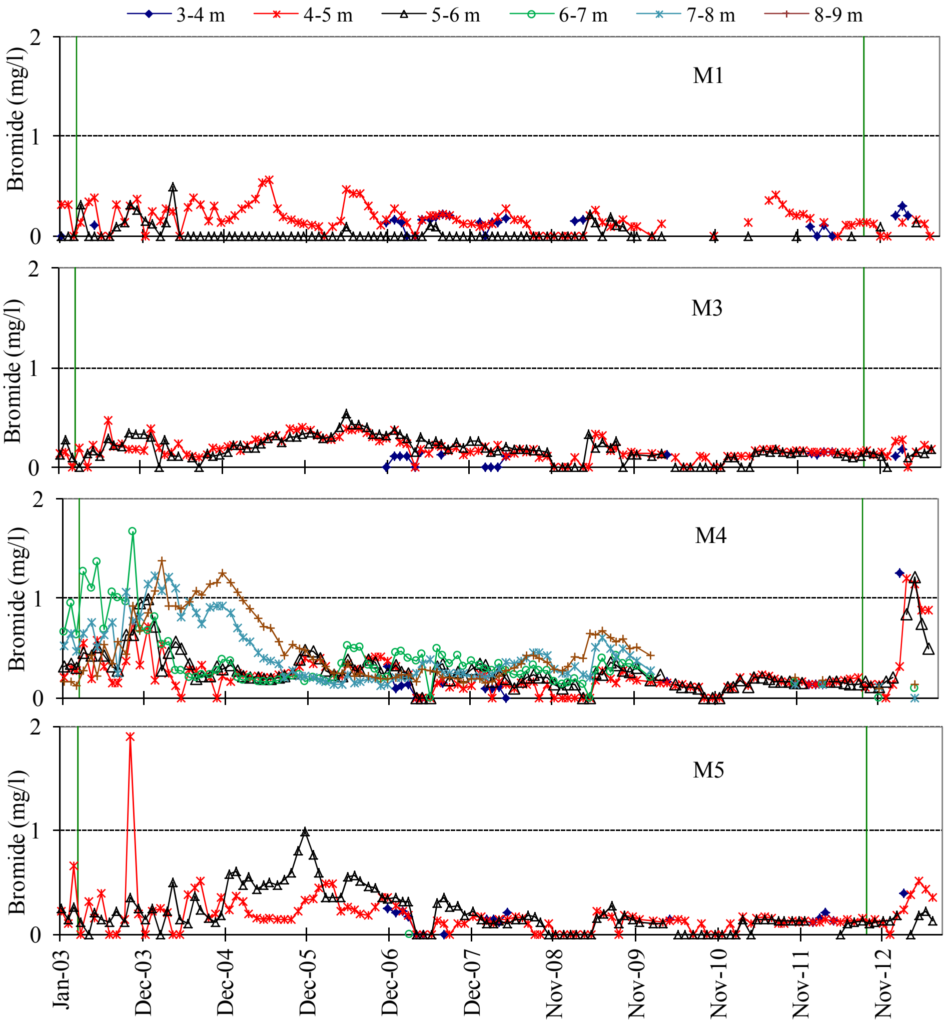

Figure 2.4. Bromide concentration in the groundwater at **Tylstrup.** The data derive from monitoring wells M1–M5. Screen depth is indicated in m b.g.s. The green vertical lines indicate the dates of bromide applications.

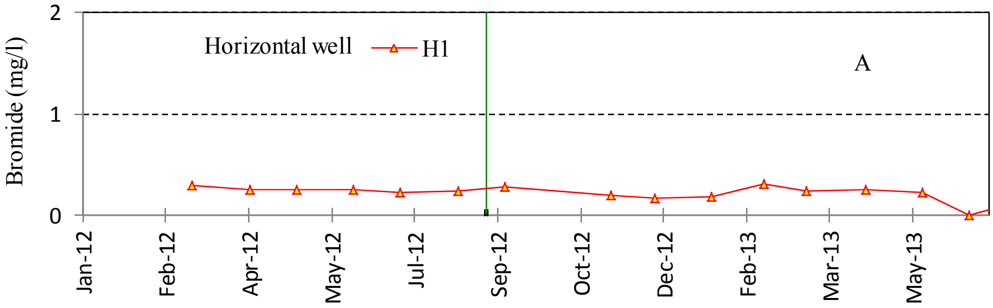

Figure 2.5. Bromide concentration in the groundwater at **Tylstrup.** The data derive from horizontal monitoring well H1. The green vertical lines indicate the date of bromide application.

2.2.3 Pesticide leaching

Monitoring at Tylstrup began in May 1999 and encompasses the pesticides and degradation products shown in Appendix 7. Pesticide applications during the latest growing seasons are listed in Table 2.2 and are shown together with precipitation and simulated precipitation in Figure 2.6.

It should be noted that precipitation in Table 2.2 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. Pesticides applied later than April 2013 are not evaluated in this report and hence are not included in Table 2.2 and Figure 2.6.

The current report focuses on the pesticide applied from 2011 and onwards, while leaching risk of pesticides applied before 2011 has been evaluated in previous monitoring reports (see http://pesticidvarsling.dk/publ_result/index.html).

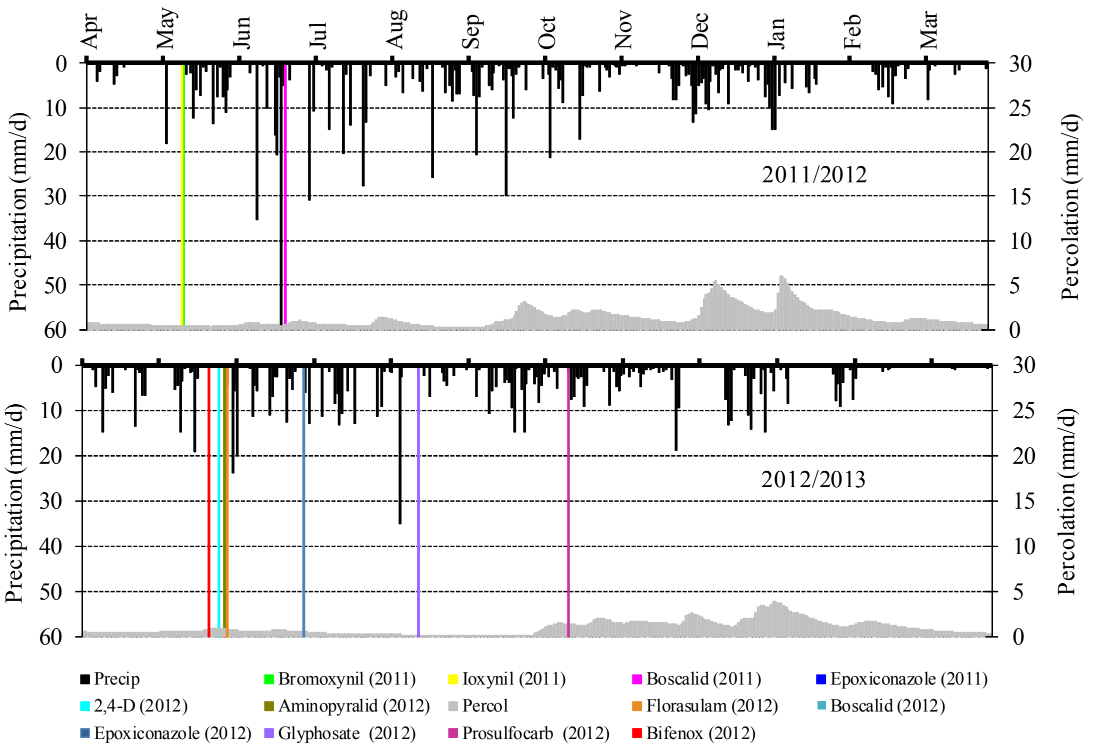

Figure 2.6. Application of pesticides included in the monitoring programme, precipitation and irrigation (primary axis) together with simulated percolation 1 m b.g.s. (secondary axis) at **Tylstrup** in 2011/2012 (upper) and 2012/2013 (lower). Boscalid 2011 included application boscalid and epoxyconazol.

Table 2.2. Pesticides analyzed 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 month) 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. (End monito) end of monitoring of pesticide (P) or degradation product (M). Bifenox (Fox 480 SC) was applied May 2012, and analyzed from May to December 2012.

Crop	Applied Product	Analyzed pesticide	Applica. date	End monito.	Y 1st precip.	Y 1st percol.	M 1st precip.	M 1st percol.	C_{mean}
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	Dec 09	1032	415	36	26	<0.01
Spring barley 2009	Amistar	Azoxystrobin(P)	Jun 09	Jun 11	909	475	138	11	<0.01
		CyPM(M)	Jun 09	Jun 11	909	475	138	11	<0.01
	Basagran M75	Bentazone(P)	May 09	Jun 12	996	488	133	22	<0.01
Potatoes 2010	Fenix	Aclonifen(P)	May 10	Jun 12	958	491	62	12	<0.01
	Titus WSB	PPU(M)	May 10	Jun 12	958	491	62	12	0.01-0.02
		PPU-desamino(M)	May 10	Jun 12	958	491	62	12	<0.01
	Ranman	Cyazofamid(P)	Jun 10	Jun 12	981	499	128	17	<0.01
	Ridomil Gold MZ Pepite	Metalaxyl-M(P)	Jul 10	Jun 12	934	514	127	43	<0.01
		CGA 108906(M)	Jul 10	Jun 12	934	514	127	43	0.03-0.12
		CGA 62826(M)	Jul 10	Jun 12	934	514	127	43	<0.01-0.02
Spring barley 2011	Bell	Boscalid (P)	Jun 11	Dec 12	959	467	106	20	<0.01
Spring barley 2012	Fox 480 SC	Bifenox(P)**	May 12	Dec 12	803	338	100	23	<0.02
		Bifenox acid(M)	May 12	Dec.12	803	338	100	23	<0.05
		Nitrofen(M)	May 12	Dec.12	803	338	100	23	<0.01
	Mustang forte	Aminopyralid(P)	May 12	Jun 13*	852	335	121	22	<0.02
Winter rye 2013	Boxer	Prosulfocarb(P)	Oct 12	Jun 13*	507	285	79	49	<0.01

Systematic chemical nomenclature for the analyzed pesticides is given in Appendix 1.
**monitoring continues the following year.*
***Bifenox (Fox 480 SC) was applied May 2012, and analyzed from May to December 2012.*

Leaching of metalaxyl-M applied in potatoes in 2010 was minor at Tylstrup. The compound was only detected in four samples collected from the variably-saturated zone, concentration level ranging from 0.018 to 0.03 µg/L (Figure 2.7). However, two degradation products of metalaxyl-M (CGA62826 and CGA108906) leached from the root zone (1 m b.g.s.), the latter in average concentrations exceeding 0.1 µg/L (Table 2.2 and Figure 2.7). Both compounds were found in suction cups 1 m b.g.s. in 2010, 2011, 2012 and 2013 and the leaching of CGA108906 has not yet ceased. In the second monitoring year CGA108906 was found in even higher concentrations in the suction cups, with maximum concentrations of 2.5 and 4.8 µg/L in S1 and S2, respectively, but in the monitoring period 2012-2013 the concentrations have fallen below 0.1 µg/L, Figure 2.7.

In the saturated zone neither metalaxyl-M nor CGA62826 was found in any samples collected from the wells situated downstream the field site before spraying, whereas both compounds were found in samples collected from M1 situated upstream of the field site (Figure 2.8). 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 show that these compound have leached from previous application occurring at these upstream neighbouring fields, where metalaxyl and metalaxyl-M have been applied (Brüsch et al., 2013, Appendix 7).

In the period April 2010 to June 2013, CGA108906 was found in 90% of the analyzed groundwater samples. In 21% of the analyzed samples concentrations exceed 0.1 µg/L. Similar to the other compounds, CGA108906 was detected in samples from the upstream well M1. Moreover, it was present in the groundwater before metalaxyl-M was applied at the PLAP field in June 2010. The background concentration of CGA 108906 found in the monitoring wells makes it difficult to determine, whether the elevated concentrations observed in the downstream monitoring wells are due to the metalaxyl-M applied on the PLAP field site in 2010 or to previous applications on the upstream fields. However, the background concentration suggests that leaching of CGA 108906 occurs both from the test field as well as from neighbouring upstream fields. Further, with a background level of CGA108906 ranging between 0.02–0.3 µg/L, additional input via root zone leaching is likely to increase the frequency of exceedance of the 0.1 µg/L in samples collected from the groundwater monitoring wells. Findings of CGA 108109 in suction cups and in the new horizontal well H 1, Figure 2.7 and 2.8, clearly indicate that the findings originate from the test field.

Metalaxyl-M, CGA 62826 and CGA 108906 were found in up to 83% of the groundwater samples, and one of the degradation products, CGA108906, was found in 100% of the water samles from the variably-saturated zone (Table 2.3).

CGA108906 was found in concentrations up to 1.5 µg/L in downstream monitoring wells after the application in 2010, Figure 2.8D.

Metalaxyl was on the Danish market from 1980-1995, with reported maximum allowed dosage from 1984-1995 being 375 g a.i./ha. It re-entered the Danish marked in 2007 as metalaxyl-M with a maximum allowed dosage of 77.6 g a.i./ha.

Since 2006 metalaxyl-M has been applied upstream neighbouring fields. The reported dosages of these fields did not exceed the maximum allowed dosage of 77.6 g a.i./ha. Usage data from 1980-1995 are not available, but information from local farmers suggest that metalaxyl during this period was applied on some of the upstream neighbouring fields during this period.

Table 2.3. Findings of metalaxyl–M**,** CGA 62826 and CGA 108906 in groundwater samples, and in water samples from suction cups in the variably-saturated zone, **Tylstrup**. Data from June 2011 to June 2013.

June 2011- June 2013		Number of samples			in %		
		Analyzed	> D. L.	≥ 0.1 µg/L	0.01/0.02–0.1µg/L	≥ 0.1 µg/L	Total
Groundwater	Metalaxyl -M	146	7	0	4.8	0	4.8
	CGA 62826	146	14	0	9,6	0	9.6
	CGA 108906	146	121	23	67.1	15.8	82.9
Variably-saturated zone	Metalaxyl -M	64	0	0	0	0	0
	CGA 62826	64	17	3	21,9	4,7	26.6
	CGA 108906	64	64	7	89.1	10.9	100

D.L. – detection limit: Metalaxyl-M - 0.01 µg/L, degradation products – 0.02 µg/l.

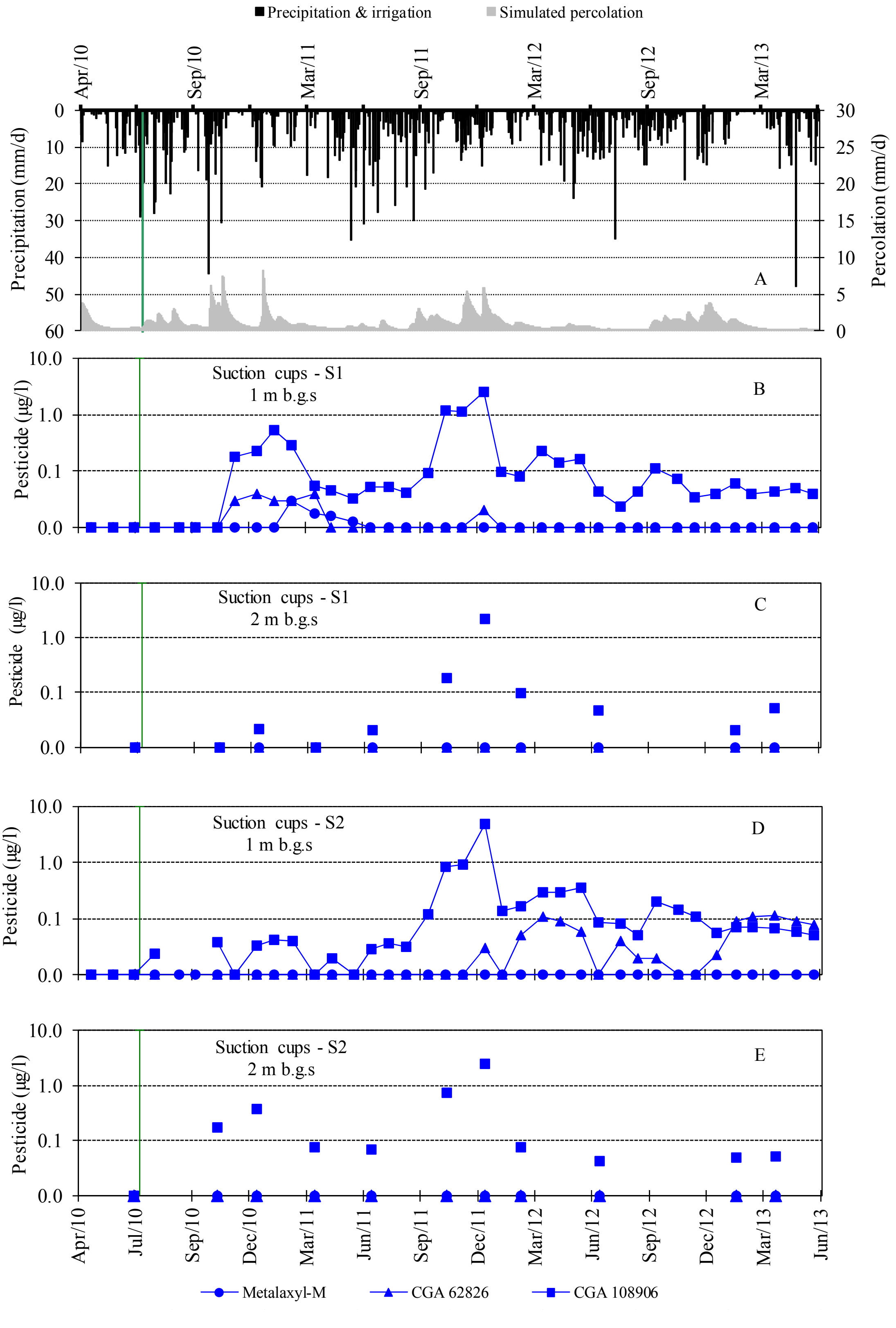

Figure 2.7. Precipitation, irrigation and simulated percolation 1 m b.g.s. (A) together with measured concentration of *metalaxyl-M, CGA62826* and *CGA108906* (µg/L) in suction cups installed at location S1 at 1 m b.g.s. (B) and 2 m b.g.s. (C) and location S2 at 1 m b.g.s. (D) and 2 m b.g.s. (E) at **Tylstrup**. The green vertical line indicates the date of pesticide application.

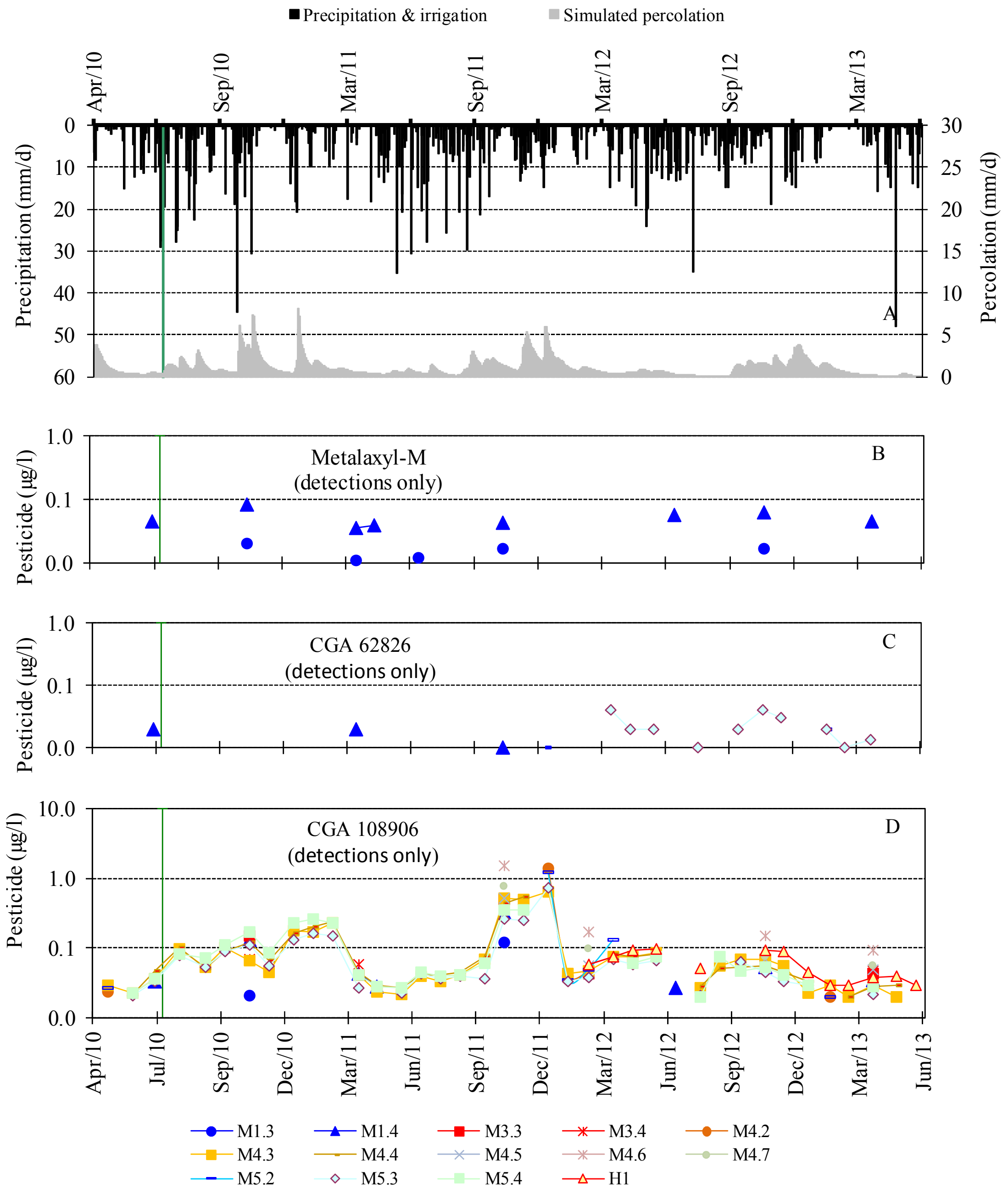

Figure 2.8. Precipitation, irrigation and simulated percolation 1 m b.g.s. (A) together with measured concentration of *metalaxyl-M* (B), *CGA62826* (C) and *CGA108906* (D) (µg/L) in horizontal and monitoring wells at **Tylstrup**. The green vertical line indicates the date of pesticide application.

Based on the available data it is concluded that residues detected in the groundwater are most likely to derive from current usage of metalaxyl-M allowed since 2007 and not previous usage of metalaxyl allowed from 1980–1995. With an average travel time to all monitoring wells being less than four years (Appendix 9) it is unlikely that water sampled from these screens have infiltrated the variably-saturated zone before 1995. A possibility could, however, be that the residues originating from the initial usage of 375 g a.i./ha (allowed in 1980-1995) were left in the soil and continued to leach 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. This assumption does not correspond with the regulatory assessment, where final endpoints for DT_{50} were less than 18 days (Danish EPA, 2007).

Boscalid was applied to spring barley in June 2011 and 2012. There have been no findings neither the saturated nor in the variably-saturated zone in Tylstrup between April 2011 and until the monitoring stopped in December 2012.

Aminopyralid was applied on spring barley in May 2012. In the monitoring period there have been no detections in the variably-saturated zone or in the groundwater.

Prosulfocarb was applied on winter rye October 2012, and there have been four findings in groundwater, all below 0.1 µg/L. Prosulfocarb was not found in the variably-saturated zone.

Bifenox was applied on spring barley in May 2012. The monitoring of bifenox and the two degradation products stopped in December 2012 after bifenox was taken from the market. Bifenox and the two degradation products were not found in concentrations exceeding the detection limits.

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 1.1). 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 3.2B) The overall direction of groundwater flow is towards the northwest (Figure 3.1). 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 1.1). 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 and the analysis methods in Kjær et al. (2002). The monitoring design and test site are described in detail in Lindhardt et al. (2001). In September 2011, the monitoring system was extended with three horizontal screens (H1) 2.5 m b.g.s. in the South-Eastern corner of the field (Figure 3.1). A brief description of the drilling and design of H1 is given in Appendix 8.

3.1.2 Agricultural management

Management practice during the 2012-2013 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.

Ploughing of the field was done on 30 March 2012 followed by sowing of maize (cv. Atrium) on 3 May. The maize emerged on 17 May. Spraying of weeds was done thrice using bentazone on 26 May, mesotrione on 5 June, as well as fluroxypyr, florasulam, and 2,4-D on 15 June. Mesotrione and two of its degradation products, as well as bentazone were included in the monitoring. On 8 October 2012, 151.4 hkg/ha (100% dry matter) of whole crop maize was harvested.

The field was ploughed 6 April 2013 and a crop of pea (cv. Alvesta), were sown on 14 April and emerged on 26 April. The herbicides, pendimethaline and bentazone were applied twice; on 7 and 16 May 2013. Only the bentazone was included in the monitoring programme. Irrigation of the pea was done twice, using 30 mm on both 6 June and 9 July.

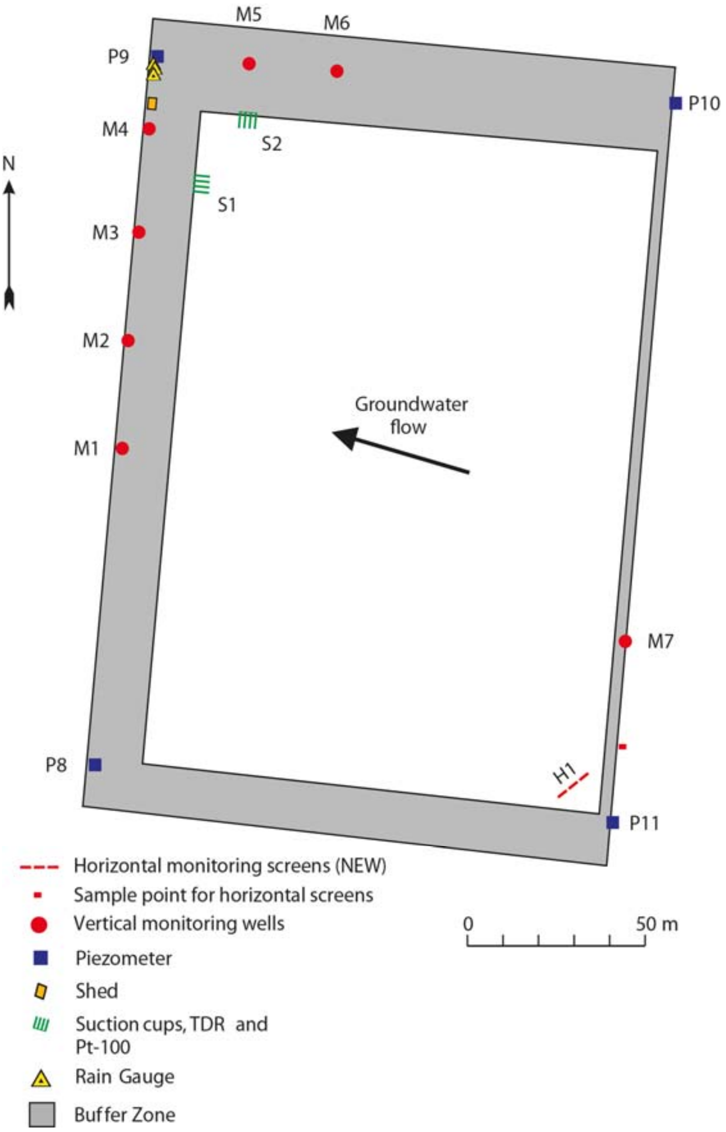

Figure 3.1. Overview of the **Jyndevad** site. The innermost white area indicates the cultivated land, while the grey area indicates the surrounding buffer zone. The positions of the various installations are indicated, as is the direction of groundwater flow (by an arrow). Pesticide monitoring is conducted monthly and half-yearly from selected horizontal and vertical monitoring screens and suctions cups as described in Table A2.1 in Appendix 2.

3.1.3 Model setup and calibration

The numerical model MACRO (version 5.2, 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 variably-saturated zone during the full monitoring period July 1999–June 2013 and to establish an annual water balance.

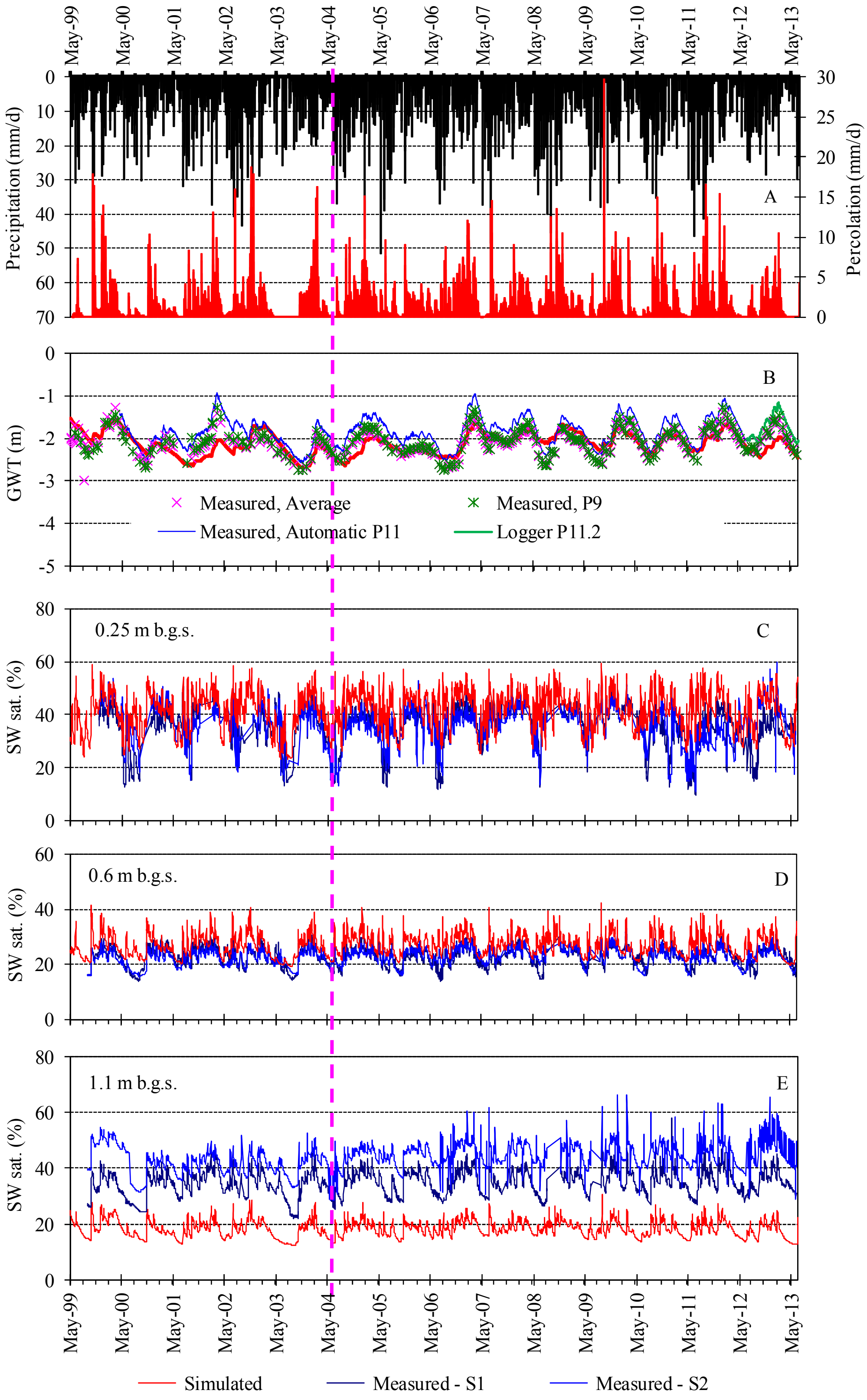

Figure 3.2. Soil water dynamics at **Jyndevad**: Measured precipitation, irrigation and simulated percolation 1 m b.g.s. (A), simulated and measured groundwater level (B), and simulated and measured soil water saturation (SW sat.) at three different soil depths (C, D and E). The measured data in B derive 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 3.1). The broken vertical line indicates the beginning of the validation period (July 2004-June 2013).

Compared with the setup in Brüsch *et al.* (2013b), 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 2013. 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 3.1), and the bromide concentration measured in the suction cups located 1 and 2 m b.g.s. (Figure 3.3). Data acquisition, model setup as well as results related to simulated bromide transport are described in Barlebo *et al.* (2007).

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 variably-saturated zone (Figure 3.2). The dynamics of the simulated groundwater table were well described with MACRO 5.1 (Figure 3.2B). No measurements of the water saturation were obtained during the following two periods: 1 June to 25 August 2009 (given degradation in the TDR measuring system) and 7 February to 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 3.2E) 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 0°C). The water flow through the soil profile will hereby be delayed – a delay, which cannot be captured by the MACRO-setup.

The resulting water balance for Jyndevad for all the monitoring periods is shown in Table 3.1. Compared with the previous thirteen years, the latest hydraulic year, July 2012-June 2013, was characterised by having low precipitation, low simulated actual evapotranspiration, low irrigation values and low groundwater recharge. Monthly precipitation in the latest hydraulic year was characterised as being low to medium and March was being the driest month monitored at this site with only 13 mm of precipitation (Appendix 4). Artificial irrigation was however only needed twice during summer with pea being sown in April. Continuous percolation 1 m b.g.s. was simulated for this hydraulic year.

Table 3.1. 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
1.7.11–30.6.12	995	1159	30	490	699
1.7.12–30.6.13	995	991	60	478	572

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

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

3.2.2 Bromide leaching

Bromide has now been applied three times at Jyndevad. The bromide concentrations measured until April 2003 (Figure 3.3, Figure 3.4 and Figure 3.5) 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).

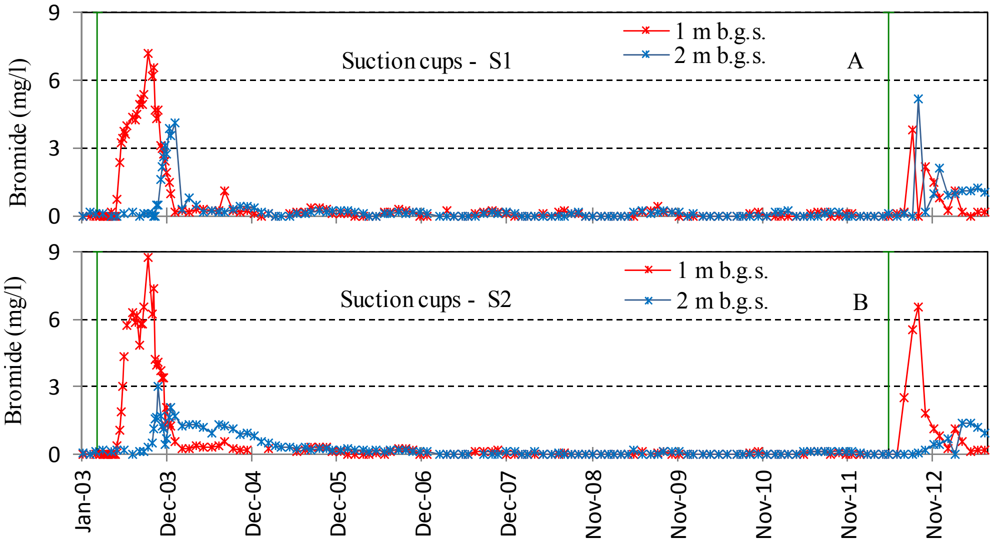

Figure 3.3. Bromide concentration in the variably-saturated zone at **Jyndevad**. The measured data derive from suction cups installed 1 m b.g.s. (upper) and 2 m b.g.s. (lower) at locations S1 and S2 (Figure 3.1). The green vertical lines indicate the dates of bromide applications.

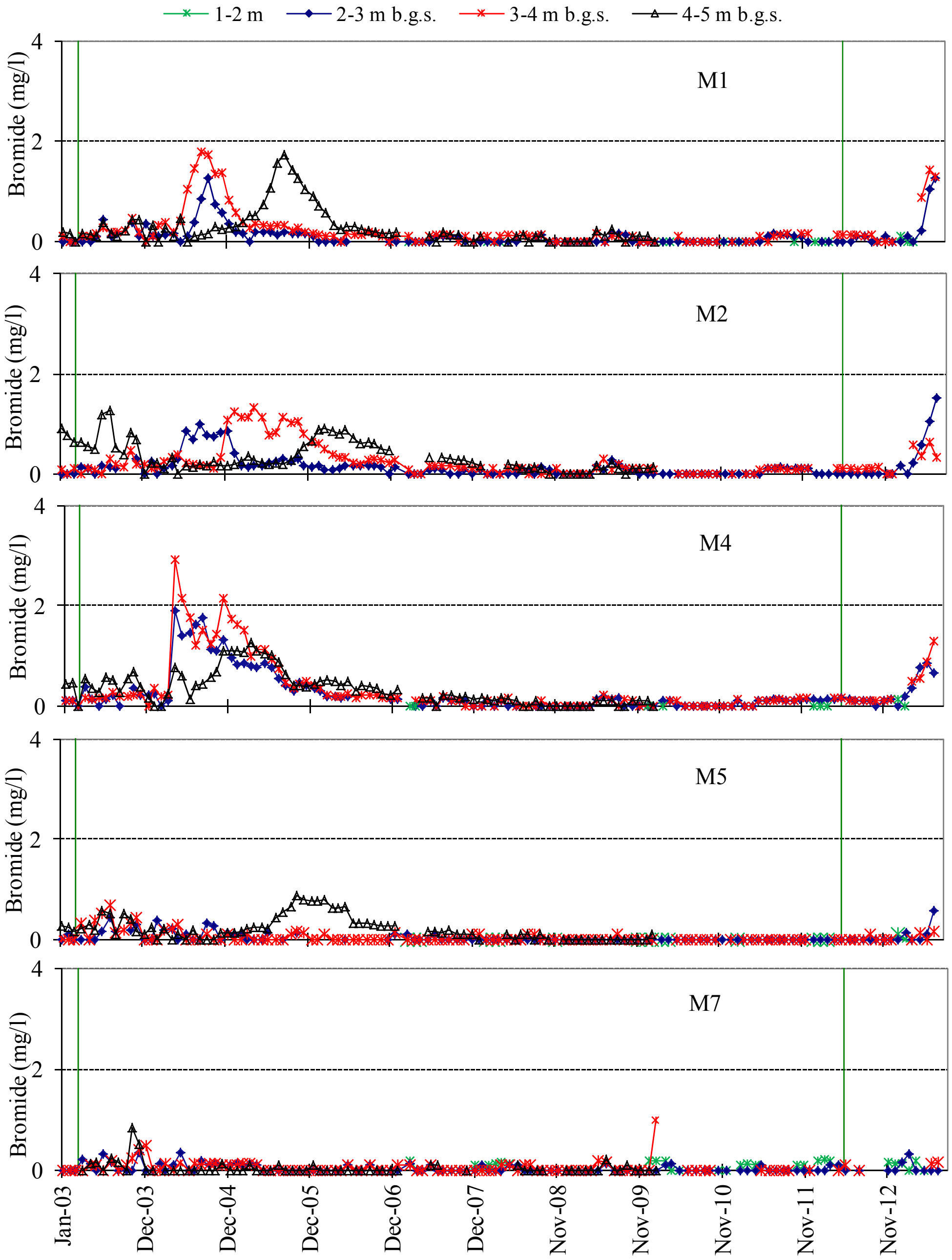

Figure 3.4. Bromide concentration in the groundwater at **Jyndevad**. The data derive from monitoring wells M1, M2, M4, M5, and M7. Screen depth is indicated in m b.g.s. The green vertical lines indicate the dates of bromide applications.

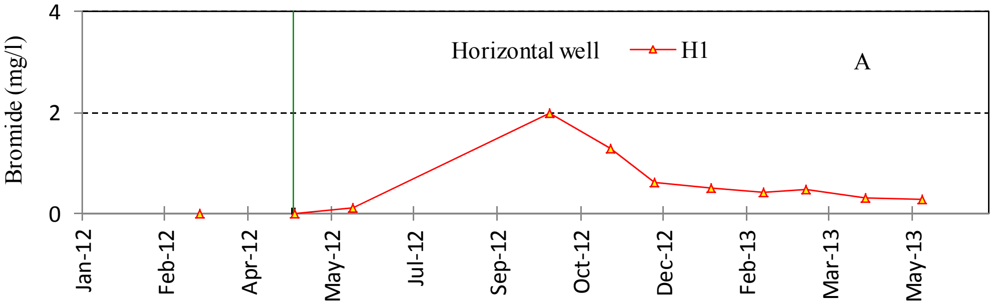

Figure 3.5 Bromide concentration in the groundwater at **Jyndevad.** The data derive from the horizontal monitoring well H1. The green vertical line indicates the date of bromide application.

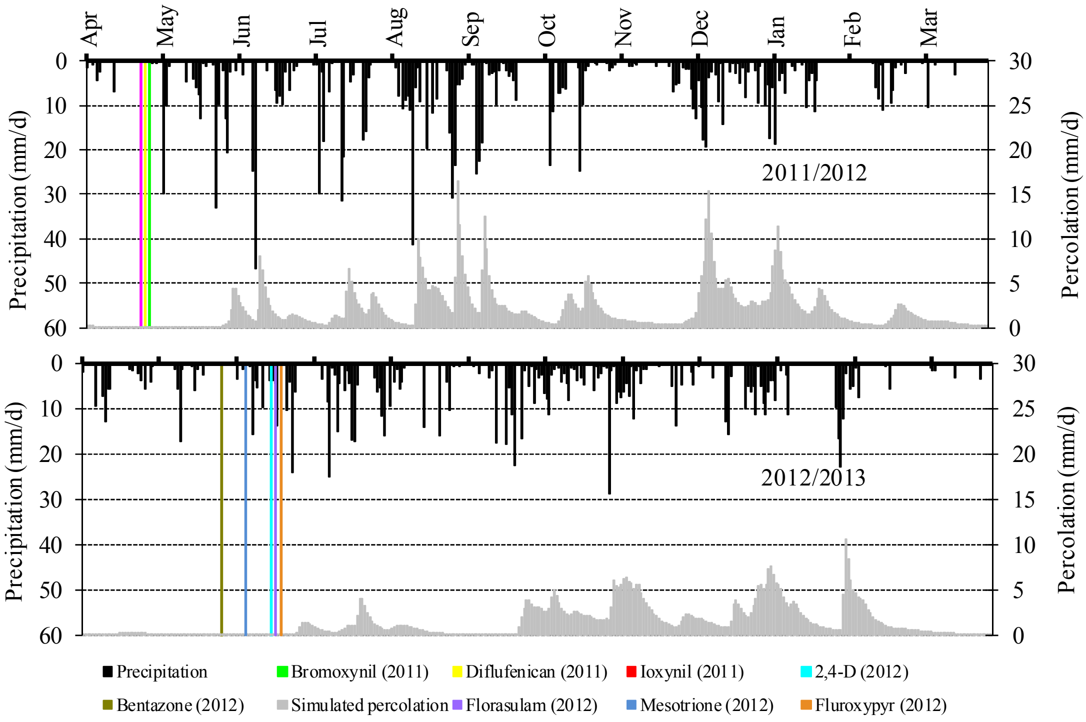

Figure 3.6. Application of pesticides included in the monitoring programme, precipitation and irrigation (primary axis) together with simulated percolation 1 m b.g.s. (secondary axis) at **Jyndevad** in 2011/2012 (upper) and 2012/2013 (lower).

3.2.3 Pesticide leaching

Monitoring at Jyndevad began in September 1999 and encompasses the pesticides and degradation products, as indicated in Appendix 7. Pesticide application during the most recent growing seasons is listed in Table 3.2 and shown together with precipitation and simulated precipitation in Figure 3.6. 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 (Table 3.2). Pesticides applied later than May 2013 are not evaluated in this report and not included in Table 3.2.

The current report focuses on the pesticides applied from 2011 and onwards, while leaching risk of pesticides applied before 2011 has been evaluated in previous monitoring reports (see http://pesticidvarsling.dk/publ_result/index.html).

Table 3.2. Pesticides analyzed 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 month) 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. (End monito.) end of monitoring of pesticide (P) or degradation product (M).

Crop	Applied product	Analyzed pesticide	Applica. date	End monito.	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	Dec 09	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 12	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 12	1206	630	106	3	<0.02
	Fox 480 SC	Bifenox acid(M)	Apr 09	Jun 12	1206	630	106	3	<0.05
	Fox 480 SC	Nitrofen(M)	Apr 09	Jun 12	1206	630	106	3	<0.01
Potatoes 2010	Fenix	Aclonifen(P)	May 10	Jun 12	1149	567	123	10	<0.01
	Ranman	Cyazofamid(P)	Jun 10	Jun 12	1188	627	125	16	<0.01
	Titus WSB	PPU(M)	Jun 10	Jun12	1160	592	137	13	0.02 1)
		PPU-desamino(M)	Jun 10	Jun12	1160	592	137	13	<0.01 1)
	Ridomil Gold MZ Pepite	Metalaxyl-M(P)	Jul 10	Jun13	1073	613	161	41	0.02 1)
		CGA108906(M)	Jul 10	Jun13	1073	613	161	41	0.37-0.6
		CGA62826(M)	Jul 10	Jun13	1073	613	161	41	0.16-0.19
Spring barley 2011	DFF	Diflufenican(P)	Apr 11	Jun13	1315	742	126	3	<0.01
		AE-05422291(M)	Apr 11	Jun13	1315	742	126	3	<0.01
		AE-B107137(M)	Apr 11	Jun 13	1315	742	126	3	<0.01
Maize 2012	Callisto	Mesotrione (P)	Jun 12	Jun 13*	993	512	109	11	<0.01
	Callisto	AMBA(M)	Jun 12	Jun 13*	993	512	109	11	<0.01
	Callisto	MNBA(M)	Jun 12	Jun 13*	993	512	109	11	<0.01
	Fighter 480	Bentazone(P)	Jun 12	Jun 13*	994	513	114	2	0.04-0.24
Peas 2013	Fighter 480	Bentazone(P) 2)	May 13	Jun 13*	220	26	84	0	0.01-0.09

Systematic chemical nomenclature for the analyzed pesticides is given in Appendix.

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

2) *Bentazone applied on 7May and 16 May.*

* *monitoring continues the following year.*

In Table 3.2 weighted average concentrations 1 m b.g.s. (C_{mean}) is calculated from both S1 and S2. When these values are reported as a range it indicates that C_{mean} in S1 and S2 differs from each other. During the monitoring period 2011/2012 it was unfortunately not possible to extract sufficient water from S2 to perform all pesticide analyzes. For some of the compounds (metalaxyl-M, PPU, PPU-desamino) there was not sufficient data to calculate weighted leachate concentration, why reported 2010 values in Table 3.2 refers to suction cups S1 only. For the same reason concentration of CGA62826 and CGA108906 in S2 was not measured in S2 during the first months after applications. The calculated concentration of CGA62826 and CGA108906 was 0.16-0.19 and 0.37-0.6, respectively (Table 3.2) and refers to average leaching concentration from date of first analysis on 4 November 2010 until 1 July 2011.

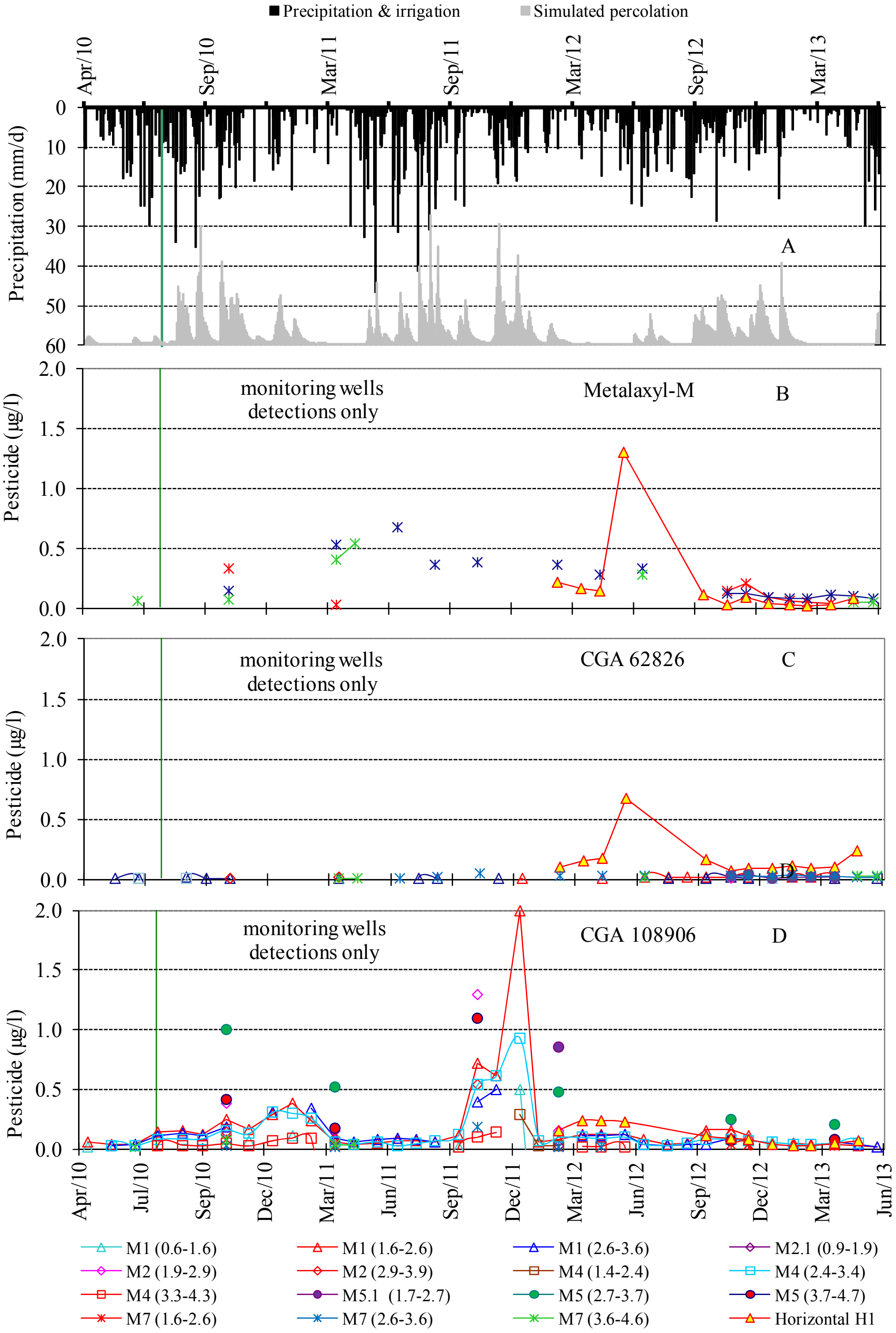

Figure 3.7. Precipitation, irrigation and simulated percolation 1 m b.g.s. in Jyndevad. (A) together with measured concentrations (µg/L) in downstream (M1, M2, M4 and H1) and upstream horizontal and monitoring wells (M7) of *metalaxyl-M* (B), CGA 62826 (C) and CGA 108906 (D) at **Jyndevad**. The numbers in parentheses indicate the depths of the analyzed screens. The green vertical line indicates the date of pesticide application.

Both metalaxyl-M applied on potatoes in July 2010 as well as two of its degradation product CGA62829 and CGA108909 leached from the root zone (1 m b.g.s.) - the two latter in average concentrations exceeding 0.1 µg/L (Table 3.2, Figure 3.7 and Figure 3.8). Both degradation products were found in water from suction cups 1 m b.g.s. at the end of the last monitoring period, indicating that leaching had not yet ceased.

Results from the saturated zone suggested that previous application occurring at up stream neighbouring fields also have induced leaching to the groundwater of metalaxyl-M, CGA62826 and CGA108906. All three compounds were present in the groundwater before metalaxyl-M was applied to the field. They were also detected in water collected from M7 situated upstream of the test field (Figure 3.7). CGA108906 was also found in M5 located north of the field. The tracer test suggested that water sampled in M7 and M5 (uppermost three filters) had not infiltrated at the PLAP site, but originated from the upstream neighbouring fields, where metalaxyl-M have also been applied (Brüsch et al., 2013).

CGA 62826 and CGA 108906 were detected in approximately 80% of the samples from the variably-saturated zone and in up to 75% of the groundwater samples (Table 3.3).

Table 3.3. Findings of metalaxyl–M**,** CGA 62826 and CGA 108906 in groundwater samples, and in water samples from suction cups in the variably-saturated zone, **Jyndevad**. Data from June 2011 to June 2013.

June 2011- June 2013		Number of samples			in %		
		Analyzed	> D. L.	≥ 0.1 µg/L	0.01/0.02–0.1µg/L	≥ 0.1 µg/L	Total
Groundwater	Metalaxyl -M	146	35	18	11.6	12.3	24
	CGA 62826	147	61	8	36.1	5.4	41.5
	CGA 108906	147	109	42	45.6	28.6	74.1
Variably-saturated zone	Metalaxyl -M	36	3	0	8.3	0	8.3
	CGA 62826	46	38	8	65.2	17.4	82.6
	CGA 108906	46	36	17	41.3	37.0	78.3

D.L. – detection limit: Metalaxyl-M - 0.01 µg/L, degradation products – 0.02 µg/l.

The background concentration of CGA108906, found in water from all monitoring wells, makes it difficult to determine, whether the elevated concentrations observed in downstream monitoring wells during the two year monitoring period, are due to the metalaxyl-M applied on the PLAP test site in 2010, or to previous application on the upstream fields. However, with a background level of CGA 108906 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 exceedance of the 0.1 µg/L in collected groundwater samples.

In the horizontal well, H1, CGA 108906 was found in 15 analyzed samples between March 2012 and October 2013 in concentrations from 0.03-0.24 µg/L (Figure 3.7). The average concentration was 0.11 µg/L. The findings in mixed samples from three screens in the horizontal well indicate clearly that CGA 108906 originate from the test field.

Metalaxyl-M was detected in water from the upstream groundwater monitoring well M7 in high concentrations reaching 0.68 µg/L, but it was not detected in water from the downstream groundwater monitoring wells. Metalaxyl-M was found in 12 water samples, collected from the horizontal well H1, had concentrations reaching 1.3 µg/L in June 2012. CGA62826 was only found in small concentrations in water from the vertical groundwater wells, whereas it was found in increasing concentrations (between

0.11µg/L and 0.68 µg/L) in water from H1 in the same period (March 2012 to June 2012). In the following period (July 2012 to June 2013) CGA62826 was found in all eight analyzed water samples from H1, maximum being 0.24 µg/L in May 2013.

Metalaxyl was on the Danish market from 1980-1995, in a maximum allowed dosage from 1984-1995 of 375 g a.i./ha. It was then banned, but re-entered the Danish marked in 2007 as metalaxyl-M with a maximum allowed dosage of 77.6 g a.i./ha. Since 2006 metalaxyl-M was applied at upstream neighbouring 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 to 1993 was also reported. For putting the results into a regulatory context it would thus be important to assess, if the pesticide residues measured in groundwater originate from the 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. With an average travel time to all monitoring wells being less than 3 years (Appendix 9) it is unlikely that water sampled from these screens have infiltrated from the variably-saturated zone before 1995, 17 years ago. Based on available data, it is likely that the residues detected in the groundwater originate from the current usage of metalaxyl-M (allowed since 2007) and not the initial usage allowed from 1980–1995.

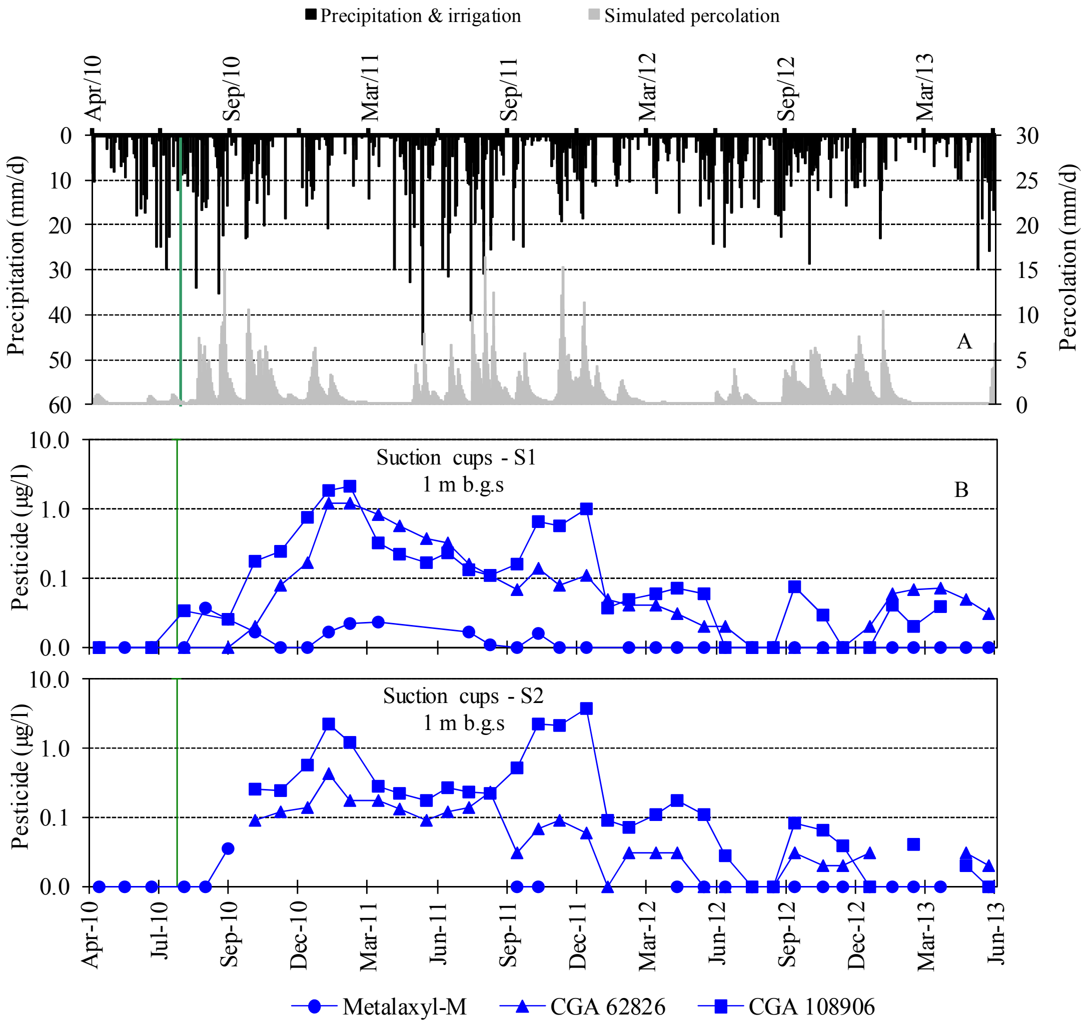

Figure 3.8. Precipitation, irrigation and simulated percolation 1 m b.g.s. (A) together with measured concentrations of *Metalaxyl-M,* CGA 62826 and CGA 108906 at **Jyndevad**. The green vertical line indicates the date of pesticide application.

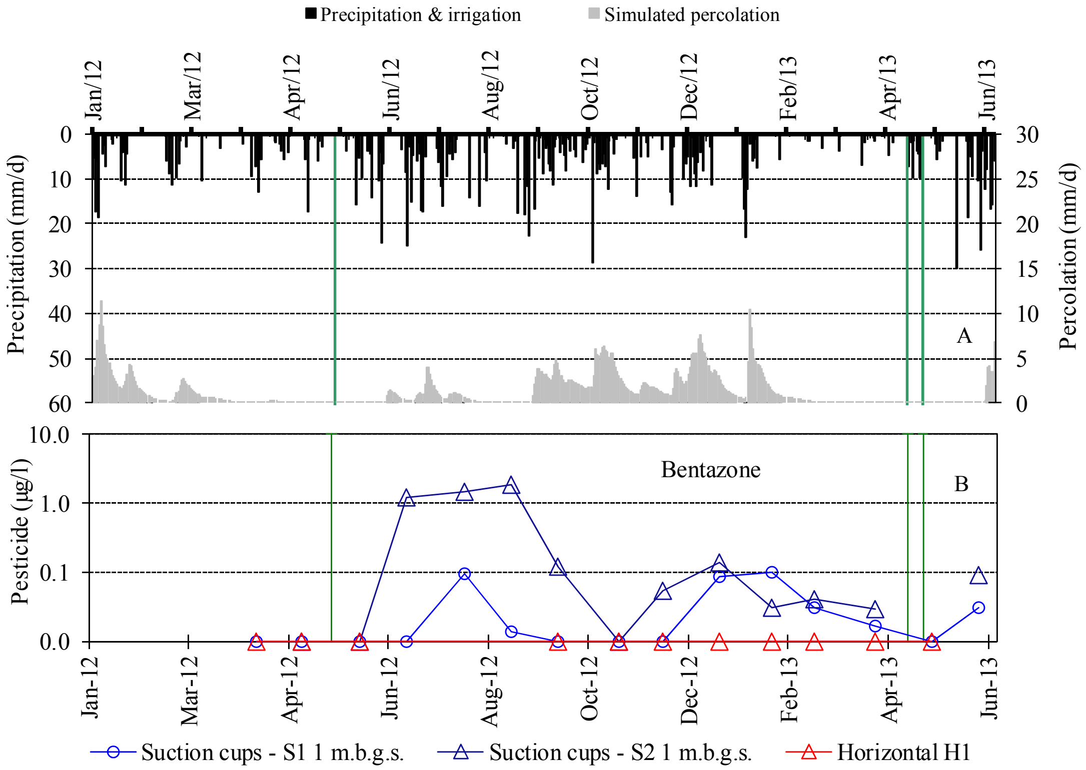

Figure 3.9. Precipitation, irrigation and simulated percolation 1 m b.g.s. (A) together with measured concentrations of bentazone in suction cups S1 and S2 and horizontal well H1 at **Jyndevad**. The green vertical lines indicate the dates of bentazone application.

A possibility could however be that the residues originating from the initial usage of 375 g a.i./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 not corresponding to the regulatory assessment, reporting the final endpoints for DT_{50} to be less than 18 days (Danish EPA, 2007).

Bentazone was not detected in any of the samples from the vertical monitoring wells, whereas 0.01 µg/L was found in H1 on 14 February 2013, after the application on maize in June 2012.

However, it was found frequently in samples from suction cups, reaching a maximum of 1.9 µg/L in September 2012 (Figure 3.9.b). The bentazone leached from the variably-saturated zone in average concentrations between 0.04 and 0.24µg/L. Except for one groundwater sample containing 0.01 µg/L collected September 2008, epoxiconazole did not leach at Jyndevad.

Diflufenican, used in spring barley in 2011, and two of its degradation products AE-05422291 and AE-B107137, were not detected in the variably-saturated zone or saturated zone between April 2011 and June 2013.

Mesotrione was applied on maize in June 2012, and neither mestotrione nor two of its degradation products AMBA and MNBA were detected in water samples from the variably-saturated or saturated zone.

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 the city Thisted in North-Western Jutland (Figure 1.1). The cultivated area is 1.7 ha (91 x 185 m) and slopes gently 1–2° to the north (Figure 4.1). 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 1.1). 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 and the analysis methods in Kjær et al. (2002). The monitoring design and test site are described in detail in Lindhardt et al. (2001). In September 2011, the monitoring system was extended with three horizontal screens (H3) 2 m b.g.s. in the North-Eastern corner of the field (Figure 4.1) - one of the screens should be located just below the drain line (a lateral) 1.1 m b.g.s and two screens between the laterals. A brief description of the drilling and design of H3 is given in Appendix 8.

4.1.2 Agricultural management

Management practice during the 2012-2013 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.

The crop of the field was a third year crop of red fescue (cv. Jasperina) that had been under sown in spring barley on 11 April 2009. After trimming of the grass on 17 August 2011 the field was sprayed with the herbicide bifenox on 16 September. Pig slurry was applied in the autumn, on 5 October 2011. Spraying against weeds was done twice using diflufenican on 13 April and fluazifop-P-butyl on 19 April 2012, both compounds included in the monitoring. The fungicide tebuconazole was applied on 18 May 2012, and its degradation product 1,2,4-triazol, was planned included in the monitoring programme, but problems in the analytical method development, meant that 1,2,4-triazol was omitted from the program until next monitoring year.

An amount of 14.16 hkg/ha of grass seed (87% dry matter) was harvested and 48.3 hkg/ha of straw (100% dry matter) removed from the field on 25 July 2012. The grass field was desiccated on 10 September 2012 using glyphosate. Ploughing was done 8 October 2012 and the following day the field was sown with winter wheat (cv. Hereford), which emerged on 24 October. Spraying of weeds was done on 9 November 2012 using ioxynil, bromoxynil and diflufenican of which only the latter was included in the monitoring.

Due to a combination of late sowing as well as harsh winter conditions, very few winter wheat plants survived, and the winter wheat was therefore replaced by a crop of spring barley (cv. Quenc) sown on 3 May 2013 and emerging on 16 May.

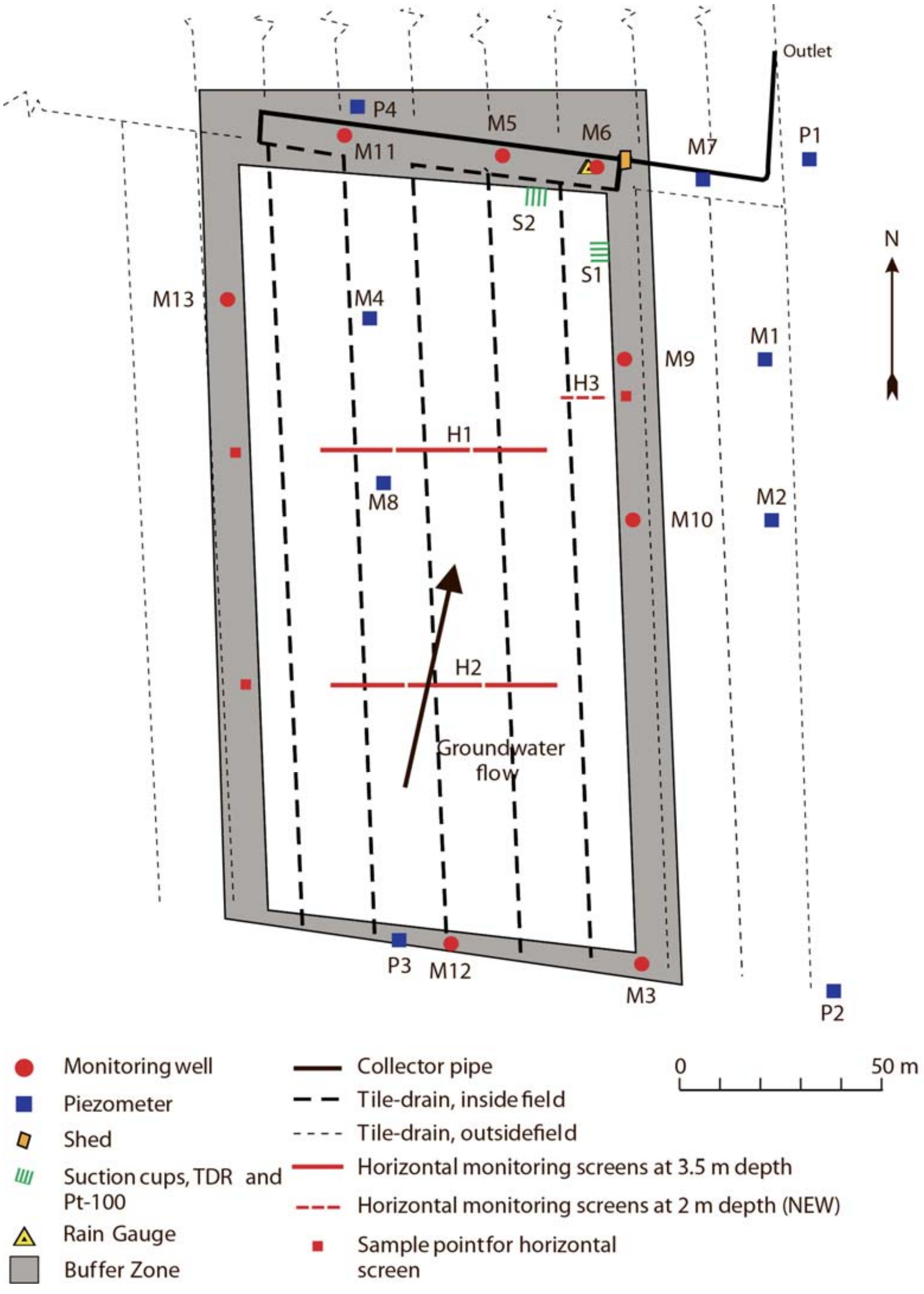

Figure 4.1. Overview of the **Silstrup** site. The innermost white area indicates the cultivated land, while the grey area indicates the surrounding buffer zone. The positions of the various installations are indicated, as is the direction of groundwater flow (by an arrow). Pesticide monitoring is conducted weekly from the drainage system (during period of continuous drainage runoff) and monthly and half-yearly from selected vertical and horizontal monitoring screens as described in Table A2.1 in Appendix 2.

4.1.3 Model setup and calibration

Compared with the setup in Brüsch *et al.* (2013b), 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 2013. 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 4.1), 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 from 15 December 2009 to 20 March 2010 were discarded given freezing soils (soil temperatures at or below 0° C). 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 consistent with the observed data, thus indicating a reasonable model description of the overall soil water dynamics in the variably-saturated zone (Figure 4.2). As in Brüsch *et al.* (2013b), 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 4.2B and 4.2C). The drainage flow period of the past year was well captured by the model (Figure 4.2C). As in the previous monitoring periods, the overall trends in soil water content were described reasonably well (Figure 4.2D, 4.2E and 4.2F), although the model describe the topsoil as being more wet during the summer period than actually measured by the upper TDR probes (Figure 4.2D).

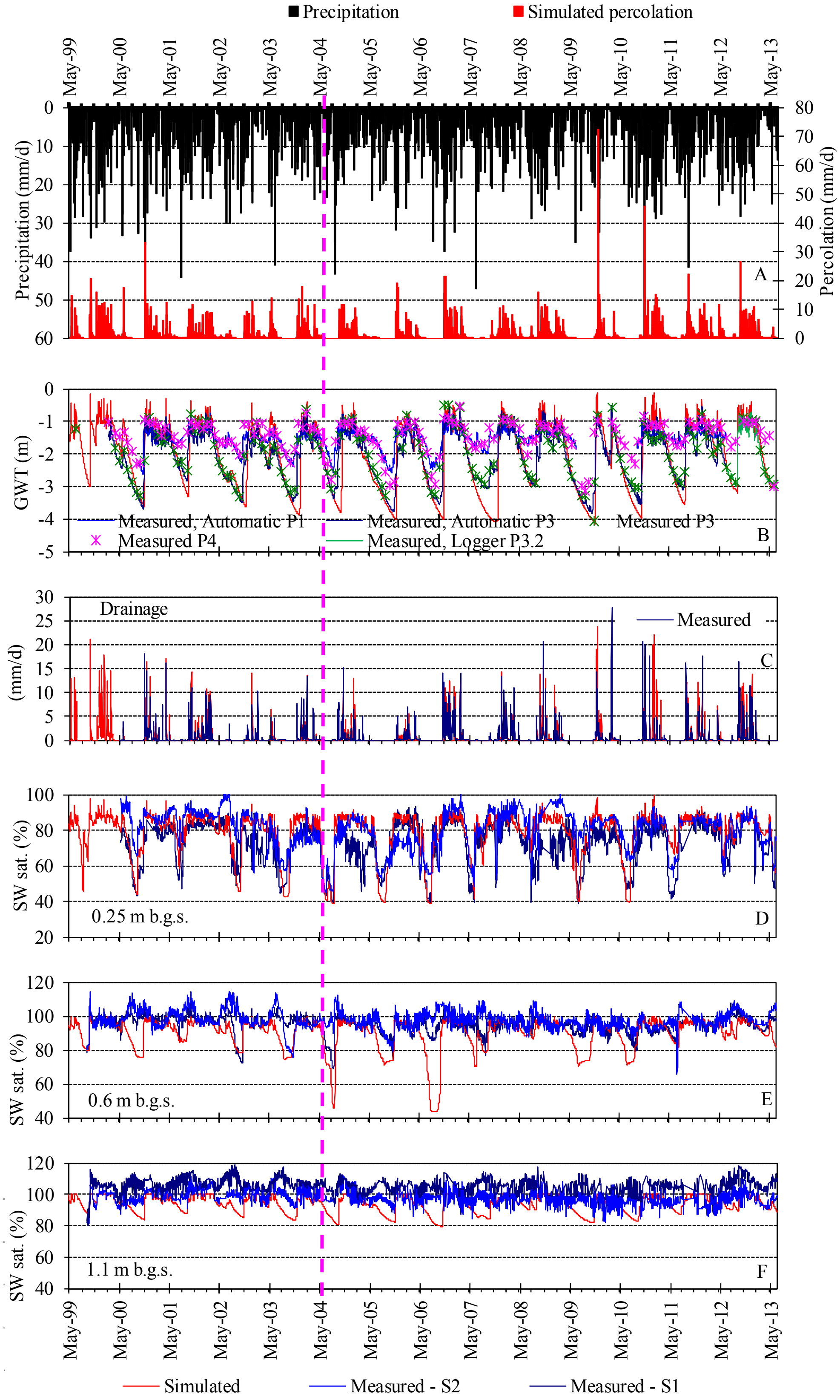

Figure 4.2. Soil water dynamics at **Silstrup**: Measured precipitation and simulated percolation 1 m b.g.s. (A), simulated and measured groundwater level GWT (B), simulated and measured drainage flow (C), and simulated and measured soil water saturation (SW sat.) at three different soil depths (D, E 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 4.1). The dotted vertical line indicates the beginning of the validation period (July 2004-June 2013).

Table 4.1. 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
1.7.11–30.6.12	976	1103	432	230	321	444
1.7.12–30.6.13	976	1020	466	249	333	306

[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 4.1. Compared with the previous 13 years, the recent hydraulic year July 2012-June 2013 was characterised by having medium precipitation, medium simulated actual evapotranspiration, and the second highest measured drainage. Precipitation of this year was characterised by February-March being the driest since the monitoring started and a very wet September-October (Appendix 4). Due to this precipitation pattern continuous percolation was simulated for the whole hydrological year except for a few days in June (Figure 4.2A). The climatic setting of this year gave rise to a continuous period with the groundwater table just above the drainage level, causing the second largest measured drainage compared to the other hydrological years (Figure 4.2B and 4.2C). Compared to the hydrological year July 2011 – June 2012, less water was entering the soil media and more water was entering the drainage system leaving less water to percolate to the groundwater resulting in less groundwater recharge.

The simulated drainage (Figure 4.2C) matched the measured drainage flow quite well except for a later initiation of drainage in autumn 2012. Drainage flow measured in connection with the minor degree of snowmelt present, this hydrological year seems also to be captured by MACRO.

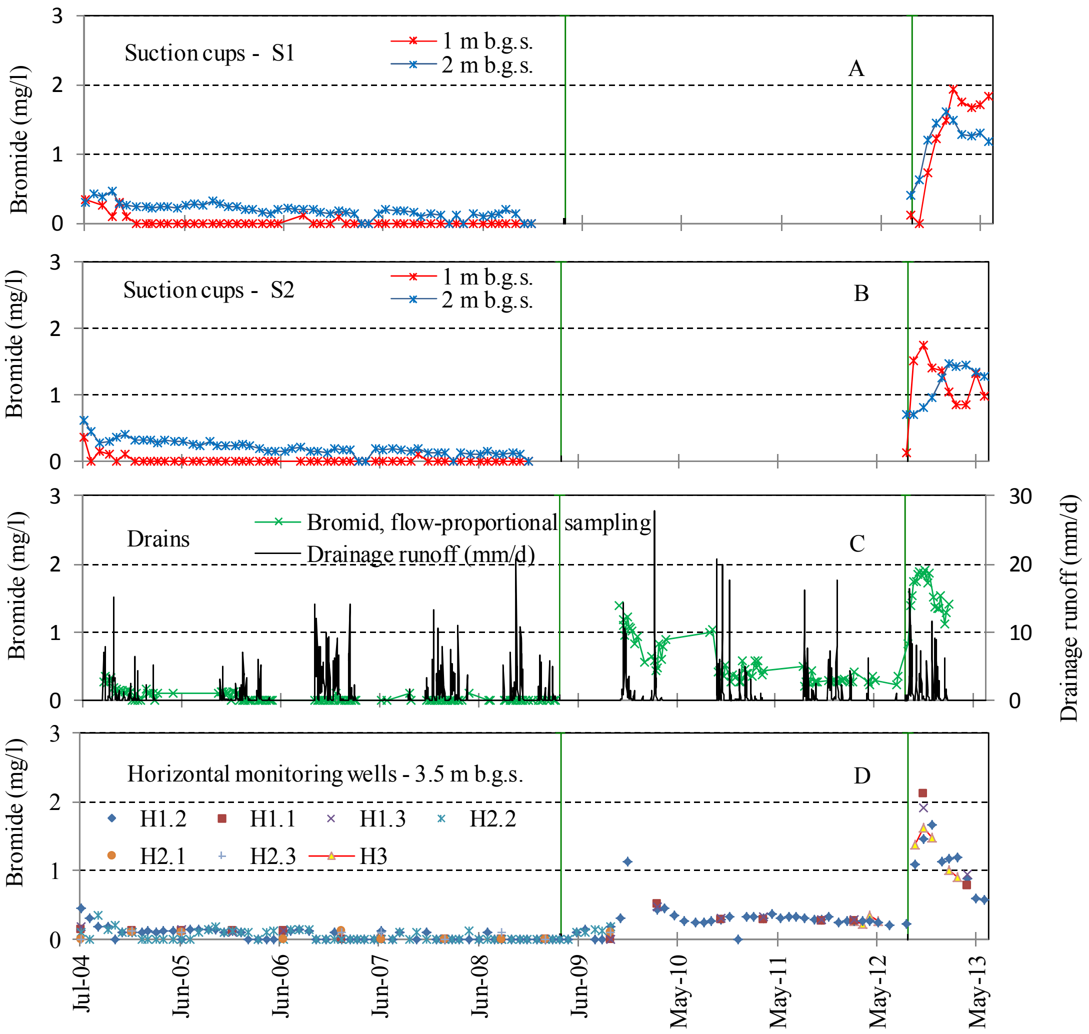

Figure 4.3. Bromide concentration at **Silstrup**. A and B refer to suction cups located at S1 and S2 (see Figure 4.1). The bromide concentration is also shown for drainage runoff (C) and the horizontal monitoring wells H1, H2 and H3 (D). From January 2009 to September 2012, bromide measurements in the suction cups were suspended. The green vertical lines indicate the dates of bromide applications.

4.2.2 Bromide leaching

The bromide concentrations prior March, shown in Figure 4.3 and Figure 4.4, 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 March 2009, bromide measurements in the suction cups and monitoring wells M6 and M11 were suspended. In September 2012 a third application of potasium bromide was done, 30.5 kg/ha.

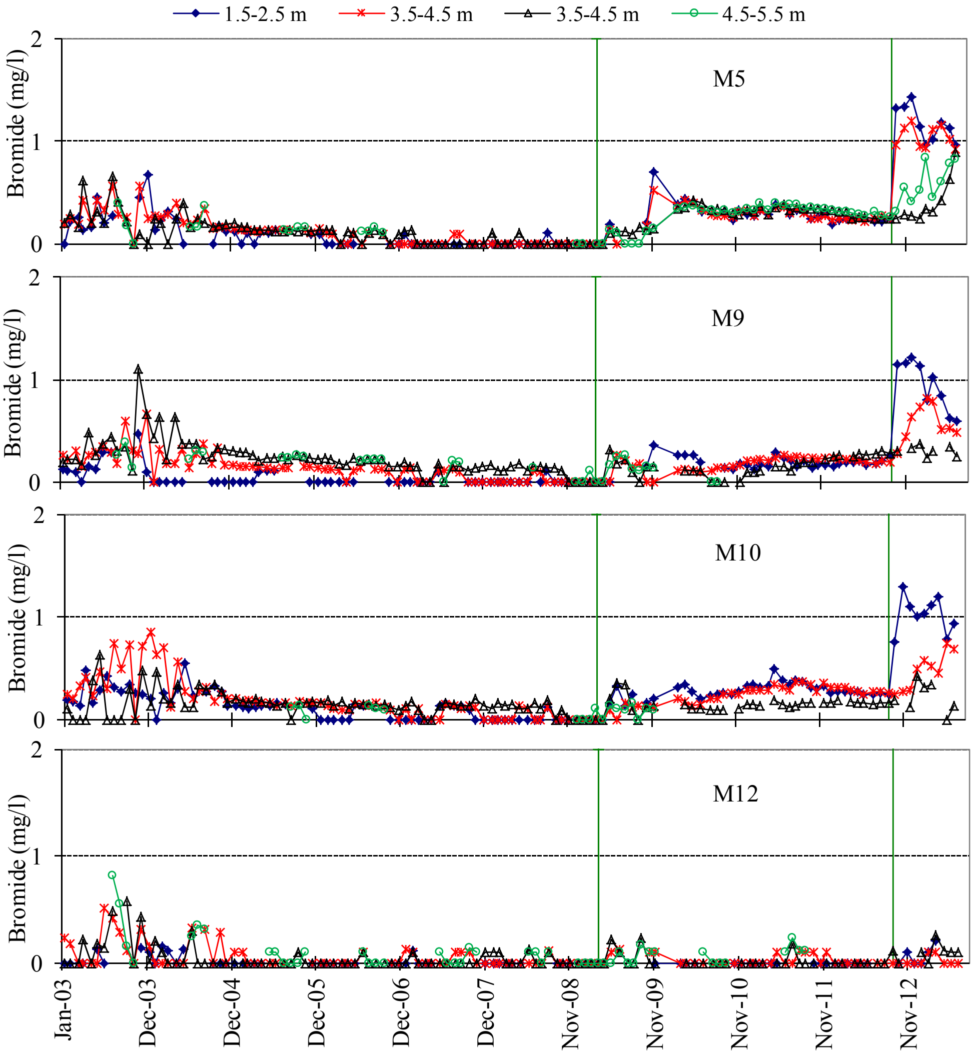

Figure 4.4. Bromide concentration at **Silstrup**. The data derive from the vertical monitoring wells (M5–M12). In September 2008, monitoring wells M6 and M11 were suspended (Appendix 2). Screen depth is indicated in m b.g.s. The green vertical lines indicate the dates of bromide applications.

4.2.3 Pesticide leaching

Monitoring at Silstrup began in May 2000 and the pesticides and degradation products monitored are given in Appendix 7. Pesticide application from 2007 and during the most recent growing seasons, 2011/2012 and 2012/2013 is listed in Table 4.2 and shown together with precipitation and simulated percolation in Figure 4.5. It should be noted that precipitation in Table 4.2 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 2013 are not evaluated in this report and hence not included in Table 4.2.

Table 4.2. Pesticides analyzed 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 month) 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. (End monito.) end of monitoring of pesticide (P) or degradation product (M).

Crop	Applied product	Analyzed pesticide	Applica. date	End Monito.	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 12[*]	985	494	105	21	<0.01
		TFMP(M)	Jul 08	Jun 12[*]	985	494	105	21	0.24
	Goliath	Metamitron(P)	May 08	Dec 10	969	498	43	4	0.01
		Desamino-metamitron(M)	May 08	Dec 10	969	498	43	4	0.02
	Safari	Triflusulfuron-methyl(P)	May 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	Mar 12	835	390	61	0	0.01
		CyPM(M)	Jun 09	Mar 12	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 12[*]	888	390	56	0	<0.02
		Bifenox acid(M)	Sep 09	Jun 12[*]	888	390	56	0	2.26
		Nitrofen(M)	Sep 09	Jun 12[*]	888	390	56	0	<0.01
	Fusilade Max	Fluazifop-P(M)	May 10	Jun 12[*]	1027	520	53	2	<0.01
		TFMP(M)	May 10	Jun 12[*]	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(M)	May 10	Dec 10	1024	520	49	1	<0.01
Red fescue 2011	Fusilade Max	TFMP(M)	May 11	Jun 12[*]	1043	550	26	4	0.003
	Fox 480 SC	Bifenox(P)	Sep 11	Dec 12[*]	989	493	101	68	0.014
		Bifenox acid(M)	Sep 11	Dec 12[*]	989	493	101	68	0.25
		Nitrofen(M)	Sep 11	Dec 12[*]	989	493	101	68	0.03
Red fescue 2012	DFF	Diflufenican(P)	Apr 12	Jun 13[*]	1067’	584	112	56	0.009
		AE-05422291(M)	Apr 12	Jun 13[*]	1067	584	112	56	<0,01
		AE-B107137(M)	Apr 12	Jun 13[*]	1067	584	112	56	0.007
	Folicur	Tebuconazole(P)	May 12	Dec 12	1024	532	48	11	0.003
	Fusilade Max	TFMP(M)	Apr 12	Jun 13[*]	1073	581	127	64	0.074
Winter wheat 2013	Glyfonova 450 Plus	Glyphosate(P)	Sep 12	Jun 13[*]	836	514	207	121	0.15
Spring barley[**]		AMPA(M)	Sep 12	Jun 13[*]	836	514	207	121	0.067
	Oxitril CM	Bromoxynil(P)	Nov 12	Jun 13[*]	463	270	68	69	<0.01
	Oxitril CM	Ioxynil(P)	Nov 12	Jun 13[*]	463	270	68	69	<0.01
	DFF	Diflufenican	Nov 12	Jun 13[*]	463	270	68	69	0.006
	DFF	AE-05422291(M)	Nov 12	Jun 13[*]	463	270	68	69	<0.01
	DFF	AE-B107137(M)	Nov 12	Jun 13[*]	463	270	68	69	0.001

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

[*] *monitoring continues the following year.*

[**] *On 3 May 2013: Sowing spring barley, replacing winter wheat injured by frost.*

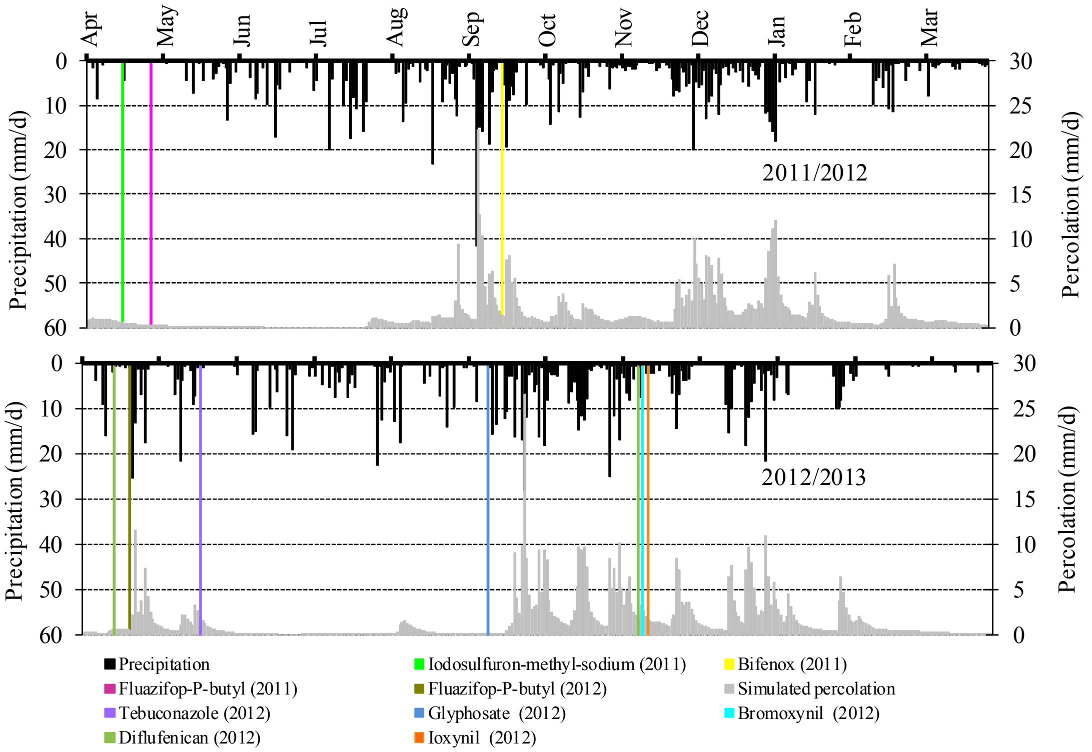

Figure 4.5. Pesticides included in the monitoring programme, precipitation and irrigation (primary axis) and simulated percolation 1 m b.g.s. (secondary axis) at **Silstrup** in 2011/2012 (upper) and 2012/2013 (lower).

The current report focuses on the pesticides applied from 2011 and onwards, while the leaching risk of pesticides applied in 2011 and before has been evaluated in previous monitoring reports (see http://pesticidvarsling.dk/publ_result/index.html).

The herbicide fluazifop-P-butyl has been included in the PLAP at Silstrup in total five times, and as fluazifop-P-butyl is rapidly degraded, main focus has been on its degradation products, firstly fluazifop-P (free acid) and lately TFMP (Table 4.2). The degradation product fluazifop-P (free acid) was only detected once in groundwater. Since the 2008 application in fodder beet focus has been on the degradation product TFMP. In Figure 4.6A, B and C it can be seen that an application of 375 g a.i./ha of fluazifop-P-butyl (3.0 l/ha Fusilade Max) in 2008 lead to TFMP concentrations above 0.1 µg/L in both drainage and groundwater. Further, a concentration of 0.1 µg/L was exceeded first in the groundwater and then later in the drainage water, which indicate a preferential transport of TFMP. Subsequently, the Danish EPA has restricted the use of fluazifop-P-butyl regarding dosage, crop types and frequency of applications.

When fluazifop-P-butyl was used for the third and fourth time, April 2010 and April 2011, the Danish EPA had restricted its use regarding applicable amounts, crop types and frequency of applications, and as can be seen in Figure 4.6B, this seemed to have reduced the environmental impact. However, a fifth application in April 2012, shows that there still might be a problem, even when used in the low dosage and in a dense grass crop. This may, very likely, relate to differences in the hydrological regimes at the time of the third and fourth application, as compared to that of the fifth application in 2012.

As can be seen from Figure 4.6A, there was no instant leaching of TFMP to the drainage system in neither 2010 nor in 2011. Thus, the concentrations in drainage never exceeded 0.1 µg/L and TFMP was not detected in the groundwater. At the time of the application in the spring of 2010 and 2011 sprayings and throughout most of following summer there was virtually no percolation or drainage flow (Figure 4.6A). In 2010 it took five months before 0.06 µg/L of TMP was detected in the drainage water and in 2011 four months before 0,05 µg/L was found. In 2012, the same amount of fluazifop-P-butyl was applied on 19 April, again in a dense stand of red fescue grass, but this year there was percolation and drainage flow. At the first sampling following the application, TFMP could be found in both drainage and groundwater, Figure 4.6B and 4.6C in concentrations exceeding the 0.1 µg/L in both drainage and groundwater. One month after the spraying, on 23 May 2012, the maximal concentrations were reached in drain and wells. Last exceedance of the limit for groundwater was 0.11µg/L on 3 October 2012. TFMP continued to leach to the groundwater until 15 May 2013 were 0.023 µg/L was found.

Tebuconazole was applied on red fesque in May 2012. Tebuconazole was found in two drainwater samples in August and September 2012 (0.013 and 0.084 µg/L). Analyze of the degradation product, 1,2,4–triazole, was not possible in this monitoring period.

Since the most recent application (16 September 2011) of the herbicide bifenox in red fescue, there have been numerous detections of bifenox acid in both drainage water and groundwater (data not shown). The highest concentration in drainage water was 4.8 µg/L of bifenox acid sampled on 29 September 2011 and 1.2 µg/L of bifenox acid in groundwater sampled November 2011 from the uppermost screen of monitoring well M5. Bifenox itself has only been found a few times in the drainage water between 22 September and 19 October 2011, concentrations ranging from 0.023 to 0.38 µg/L. Another degradation product nitrofen was solely found in drainage in the same period, in concentrations ranging between 0.045 and 0.34 µg/L. The last measurement of bifenox acid was done on 3 October 2012 showing 0.053 µg/L in groundwater, whereas the last measurement in drainage showed 0.11 µg/L on 2 May 2012. Due to data from the PLAP monitoring the Danish EPA has now banned all use of bifenox in Denmark.

Azoxystrobin has been applied at Silstrup three times since 2004 (Figure 4.7). The last application (24 June 2009) still causes leaching of the degradation product CyPM to the drainage (Figure 4.7C), whereas leaching of azoxystrobin itself seems to have ended, the most recent detection was 0.011 µg/L on 24 March 2010 (Figure 4.7B). The concentrations of CyPM were generally higher than the concentration of the parent compound. Whereas there have been no detections of azoxystrobin in the groundwater, CyPM was found in both horizontal and vertical wells, concentrations ranging from 0.013 to 0.086 µg/L and 0.011 to 0.1 µg/L, respectively. Latest detection of CyPM in groundwater was 0.012 µg/L on 19 May 2010 (Figure 4.7D) and 0.01 µg/L in drainage on 3 January 2013 (Figure 4.7C).

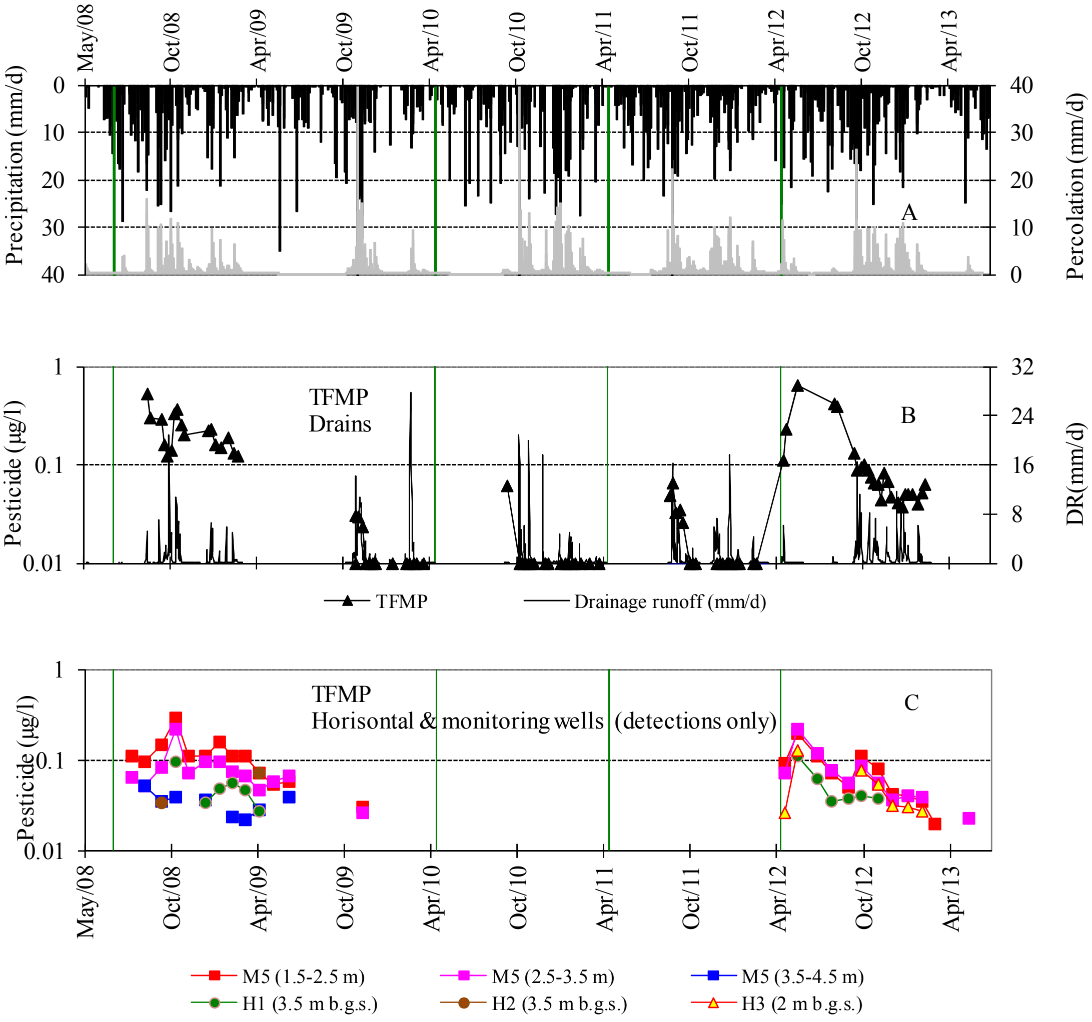

Figure 4.6. Precipitation and simulated percolation 1 m b.g.s. (A) together with the concentration of TFMP (B) in the drainage runoff, and the concentration of TFMP (C) in the groundwater horizontal and monitoring screens at **Silstrup**. The green vertical lines indicate the dates of fluazifop-P-butyl applications. Values below the detection limit of 0.01 µg/L are shown as 0.01 µg/L (all graphs) and further represented by open symbols in A, B and C.

Diflufenican was applied in April 2012 and in November 2012 (red fescue and winter wheat). Diflufenican was detected in nine drainage water samples, and one drainage water sample exceeded 0.1 µg/L (0.12 in April). Diflufenican was detected in one groundwater sample in November (0.47 µg/L). The break down product AE-B107137 was detected in five drainage water samples where one sample exceeded 0.1 µg/L (0,13 µg/L). The other break down product AE-05422291 was not detected.

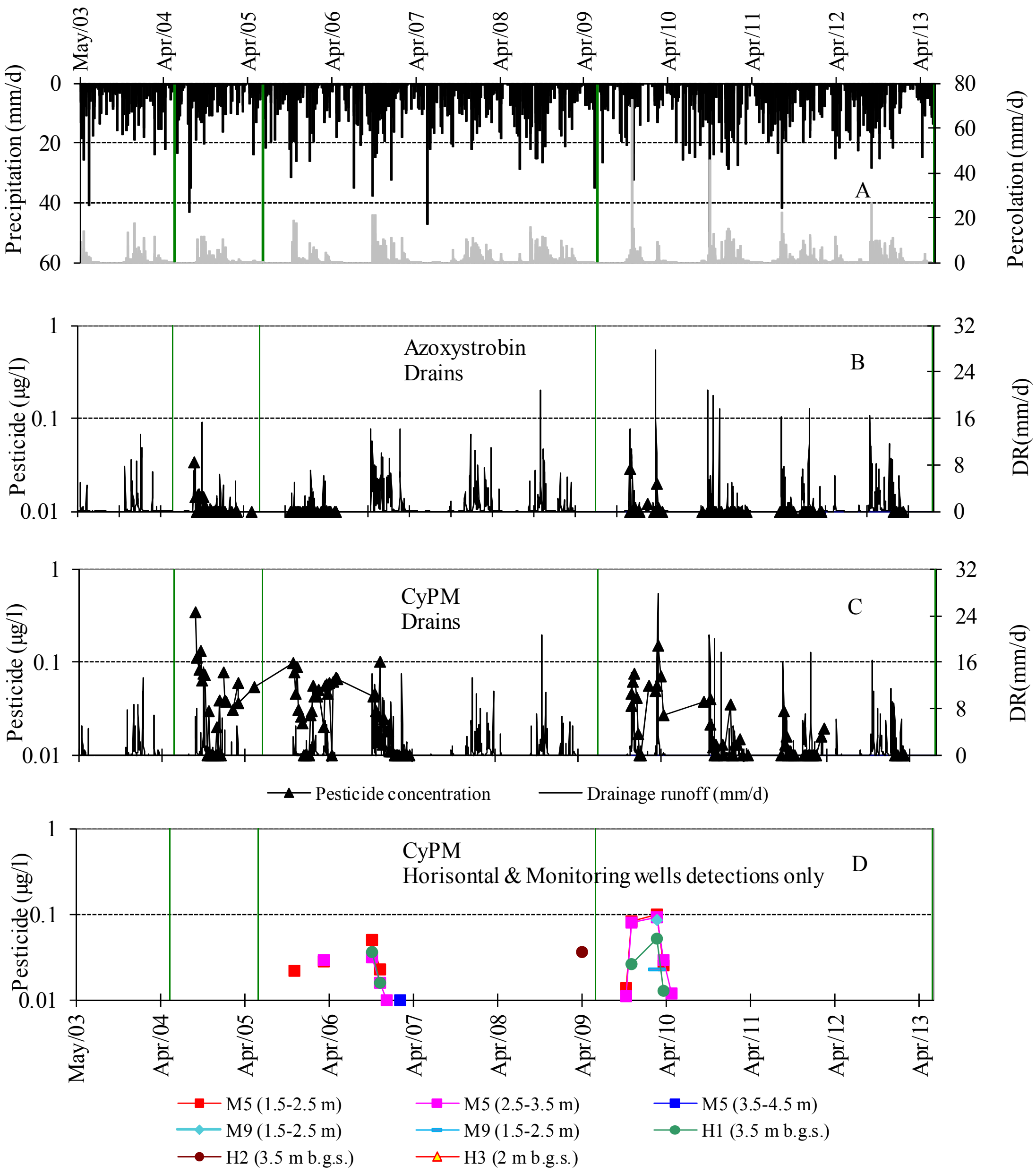

Figure 4.7. Precipitation and simulated percolation 1 m b.g.s. (A) together with the concentration of azoxystrobin (B) and CyPM (C) in the drainage runoff, and the concentration of CyPM (D) in the groundwater monitoring screens at **Silstrup**. The green vertical lines indicate the dates of bentazone and azoxystrobin applications. Values below the detection limit of 0.01 µg/L are shown as 0.01 µg/L (all graphs).

Glyphosate was applied on 10 September 2012, killing the red fescue, and both glyphosate and AMPA were found in drainage nine days later. Glyphosate was found in concentrations up to 0.66 µg/L (Figure 4.8) and AMPA in concentrations up to 0.13 µg/L. Glyphosate was found in ten groundwater samples from the monitoring wells, and in three groundwater samles from the new horizontal well in small concentrations below 0.1 µg/L. AMPA was found in two water samples from groundwater and in three water samples form the horizontal well, also in small concentrations ≤ 0.1 µg/L. After February 2013 glyphosate and AMPA were found in monitoring wells, but not in the drainage water (Figure 4.8). The average glyphosate concentration in the drainage water was 0.15 µg/L, while the average AMPA concentration was 0.067 µg/L.

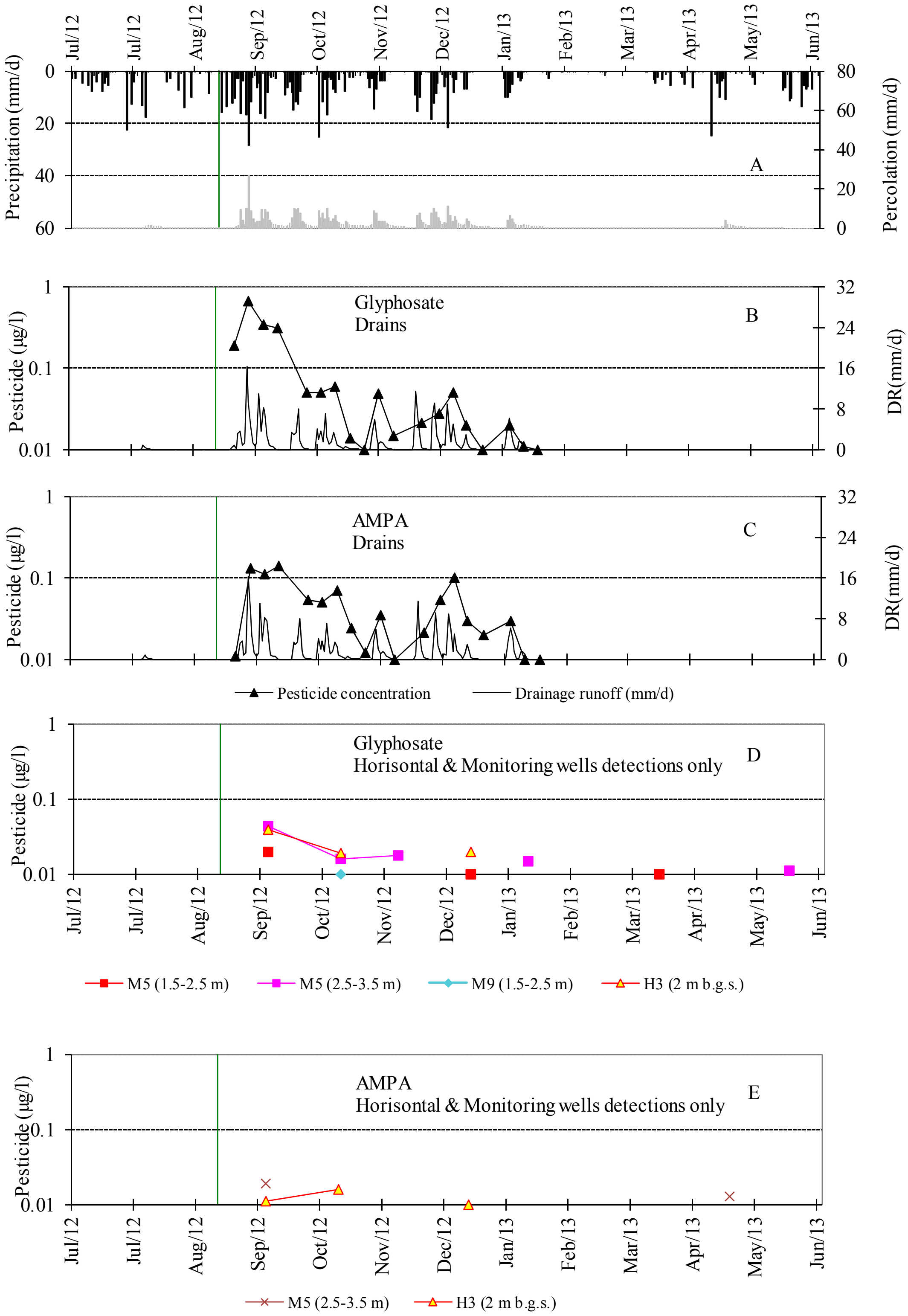

Figure 4.8. Precipitation and simulated percolation 1 m b.g.s. (A) together with the concentration of glyphosate (B) and AMPA (C) in the drainage runoff, and the concentration of glyphosate (D) and AMPA (E) in the groundwater monitoring screens at **Silstrup**. The green vertical lines indicate the dates of glyphosate applications. Values below the detection limit (not detected) of 0.01 µg/L, are shown as 0.01 µg/L.

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 1.1) 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 1.3 ha (105 x 120 m) and is virtually flat (Figure 5.1). 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 c haracterises 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 1.1). 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 and the analysis methods in Kjær et al. (2002). The monitoring design and test site are described in detail in Lindhardt et al. (2001). Please note that the geological conditions only allowed one of the planned horizontal wells in 3.5 m b.g.s. to be installed. In September 2011, the monitoring system was extended with three horizontal screens (H2) 2 m b.g.s. in the North-Eastern area of the field (Figure 5.1), one of the screens should be located just below a tile drain 1.1 m b.g.s., whereas two are located between tile drains. A brief description of the drilling and design of H2 is given in Appendix 8.

5.1.2 Agricultural management

Management practice during the 2012-2013 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.

The field was ploughed on 9 November 2011, rotorharrowed on 29 March 2012 and on 30 March 2012 sown with spring barley (cv. Keops), emerging on 22 April. The field was sprayed with the herbicides bifenox on 15 May and aminopyralid, florasulam and 2,4-D on 18 May. Aminopyralid and bifenox, including two degradation products of each, were included in the monitoring. On 13 June the fungicide azoxystrobin was sprayed and included. Harvest of spring barley was done on 13 August, yielding 62.9 hkg/ha of grain, whereas 41.0 hkg/ha of straw was shredded (85% and 100% dry matter, respectively).

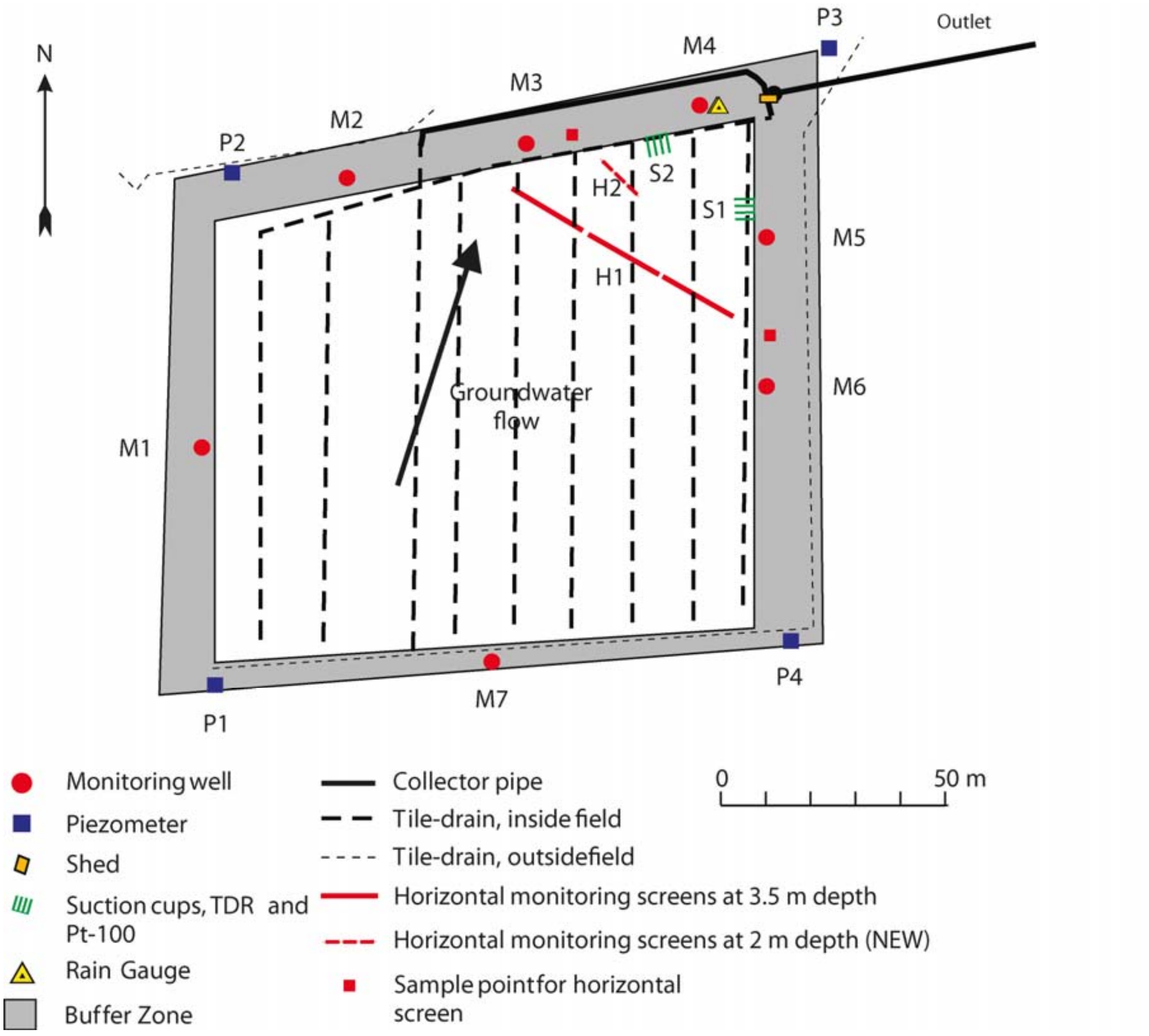

Figure 5.1. Overview of the **Estrup** site. The innermost white area indicates the cultivated land, while the grey area indicates the surrounding buffer zone. The positions of the various installations are indicated, as is the direction of groundwater flow (by an arrow). Pesticide monitoring is conducted weekly from the drainage system (during period of continuous drainage runoff) and monthly and half-yearly from selected vertical and horizontal monitoring screens as described in Table A2.1 in Appendix 2.

The field was ploughed on 8 March 2013 and sown with pea (cv. Alvesta) on 23 April, emerging on 4 May 2013. The field was sprayed with the herbicides clomazone on 25 April and bentazone on 16 May. Bentazone as well as the degradation product of clomazone FMC65317 were included in the monitoring. A spraying of aphids was done on 16 May using cypermethrin, however the substance was not monitored.

5.1.3 Model setup and calibration

The numerical model MACRO (version 5.2, 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 variably-saturated zone during the monitoring period from July 2000-June 2013 and to establish an annual water balance.

Compared to the setup in Brüsch *et al.* (2013b), 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 2013. For this purpose, the following time series have been used: the observed groundwater table measured in the piezometers located in the buffer zone (a new in situ logger allowing higher resolution has been installed instead of the diver), measured drainage flow, and soil water content measured at two depths (25 and 40 cm b.g.s.) from the soil profile S1 (Figure 5.1). 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 0° C). 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 variably-saturated zone (Figure 5.2). 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 5.2B). 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 5.2D and 5.2E), except for the drop in water saturation at 25 cm b.g.s. in April-June 2013. As in previous years (Brüsch *et al.*, 2013b), the simulated groundwater table often fluctuates slightly above the drain depth resulting in long periods with drainage.

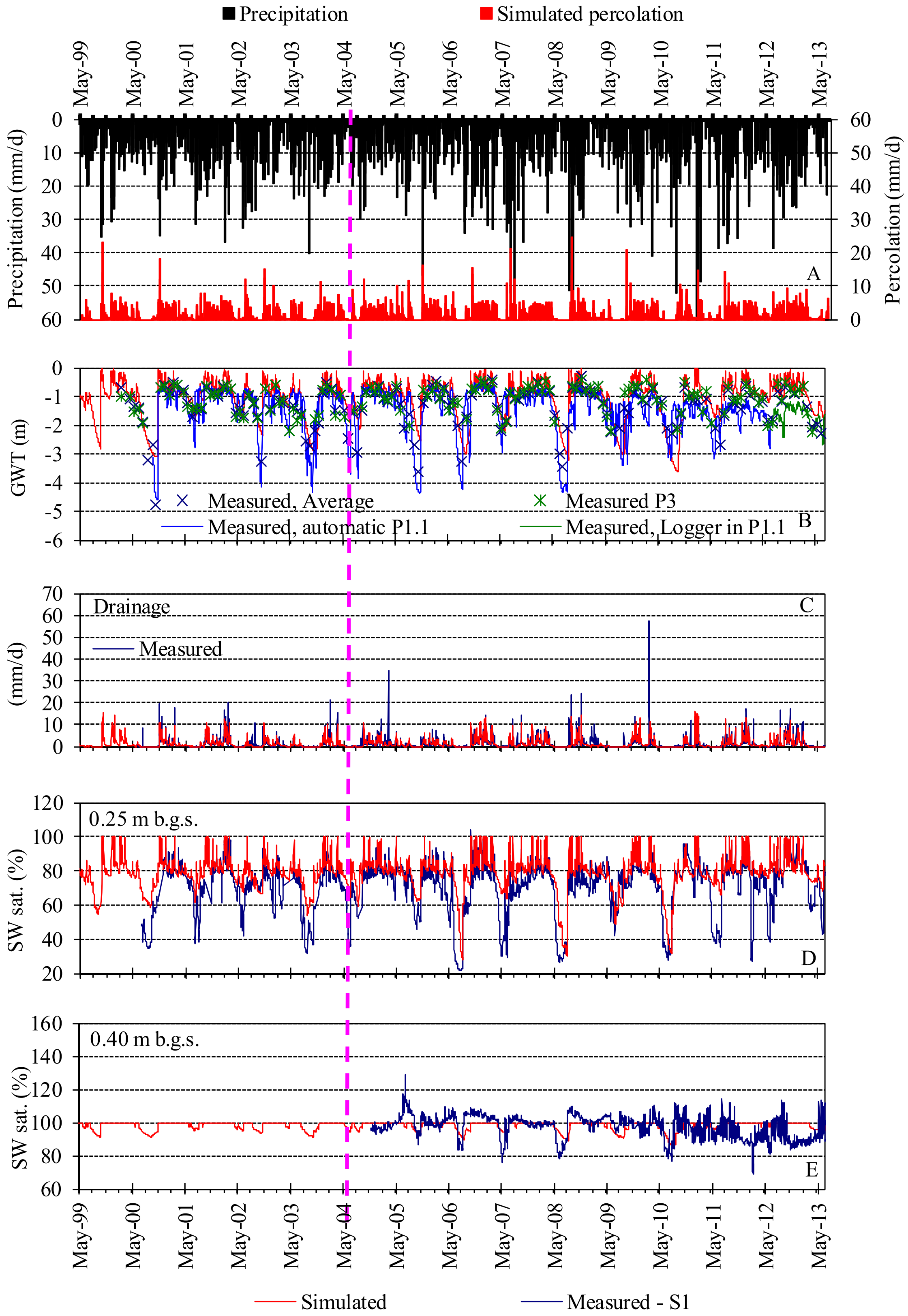

Figure 5.2. Soil water dynamics at **Estrup**: Measured precipitation and simulated percolation 0.6 m b.g.s. (A), simulated and measured groundwater level (B), simulated and measured drainage flow (C), and simulated and measured soil saturation (SW sat.) at two different soil depths (D and E). The measured 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 5.1). The dotted vertical line indicates the beginning of the validation period (July 2004-June 2013).

Table 5.1. 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
1.7.11–30.6.12	968	1222	404	479	577	3397
1.7.12–30.6.13	968	1093	386	503	564	204

[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 5.2C) matches the measured drainage flow quite well except for the drainage in July 2012 where it is overestimated. Drainage flow measured in connection with the minor degree of snowmelt within this hydrological year seems also to be captured by MACRO. Drainage was high during the whole monitoring period 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 5.1. Compared with the previous 13 years, the recent hydrological year July 2012-June 2013, was characterized by having medium precipitation, the lowest simulated actual evapotranspiration during the whole periode of PLAP monitoring, and medium measured drainage. Having hardly any snowmelt, there is a good agreement between simulated and observed drainage. The difference of 61 mm can primarily be ascribed by the July 2012 drainage event being overestimated by MACRO. Precipitation in the months of this year was characterized by medium precipitation compared to the other PLAP-years except for March 2013, being the driest since PLAP-monitoring started (Appendix 4). Due to this precipitation pattern, the simulated percolation pattern of the year July 2012-June 2013 resulted in more or less continuously percolation at 1 m depth (Figure 5.2A) with a medium input to the groundwater recharge (Table 5.1) as compared to the other PLAP-years.

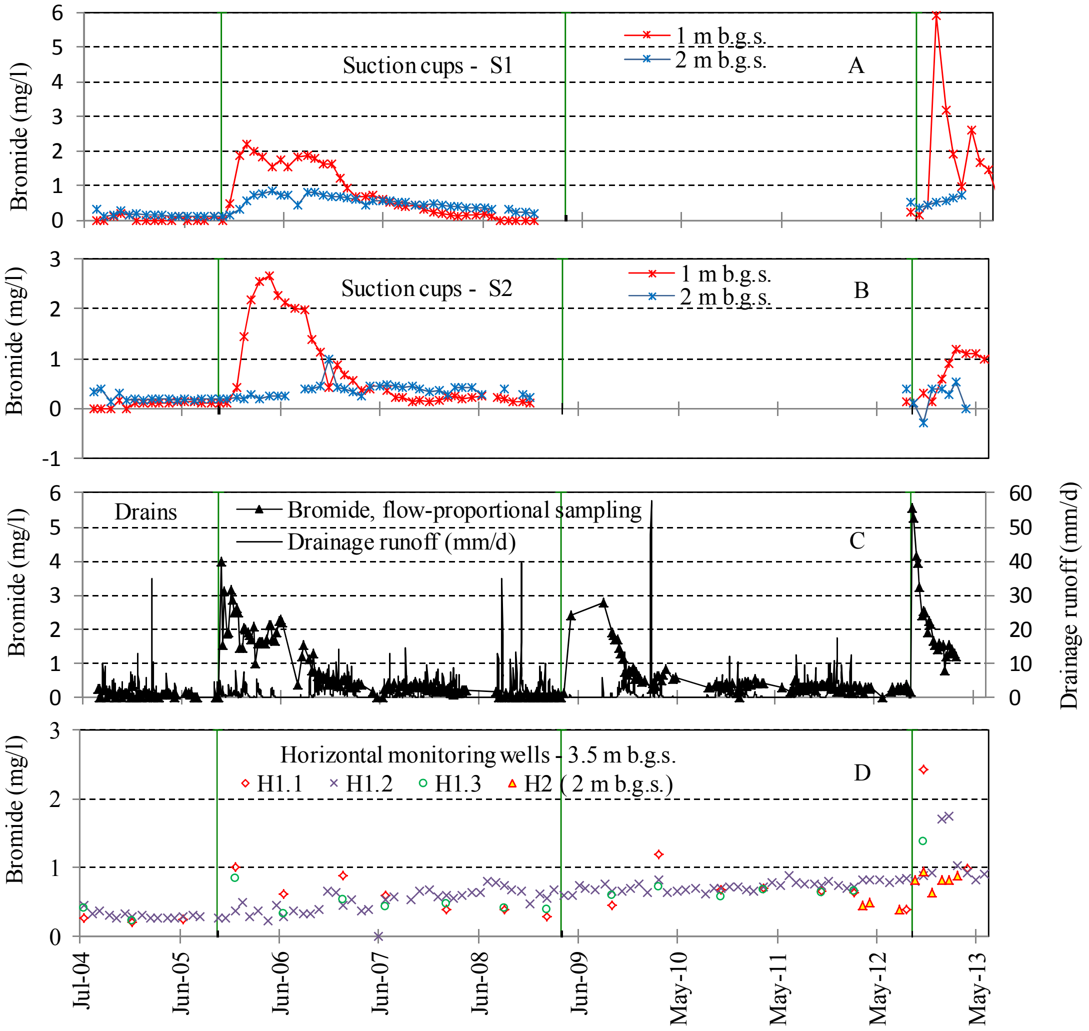

Figure 5.3. Bromide concentration at **Estrup**. A and B refer to suction cups located at S1 and S2, respectively. The bromide concentration is also shown for drainage runoff (C) and the horizontal monitoring well H1 and H3 (D). From September 2008 to August 2012, bromide measurements in the suction cups were suspended. The green vertical lines indicate the dates of bromide.

5.2.2 Bromide leaching

Bromide has now been applied four times at Estrup. The bromide concentrations measured up to October 2005 (Figure 5.3 and Figure 5.4) 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 5.3D show a very slow build up of the bromide concentrations in the horizontal screens reflecting a slow transport due to the low hydraulic conductivity.

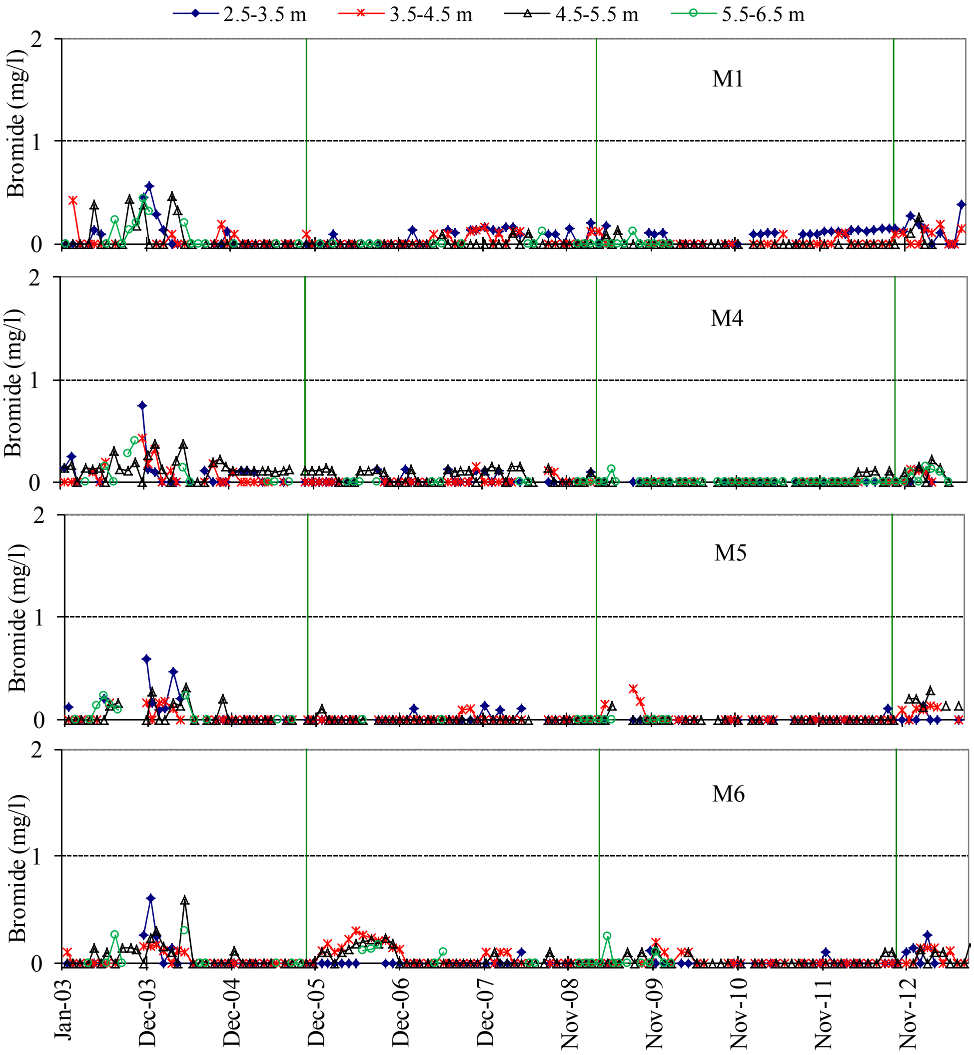

Figure 5.4. Bromide concentration at **Estrup**. The data derive from the vertical monitoring wells (M1, M4, M5 and M6). Screen depth is indicated in m b.g.s. In September 2008, monitoring wells M3 and M7 were suspended. The green vertical lines indicate the dates of the three most recent bromide applications.

5.2.3 Pesticide leaching

Monitoring at Estrup began in May 2000. Pesticides and degradation products monitored so far can be seen from Table 5.2 (2007-2013) and Table A7.4 in Appendix 7 (2000-2007). Pesticide application during the most recent growing seasons (2011/2012 and 2012/2013) is shown together with precipitation and simulated precipitation in Figure 5.5. 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 2013 are not evaluated in this report and hence not included in Table 5.2.

Table 5.2. Pesticides analyzed at **Estrup**. 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 month) 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. End Monito.- end of monitoring of pesticide(P) or degradation product(M).

Crop	Applied product	Analyzed pesticide	Applica. Date	End Monito.	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	Jul 08	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 12*	1093	232	88	0	0.06
		CyPM(M)	Jun 08	Jun 12*	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 12*	1200	261	113	29	0.19
		AMPA(M)	Sep 07	Jun 12*	1200	261	113	29	0.13
Spring barley 2009	Amistar	Azoxystrobin(P)	Jun 09	Jun 12*	1215	235	60	0	0.04
		CyPM(M)	Jun 09	Jun 12*	1215	235	60	0	0.41
	Basagran M75	Bentazone(P)	May 09	Jun 12*	1222	238	83	4	0.05
	Fox 480 SC	Bifenox(P)	May 09	Jun 12*	1243	246	87	16	<0.02
		Bifenox acid(M)	May 09	Jun 12*	1243	246	87	16	0.16
		Nitrofen(M)	May 09	Jun 12*	1243	246	87	16	<0.01
Winter rape 2010	Biscaya OD 240	Thiacloprid(P)	May 10	Mar 12	1083	196	43	0	<0.01
		M34(M)	May 10	Mar 12	1083	196	43	0	<0.02
		Thiacloprid sulfonic acid(M)	May 10	Mar 12	1083	196	43	0	<0.1
		Thiacloprid-amide(M)	May 10	Mar 12	1083	196	43	0	<0.01
Winter wheat 2011	Express ST	Triazinamin-methyl(M)1)	Sep 10	Jun 12*	823	176	97	31	0.01
	Fox 480 SC	Bifenox(P)	Apr 11	Jun 13	1217	276	45	2	<0.01
		Bifenox acid(M)	Apr 11	Jun 13	1217	276	45	2	0.003
		Nitrofen	Apr 11	Jun 13	1217	276	45	2	<0.01
	Flexity	Metrafenone(P)	May 11	Jun 13*	1219	283	114	6	0.02
Spring barley 2012	Amistar	Azoxystrobin	Jun 12	Jun 13*	1083	281	151	29	0.04
		CyPM	Jun 12	Jun 13*	1083	281	151	29	0.24
	Fox 480 SC	Bifenox	May 12	Jun 13*	1090	281	39	13	< 0.02
		Bifenox acid	May 12	Jun 13*	1090	281	39	13	0.011
		Nitrofen	May 12	Jun 13*	1090	281	39	13	< 0.02
	Mustang forte	Aminopyralid	May 12	Jun 13*	1098	285	50	14	< 0.01
	Roundup Max	Glyphosate(P)	Oct 11	Jun 13*	1150	295	94	26	0.88
		AMPA(M)	Oct 11	Jun 13*	1150	295	94	26	0.26
Pea 2013	Fighter 480	Bentazone(P)	May 13	Jun 13*					**
	Command CS	FMC-65317(M)	Apr 13	Jun 13*					**

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

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

**monitoring continues the following year.*

***Bentazone applied on 16 May 2013, and Command CS, clomazone, on 25 April 2013. Concentration will be calculated in the next monitoring period.*

The current report focuses on pesticides applied from 2011 and onwards, while leaching risk of pesticides applied in 2010 and before has been evaluated in previous monitoring reports (see http://pesticidvarsling.dk/publ_result/index.html).

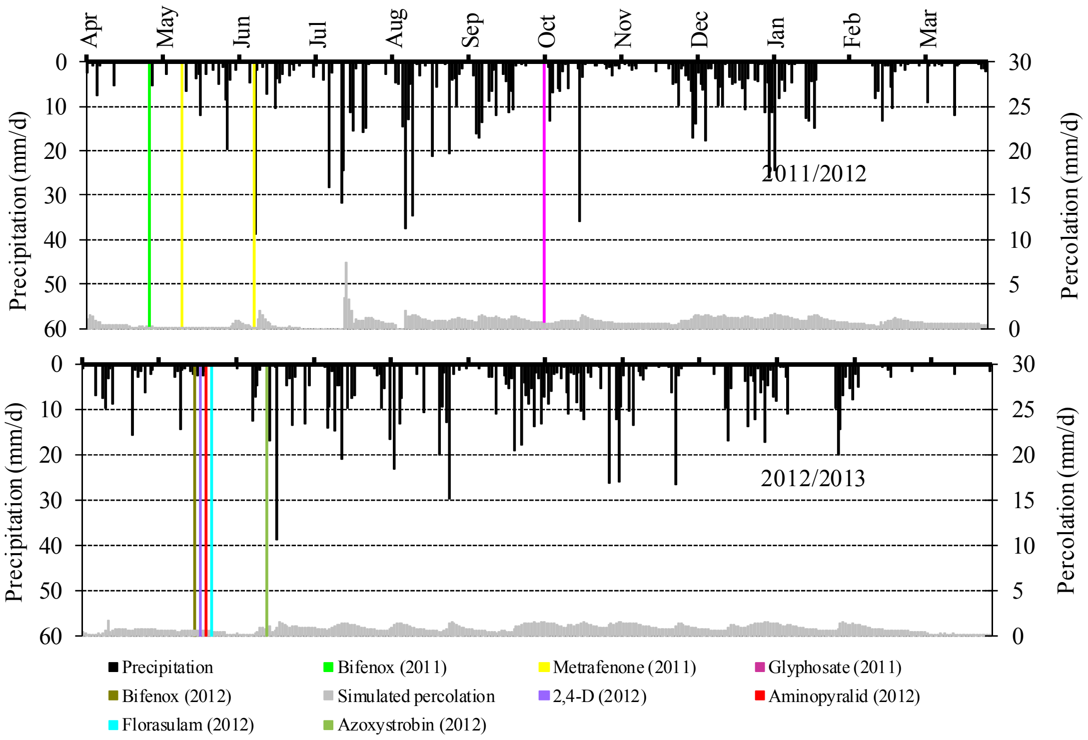

Figure 5.5. Application of pesticides included in the monitoring programme and precipitation (primary axis) together with simulated percolation 0.6 m b.g.s. (secondary axis) at **Estrup** in 2011/2012 (upper) and 2012/2013 (lower).

Azoxystrobin has now been applied five times at Estrup: on 22 June 2004, 29 June 2006, 13 June 2008, 4 June 2009 and 13 June 2012 (Figure 5.6). The last application before these five, was in June 1998 (Lindhardt *et al.*, 2001). Following all five applications azoxystrobin and its degradation product CyPM leached to the drainage at the onset of the drainage period due to infiltration of excess rain. Concentrations in drainage water of both parent and break down product are shown in Figure 5.6B and 5.6C. 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. CyPM was for the first time detected in groundwater above the limit, being 0.13 µg/L on 3 October 2012 in the new horizontal well H3 2 m b.g.s. (Figure 5.6D). Within the year of application as well as the following year, the average concentrations of CyPM in drainage were always higher than that of the parent azoxystrobin (Figure 5.6B and 5.6C), indicating its higher persistence. When drainage runoff commenced in the autumn of 2011, the third runoff season following the 2009 spraying, CyPM could still be found in the drainage water in concentrations above 0.1 µg/L, ranging between 0.022 and 0.29 µg/L. Differences in persistence for the two substances are further underlined by the fact that only two out of 566 groundwater samples contained azoxystrobin (0.04 µg/L, data not shown) whereas 18 samples contained CyPM, maximum concentration being 0.13 µg/L (Figure 5.6D and Table A5.4). The leaching pattern of azoxystrobin and CyPM is further described in Jørgensen et al., 2012a and Jørgensen et al., 2013. Following the fifth application of azoxystrobin on 13 June 2012, a similar pattern was seen in the drainage water, as that following the first four applications i.e. both parent compound and degradation product leached, the degradation product in the highest concentrations (Figure 5.6A and 5.6B).

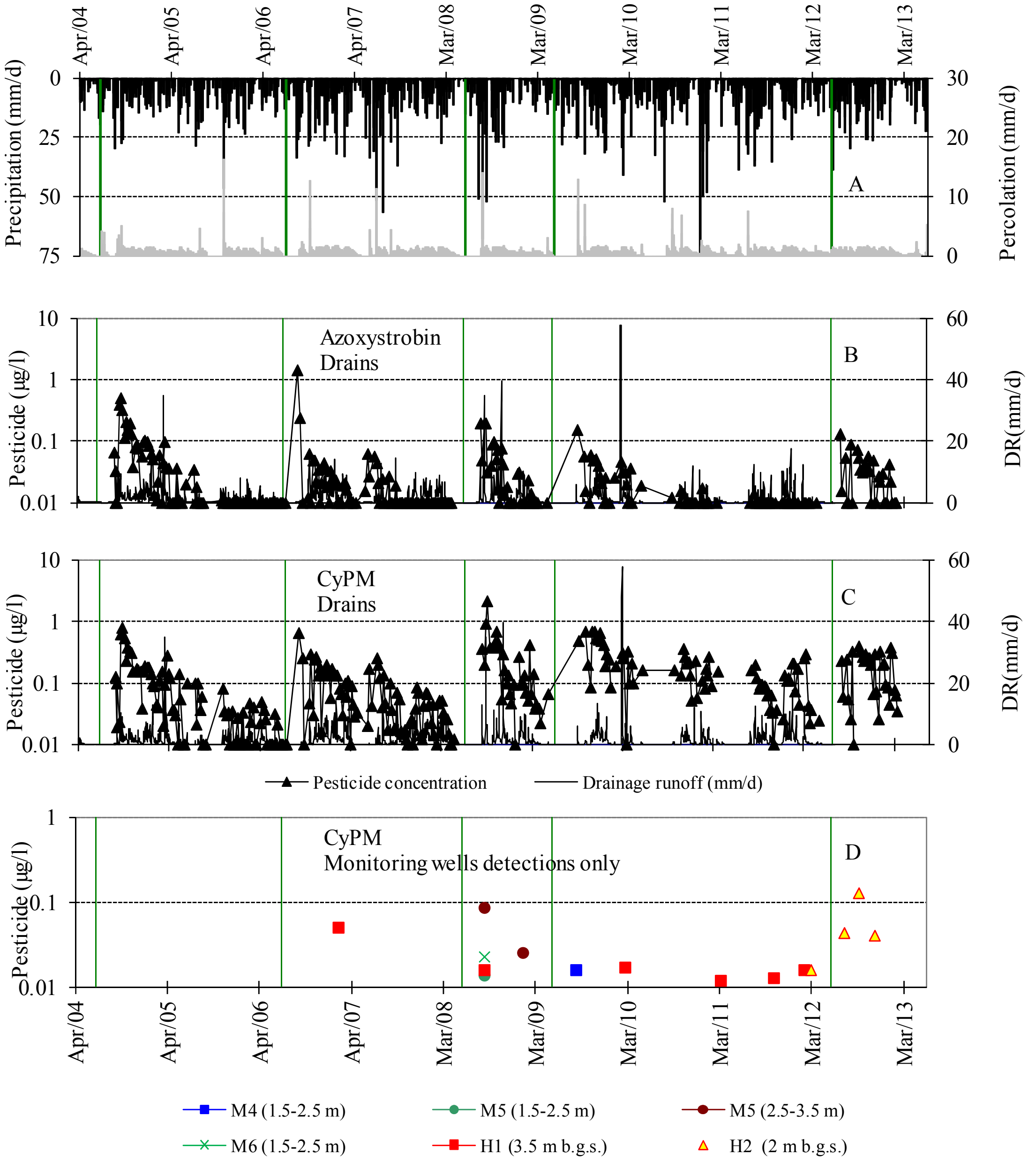

Figure 5.6. Precipitation and simulated percolation 0.6 m b.g.s. (A) together with concentration of azoxystrobin (B) and CyPM (C) in the drainage runoff (DR on the secondary axis) at **Estrup.** Detections of CyPM in groundwater monitoring screen are indicated in D. Azoxystrobin was only detected twice in groundwater horizontal and monitoring screens (see text). The green vertical lines indicate the dates of applications. Values below the detection limit of 0.01µg/L are shown as 0.01 µg/L (all graphs).

The herbicide bifenox was used on 1 May and on 30 September 2009, 26 April 2011 as well as 15 May 2012. Both applications in 2009 and May 2012 caused leaching of bifenox to the drainage. A maximum concentration of 0.15 µg/L was reached less than two weeks after the May 2009 application (data not shown, see Brüsch et al., 2013). The degradation product bifenox acid was leached to the drainage water following all four applications in concentrations larger than 0.1 µg/L (maximum concentration was 1.9 µg/L on 9 September 2009, data not shown). Only bifenox acid was found in a groundwater monitoring screen, 0.11µg/L on 25 April 2012. This elevated content probably must relate to one of the three applications done between 2009 and 2011. A second degradation product nitrofen was not found in either drainage or groundwater.

The Danish EPA has prohibited the use of bifenox in Denmark on the base of data from the PLAP.

The herbicide glyphosate has now been applied at Estrup in 2000, 2002, 2005, 2007 and 2011 (Figure 5.7 and Figure 5.8). Following all applications, both glyphosate and AMPA could be found in the drainage. Out of 480 drainage water samples analyzed for glyphosate and AMPA in the period from 31 October 2000 to 6 February 2013, the concentrations of glyphosate and AMPA exceeded 0.1 µg/L in 110 and 115 samples, respectively (Figure 5.7B, 5.8B, 5.7C and 5.8C). During the period AMPA never exceeded 0.1 µg/L in groundwater (Figure 5.7E, 5.8E and Table A5.4 in Appendix 5), whereas glyphosate did so in five samples. In a sample taken from a horizontal well on 6 October 2011 the concentration was 0.21 µg/L (Figure 5.8D and Table A5.4 in Appendix 5).

Following the glyphosate application of 3 October 2011, concentrations in drainage water of particular glyphosate increaced, reaching 4.6 µg/L in a sample from 6 October and 10 µg/L on 19 October. Concentrations of AMPA increaced less dramatically, but maintained a higher level for a longer periode of time (Figure 5.8 B and 5.8 C.) In a groundwater sample, taken from a depth of 3.5 m b.g.s., the concentration of glyphosate amounted to 0.21 µg/L three days after the spraying (Figure 5.8C). Regarding AMPA it is worth noticing that there were no detections following the 2011 application of glyphosate (Figure 5.8 E).

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 approximately two 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 in Rosenbom et al., 2010).

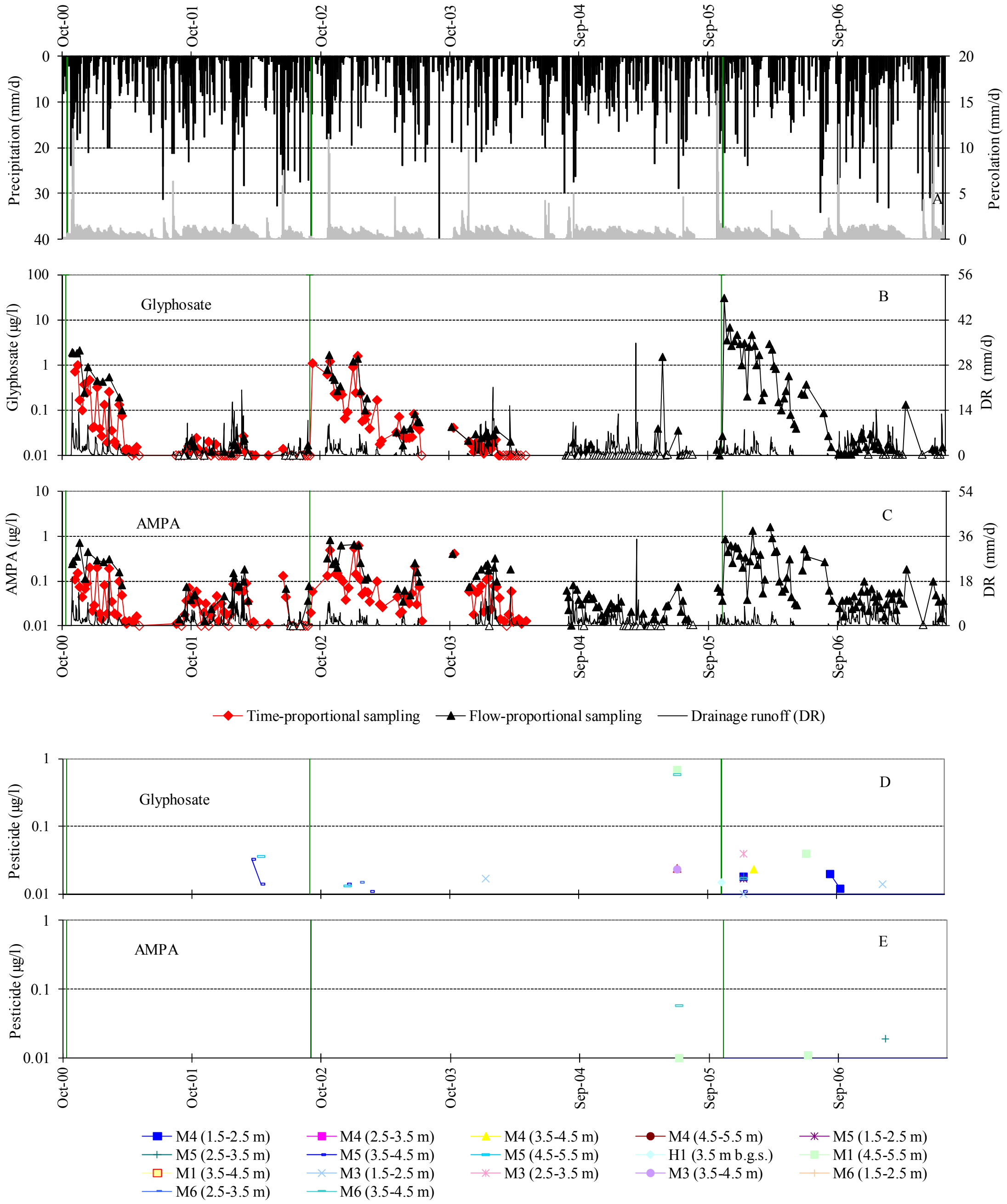

Figure 5.7. Precipitation and simulated percolation 0.6 m b.g.s. (A) together with the concentration of glyphosate (B) and AMPA (C) in the drainage runoff (DR on the secondary axis) at **Estrup** from October 2000 until July 2007. Data represent a seven-year period including four applications of glyphosate 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.

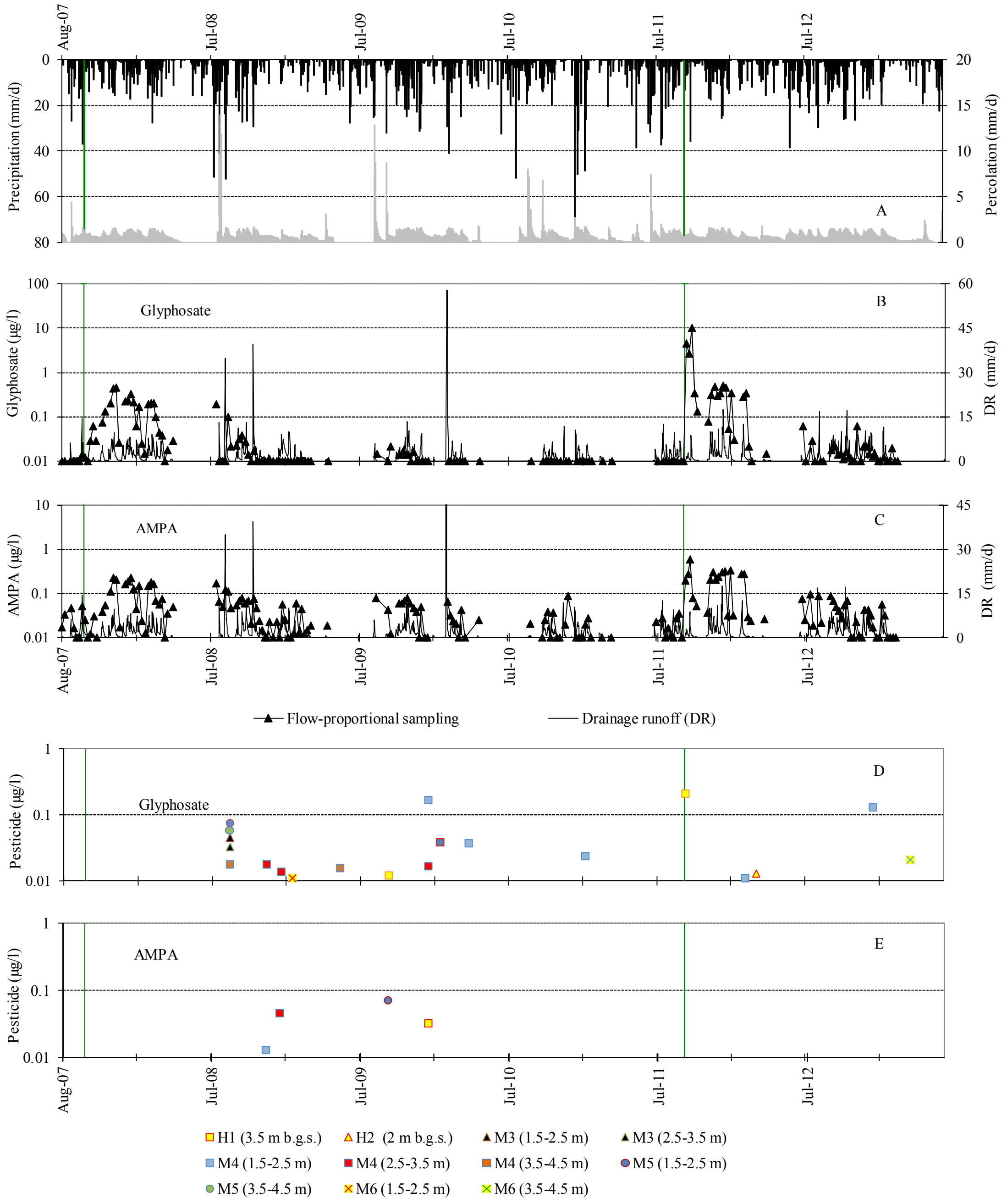

Figure 5.8. Precipitation and simulated percolation 0.6 m b.g.s. (A) together with the concentration of glyphosate (B) and AMPA (C) in the drainage runoff (DR on the secondary axis) at **Estrup** from July 2007 until June 2013. Data represent a six-year period including four applications of glyphosate 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 analytical problems caused the concentration of glyphosate to be underestimated (see text for details).

The fungicide metrafenone was applied twice on 9 May and 7 June 2011 (Fig 5.9). Between 28 July 2011 and 27 February 2013, when there was drainage flow, a total of 55 water samples were taken. Thereof 20 samples contained metrafenone, but all in concentrations below 0.1 µg/L. There was one finding of metrafenon in a total of 115 groundwater samples taken between 7 April 2011 and 12 June 2013 (data not shown). The groundwater sample contained 0.04 µg/L (7 November 2012).

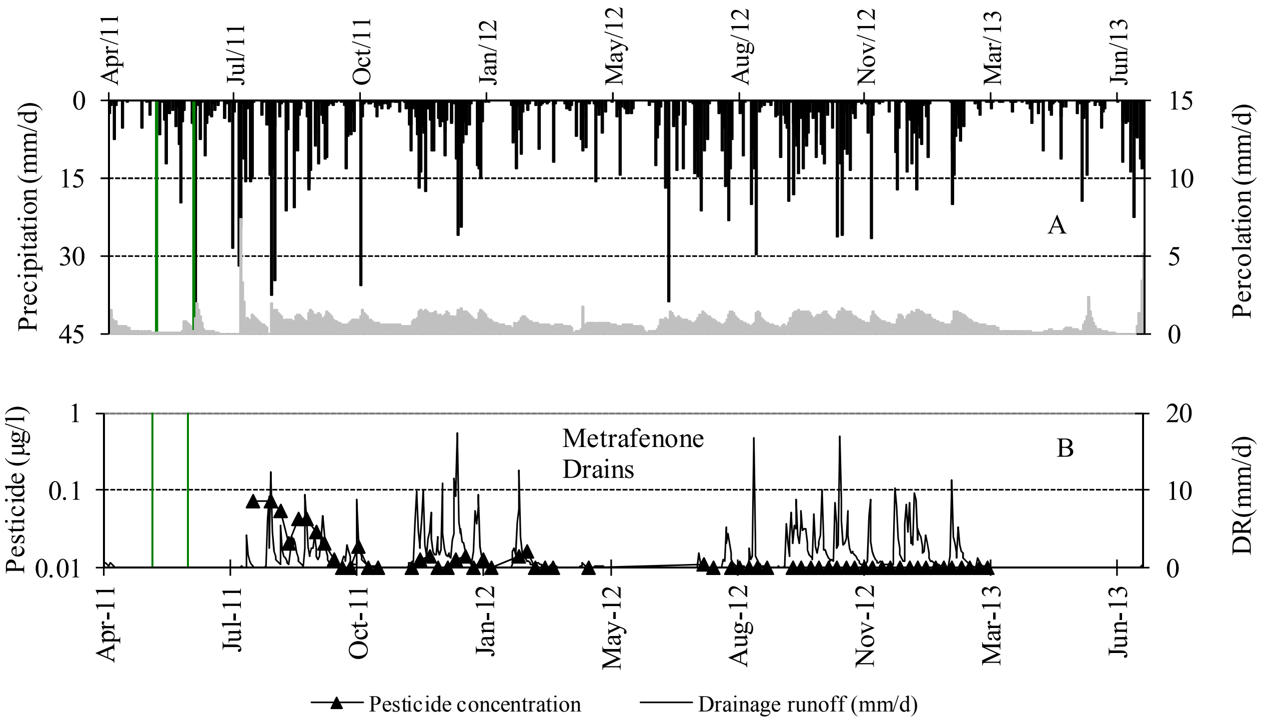

Figure 5.9. Precipitation and simulated percolation 1 m b.g.s. (A) together with the concentration of Metrafenone (B) in the drainage runoff at **Estrup**. The green vertical lines indicate the dates of Metrafenone applications.

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 6.1). The test field covers a cultivated area of 2.3 ha (150 x 160 m). The terrain slopes gently to the west by 1–3°. 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 6.1). 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 that the applied bromide reached the vertical monitoring well (M6) located in the sand-filled basin (Figure 6.4), however, not in higher concentrations compared to concentrations detected water from other vertical monitoring wells. This indicate that the 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 and the analysis methods in Kjær et al. (2002). The monitoring design and test site are described in detail in Lindhardt et al. (2001). In September 2011, the monitoring system was extended with three horizontal screens (H3) 2 m b.g.s. in the South-Western corner of the field (Figure 6.1) - one of the screens should be located just below the drain 1.2 m b.g.s. A brief description of the drilling and design of H3 is given in Appendix 8.

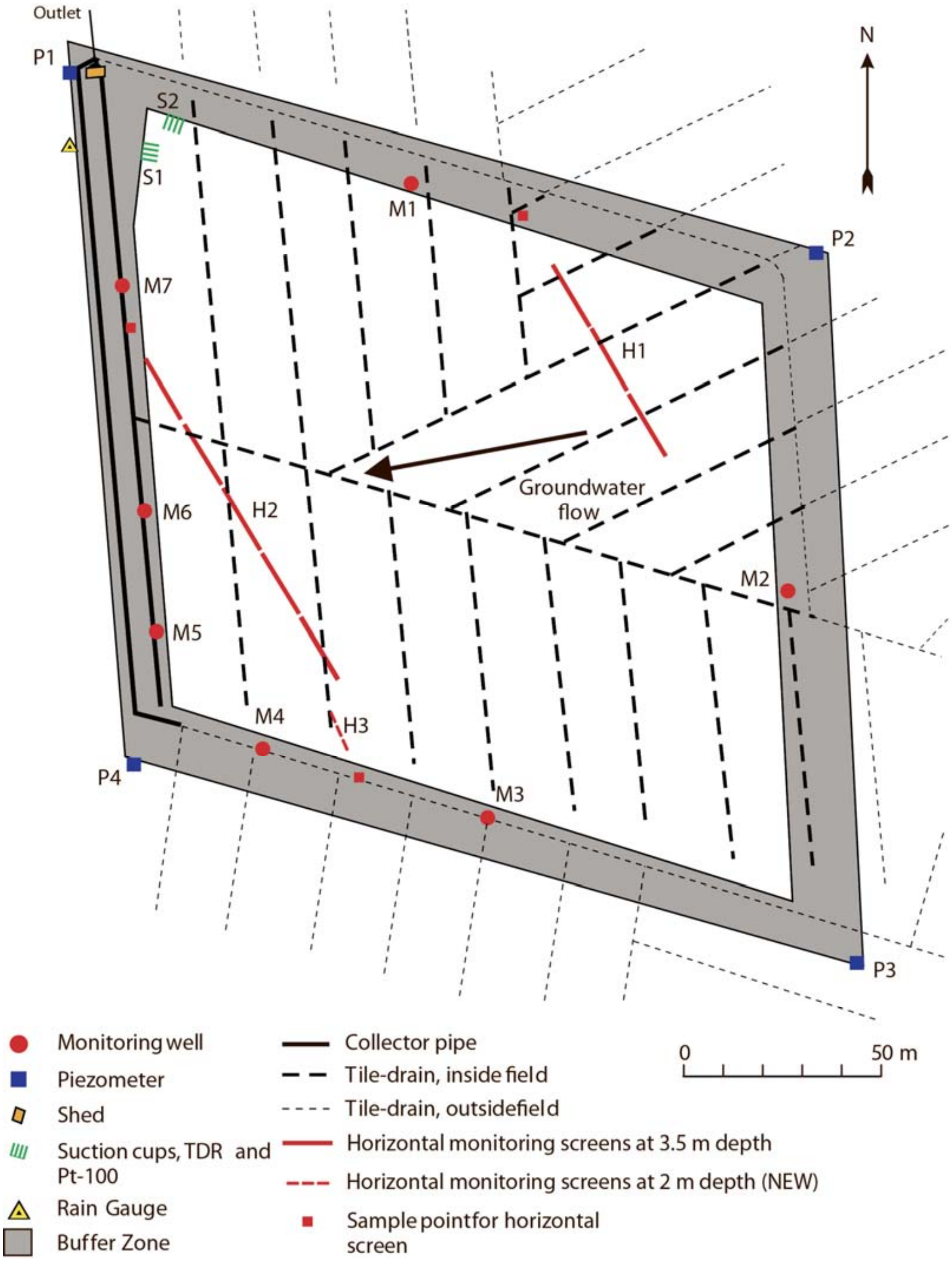

Figure 6.1. Overview of the **Faardrup** site. The innermost white area indicates the cultivated land, while the grey area indicates the surrounding buffer zone. The positions of the various installations are indicated, as is the direction of groundwater flow (by an arrow). Pesticide monitoring is conducted weekly from the drainage system (during period of continuous drainage runoff) and monthly and half-yearly from selected vertical and horizontal monitoring screens as described in Table A2.1 in Appendix 2.

6.1.2 Agricultural management

Management practice during the 2012-2013 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 4 April 2012 the field was sown with a mixture of spring barley varieties under sown with white clover (cv. Liflex) for clover seed production. The barley emerged on 19 April and the white clover on 24 April. Bentazone was used against weeds on 18 May and metrafenon against fungi on 6 June, and both substances included in the monitoring. At harvest of the spring barley on 12 August 67.5 hkg/ha of grain (85% dry matter) and 27.6 hkg/ha of straw (100% dry matter) was taken of the field. The fungicide propyzamid was applied to the white clover on 26 January 2013 and the herbicide bentazone on 14 May 2013. Bentazone and propyzamid as well as its three degradation products RH-24580, RH-24644 and RH-24655 were included in the monitoring. Pests were sprayed with lambda-cyhalothrin twice, on 31 May and 12 June, but the compound was not monitored. Clover seed yield at harvest on 28 July was 1.56 hkg/ha.

6.1.3 Model setup and calibration

The numerical model MACRO (version 5.2) 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 variably-saturated zone during the full monitoring period September 1999-June 2013 and to establish an annual water balance.

Compared to the setup in Brüsch *et al.* (2013b), 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 2013. 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 6.1) and measured drainage flow. Data acquisition and model setup are described in Barlebo *et al.* (2007).

Table 6.1. 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
1.7.11–30.6.12	626	746	400	98	106	247
1.7.12–30.6.13	626	569	453	62	92	54

[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 including the present reporting 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 2012-June 2013 were generally well described by the model (Figure 6.2D, 6.2E and 6.2F). However, for the summer period 2012 the model largely underestimated the drop in measured water saturation at 25 cm b.g.s. (Figure 6.2D).

The resulting water balance of all monitoring periods is shown in Table 6.1. Compared with the previous 13 years, the latest hydraulic year July 2012-June 2013 was characterised by having the second lowest precipitation, a medium actual evapotranspiration, and a medium measured and simulated drainage. This resulted in the second lowest groundwater recharge estimated for this site within the PLAP-period. Precipitation in this year was characterised by medium monthly precipitation compared to the other PLAP-years, although March was the driest ever registered in PLAP (Appendix 4). Due to this precipitation pattern, the duration of the simulated percolation period of the year July 2012-June 2013 was represented by continuous percolation throughout the period July-April (Figure 6.2A). Compared to the other years, the climate this year gave rise to a short period, where the groundwater table was just below drainage level, and causing medium contributions to the drains (Figure 6.2B and 6.2C).

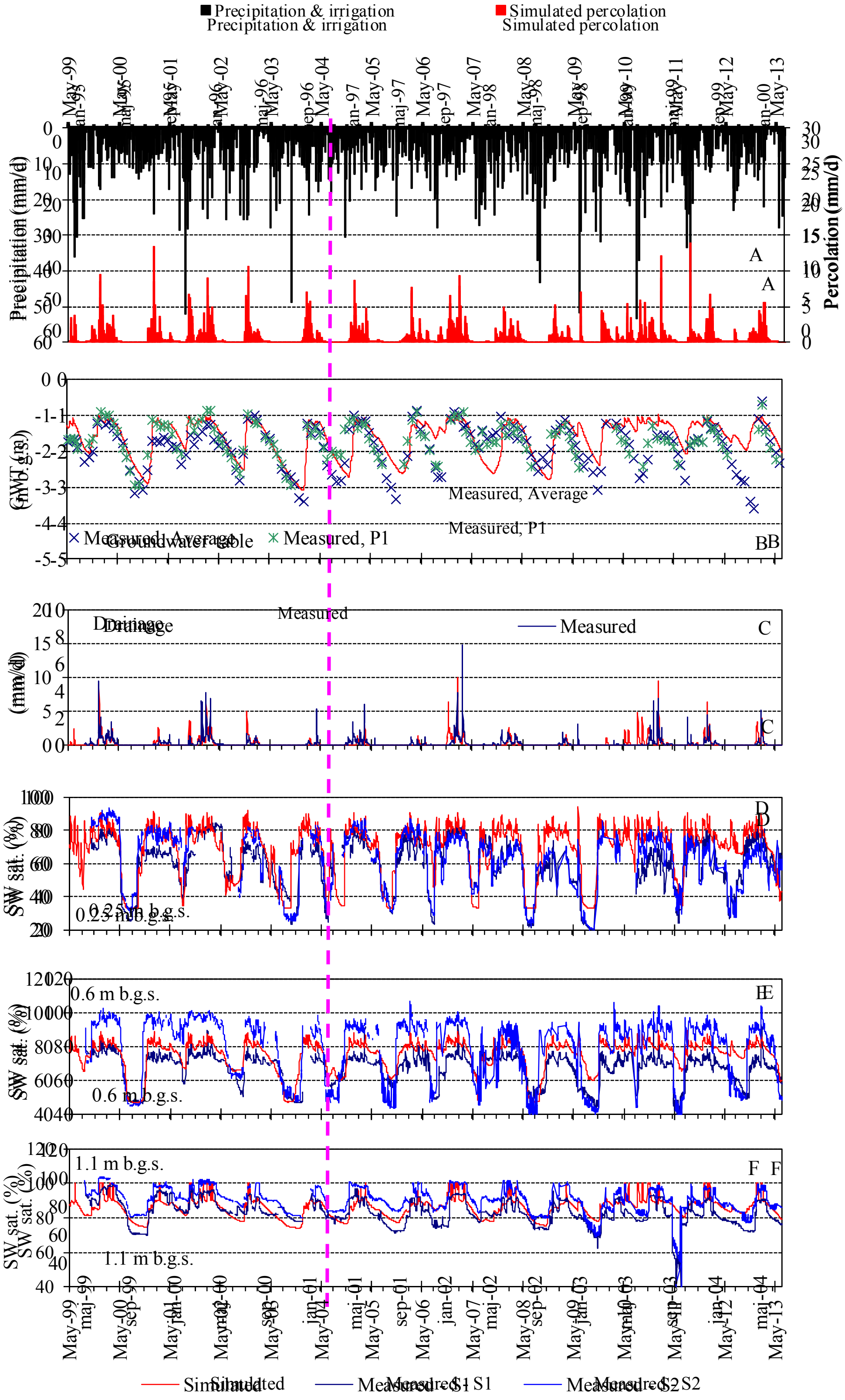

Figure 6.2. Soil water dynamics at **Faardrup**: Measured precipitation and simulated percolation 1 m b.g.s. (A), simulated and measured groundwater level GWT (B), simulated and measured drainage flow (C), and simulated and measured soil water saturation (SW sat.) at three different soil depths (D, E 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 6.1). The dotted vertical line indicates the beginning of the validation period (July 2004-June 2013).

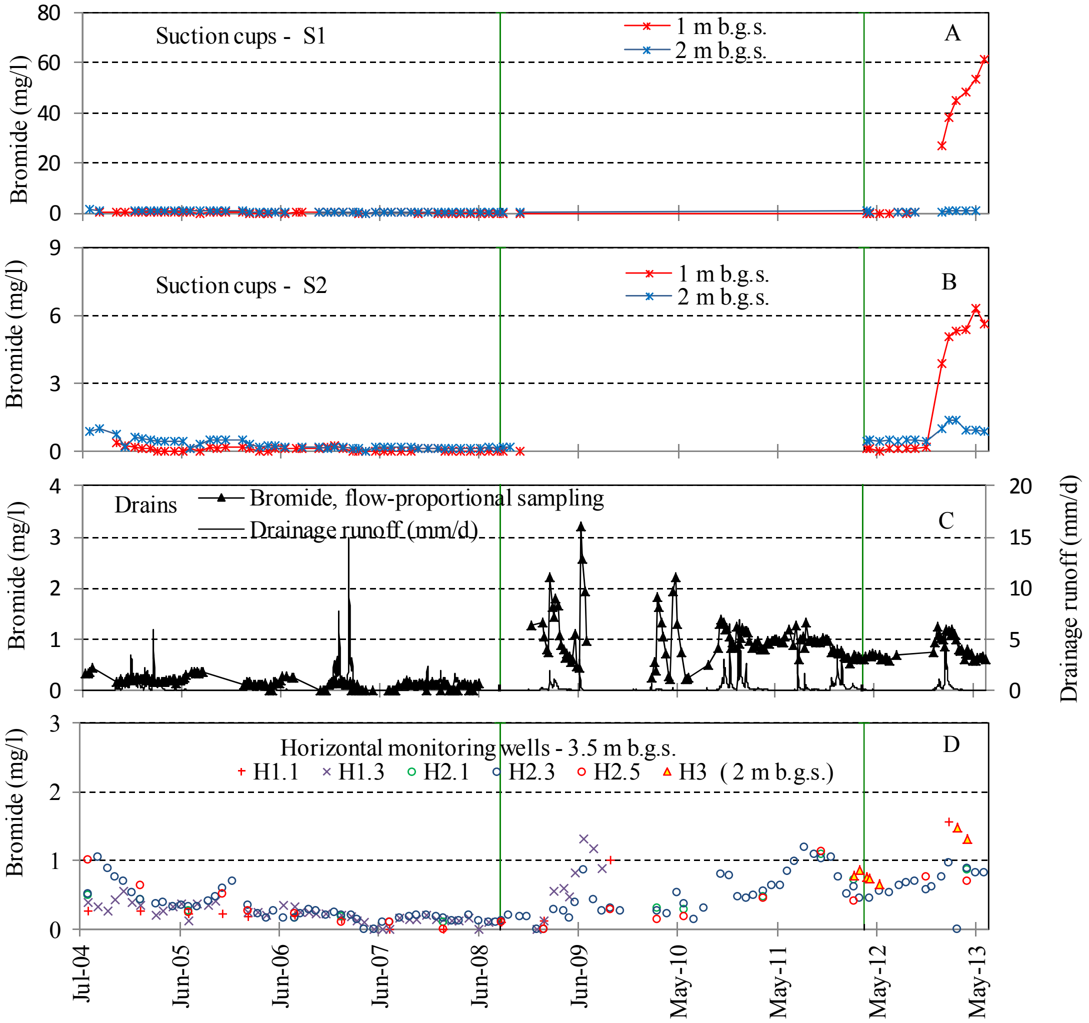

Figure 6.3. Bromide concentrations at **Faardrup**. A and B refer to suction cups located at S1 and S2. The bromide concentration is also shown for drainage runoff (C) and the horizontal monitoring wells. The horizontal wells H1 and H2 are situated 3.5 m b.g.s., and H3 in 2.5 m b.g.s. (D). From December 2008 to March 2012, bromide measurements in the suction cups were suspended. The green vertical lines indicate the dates of bromide applications.

The simulated drainage (Figure 6.2C) matched the measured drainage flow to some degree. Drainage is initiated more or less correct; however the magnitude of drainage was overestimated in the end of 2012 at the initiation of the drainage season. This discrepancy could be caused by MACRO‘s lack of ability to capture snow melting. In the periods of drainage temperature vent periodically below 0°C.

6.2.2 Bromide leaching

The bromide concentration shown in Figure 6.3 and Figure 6.4 relates to the bromide applied in May 2000 and to August 2008, where 30 kg ha^{-1} 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 6.4). On the 4 April 2012, 30 kg ha^{-1} of potassium bromide was applied, the third application.

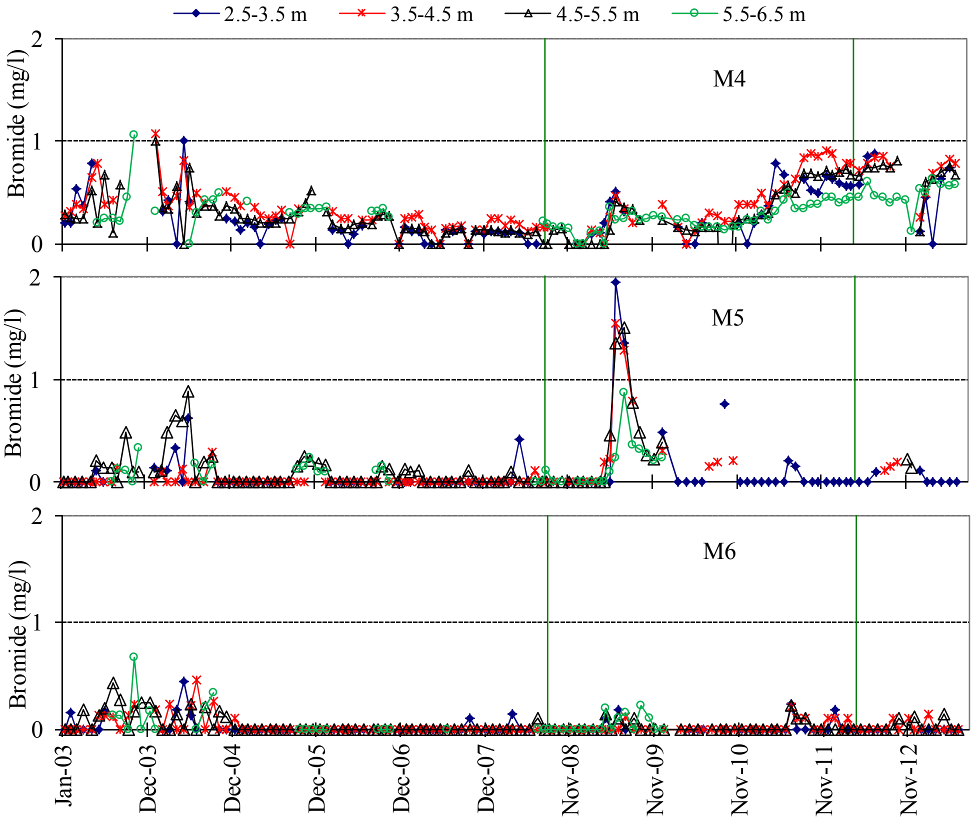

Figure 6.4. Bromide concentrations at **Faardrup**. The data derive from the vertical monitoring wells (M4, M5 and M7). Screen depth is indicated in m b.g.s. The green vertical lines indicate the dates of the two most recent bromide applications.

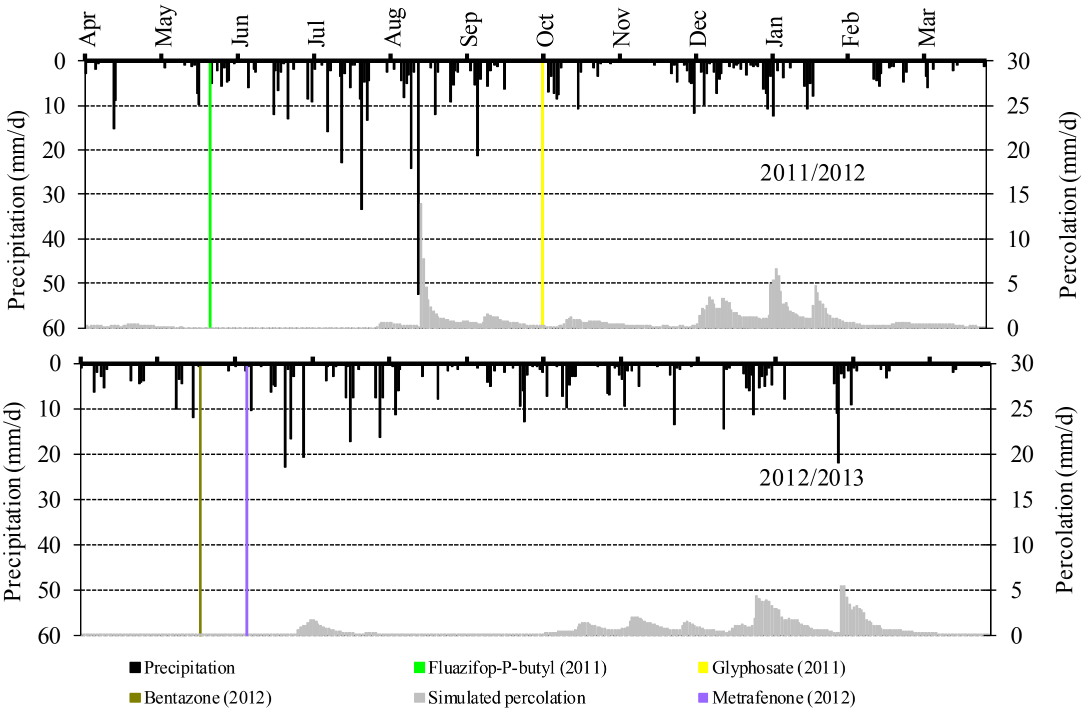

Figure 6.5. Application of pesticides included in the monitoring programme and precipitation (primary axis) together with simulated percolation (secondary axis) at **Faardrup** in 2011/2012 (upper), in 2012/2013 (lower).

6.2.3 Pesticide leaching

Monitoring at Faardrup began in September 1999. Pesticides used as well as their degradation products are shown in Table 6.2 and Table A7.5, in Appendix 7.

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 6.5. 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.

Table 6.2. Pesticides analyzed at **Faardrup**. Precipitation (precip.) and percolation (percol.) are accumulated within the first year (Y 1st precip., Y 1st percol.) and first month (M 1st precip., M 1st percol.) 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. (End monito.) end of monitoring of the pesticide (P) or their degradation products (M).

Crop	Applied product	Analyzed pesticide	Applica. Date	End monito.	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	Jun 08	806	294	57	23	<0.01
		CGA 322704(M)		Jun 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)		Mar 09	735	199	64	46	<0.01
		RH-24644(M)		Mar 09	735	199	64	46	<0.01
		RH-24655(M)		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)		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)		Jun 11	609	146	50	2	<0.01
		IN-E7710(M)		Jun 11	609	146	50	2	<0.01
		IN-M7222(M)		Jun 11	609	146	50	2	<0.02
Spring barley and	Fighter 480	Bentazone(P)	Jun 10	Jun 12*	693	327	49	29	<0.01
red fescue 2010	Fox 480 SC	Bifenox(P)	Oct 10	Jun 12	351	190	75	72	0.02
		Bifenox acid(M)		Jun 12	351	190	75	72	2.54
		Nitrofen(M)		Jun 12	351	190	75	72	0.01
Red fescue 2011	Fusilade Max	Fluazifop-P(M)	May 11	Mar 12	730	0	59	0	<0.01
	Fusilade Max	TFMP(M)		Jun 13*	730	0	59	0	<0.01
Spring barley and	Glyphogan	Glyphosate(P)	Oct 11	Aug 12	425	17	56	17	<0.01
white clover 2012	Glyphogan	AMPA(M)		Aug 12	425	17	56	17	<0.01
	Fighter 480	Bentazone(P)	May 12	Jun 13*	527	220	29	4	<0.01
	Flexity	Metrafenone(P)	Jun 12	Jun 13*	580	215	96	14	<0.01
White clover 2013	Fighter 480	Bentazone(P)	May13	Jun 13*	141	0	82	0	<0.01
	Kerb 400 SC	Propyzamid (P)	Jan 13	Jun 13*					<0,01
		RH24560 (M)		Jun 13*					<0.01
		RH24644 (M)		Jun 13*					<0.01
		RH24655 (M)		Jun 13*					<0.01

Systematic chemical nomenclature for the analyzed pesticides is given in Appendix 1.
**monitoring continues the following year.*

The current report focuses on the pesticides applied from 2011 and onwards, while the leaching risk of pesticides applied before 2011 has been evaluated in previous monitoring reports (see http://pesticidvarsling.dk/publ_result/index.html).

The following pesticides have been applied on the Faardrup field (Table 6.2) in

- 2011: Fluazifop-P-butyl and glyphosate
- 2012: Bentazone and metrafenone
- 2013: Propyzamid and bentazone.

These pesticides, except fluazifop-P-butyl, and the degradation products of fluazifop-P-butyl: fluazifop-P and TFMP, glyphosate: AMPA and propyzamid: RH24560, RH24644 and RH24655 have all been included in the PLAP-monitoring programme for Faardrup. Bentazone, fluazifop-P, glyphosate and AMPA have been tested in PLAP at Faardrup before 2011 (Table A7.5 in Appendix 7).

In the hydrological years 2010/2011, 2011/2012 and 2012/2013, bentazone was applied to test its leaching potential in cereal (spring barley) with two different under sowings (bentazone is not allowed to be used in cereal without under sowing) - red fescue in 2010 and white clover 2012 and 2013. The application onto spring barley and red fescue on 1 June 2010 was followed by a very wet July-November 2010 resulting in bentazone to be detected after 16 days in drainage water (0.11 µg/L) (Figure 6.7), and after 23 days in water from 3.5 m depth (0.052 µg/L). Four and five months later bentazone was found in water from 3.5 m depth (0.028 µg/L and 0.012 µg/L), and after five and six and a half months in drainage water 1.2 m depth (0.012 µg/L and 0.013 µg/L).

The application onto spring barley and white clover on the 18 May 2012 was followed by a dry period until the end of June (Appendix 5) and has not resulted in any detections of bentazone during the remaining part of 2012. At the end of January one detection (0.02 µg/L) in the drainage was obtained which could be the outcome of a sudden rise in the groundwater table during this month caused by high percolation (Figure 6.7). From the time of this detection until May 2013, where bentazone was applied a second time on white clover, bentazone was not detected.

Fluazifop-P-butyl has earlier (21 June 2001) been applied at Faardrup, but it has only been the degradation product fluazifop-P, which have been included in the PLAP-monitoring. This compound was found in few samples with max concentrations of 3.8 µg/L in drain water and 0.17 µg/L in groundwater. The degradation product TFMP of fluazifop-P-butyl has, however, not been included in the PLAP-monitoring at Faardrup before May 2011.

Until 2011, glyphosate has only been applied at Faardrup as weed control both in August 1999 and October 2001. On 3 October 2011 glyphosate was applied to desiccate the red fescue. Compared to the earlier applications the dose was 1.000 g active ingredient ha^{-1} higher (from 800 to 1.800 g active ingredient ha^{-1}) and plant cover larger. After three days of no precipitation, a 7 mm day^{-1} precipitation resulted in two detections, 0.019 and 0.025 µg/L, of glyphosate in groundwater samples from the two upper filters in the down gradient vertical well M4. No further detections were obtained in the hydrological year 2011/2012 and monitoring was stopped in August 2012. There has been no detections of AMPA during the samt period of time.

Metrafenone, which was applied on spring barley under sown with white clover in June 2012, has not been detected during the hydrological year 2012/2013.

At Faardrup, bifenox was detected in six water samples collected from drains from November 2010 to January 2011. The concentrations were below 0.1 µg/L (0.021-0.085 µg/L). Its degradation product bifenox-acid was found in seven samples in 2010 from the drain, but in high concentrations from 0.23-6.9 µg/L, and in one groundwater sample from the horizontal well H2 in a concentration of 0.19 µg/L (Figure 6.6). From January to August 2011 bifenox-acid was found in high, but decreasing concentrations in 11 water samples from the drain (8.6 to 0.074 µg/L). It should be noted that bifenox-acid has a high detection limit 0.05 µg/L. Another degradation product, nitrofen, was detected in five drain water samples in 2010, concentrations ranging from 0.014 to 0.16 µg/L, and in a drain water sample from 2011 (0.018 µg/L). Neither of the substances were detected in the period from August 2011 to May 2012, why monitoring for these compounds in PLAP was stopped.

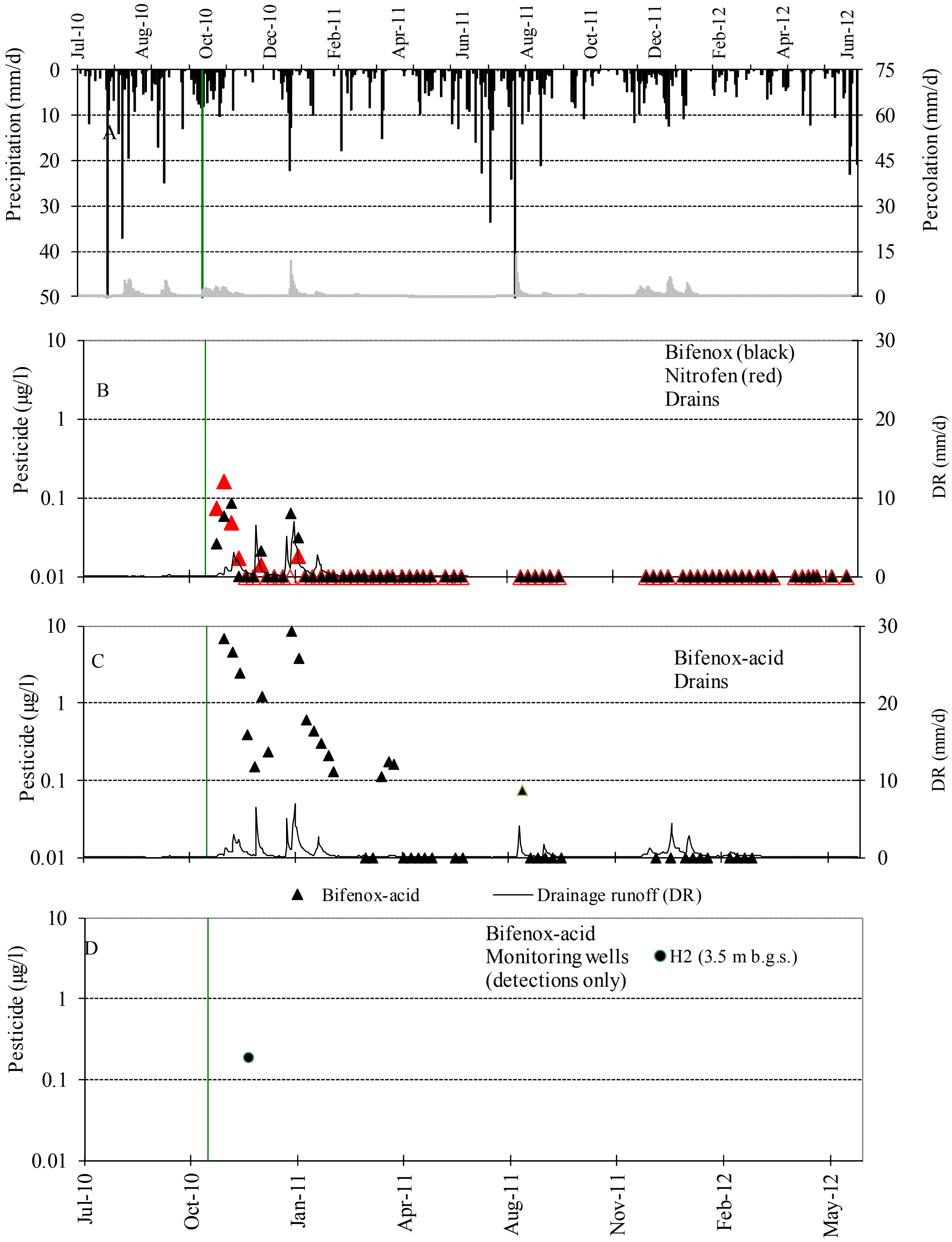

Figure 6.6. Precipitation and simulated percolation 0.6 m b.g.s. (A) together with concentration of bifenox and nitrofen (B) and bifenox-acid (C) in the drainage runoff, and the detections of bifenox-acid (E) in the groundwater monitoring screens at **Faardrup**. The green vertical line indicate the 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).

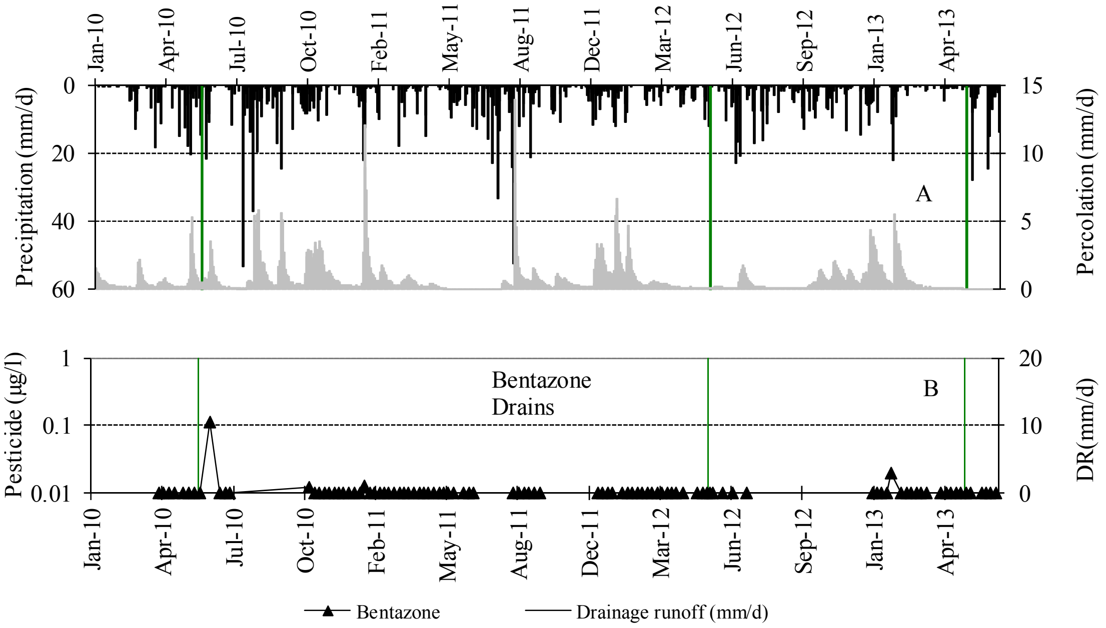

Figure 6.7. Precipitation and simulated percolation 1 m b.g.s. (A) together with the concentration of bentazone (B) in the drainage runoff at Faardrup. The green vertical lines indicate the dates of bentazone application.

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 analyzes employed. Two types of sample are used in the quality control 1) samples with known pesticide composition and concentration are used for *internal monitoring* of the laboratory method (internal QA), and 2) *externally spiked samples* that are used to incorporate additional procedures such as sample handling, transport and storage (external QA). Pesticide analysis quality assurance (QA) data for the period July 2012 to June 2013 are presented below, while those for the preceding monitoring periods are given in previous monitoring reports (available on http://pesticid-varsling.dk/publ_result).

7.1 Materials and methods

All pesticide analyzes were carried out at a commercial laboratory selected on the basis of a competitive tender. In order to assure the quality of the analyzes, 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 EPA 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 analyzed one or two control samples prepared in-house at the laboratory as part of their standard method of analysis. The pesticide concentration in the internal QA samples ranged between 0.03–0.10 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 per test field were analyzed at the laboratories along with the various water samples from the five test sites. Two stock solutions of different concentrations were prepared from standard mixtures in ampoules prepared by Dr. Ehrenstorfer, Germany (Table 7.1). 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 sealed, shaken thoroughly and shipped to the staff collecting samples on the field locations. 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 defined groundwater well in each field. After thorough mixing, the control sample was transferred to a sample bottle similar to the monitoring sample bottles and transported to the laboratory together with the regular samples.

In the present report period the final concentrations in the solutions shipped for analysis in the laboratory were 0.050 µg/L for the spiked low level control sample, and 0.117 µg/L for the high level sample. The pesticide concentration in the solution is indicated in Table 7.1.

Blank samples consisting only of HPLC water were also included as control for false positive findings in the external QA procedure every month. All samples (both spiked and blanks) included in the QA procedure were labelled with coded reference numbers, so that the laboratory was unaware of which samples were controls, blanks or true samples.

Table 7.1. Pesticides included in the **external** control samples in the period 1.7.2012-30.6.2013. Concentrations in both the original ampoules and in the resulting high-level and low-level external control samples used. *The concentrations in ampule 2 from Ehrenstorfer were not correct.

Compound	Ampoule concentration (µg/L)	Ampoule	High-level control (µg/L)	Low-level control (µg/L)
AMBA	1000	1	0.117	0.050
AMPA	1000	2^*	--	--
Aminopyralid	1000	3	0.117	0.050
Bentazone	1000	1	0.117	0.050
Bifenox acid	1000	3	0.117	0.050
Boscalid	1000	1	0.117	0.050
CGA 108906	1000	1	0.117	0.050
CyPM	1000	1	0.117	0.050
Diflufenican	1000	1	0.117	0.050
Glyphosate	1000	2^*	--	--
Metrafenone	1000	1	0.117	0.050
PPU	1000	1	0.117	0.050
RH-24644	1000	1	0.117	0.050
TFMP	1000	1	0.117	0.050
Tebuconazole	1000	1	0.117	0.050
Triazinamin-methyl	1000	1	0.117	0.050

7.2 Results and discussion

7.2.1 Internal QA

Ideally, the analytical procedure provides precise and accurate results. However, in the real world results from analysis are subject to a certain standard deviation. Such standard deviation may be the combined result of several contributing factors. Overall, the accuracy of an analytical result reflects two types of error: Random errors related to precision and systematic errors relating to bias. In a programme like PLAP it is relevant to consider possible changes in analytical "reliability over time". As random and systematic errors may both 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 provided by the laboratory 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 QA pesticide analyzes, single analyzes 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:** In brief, 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 analyzed, the QA applied is pesticide-specific. In the current reporting period internal quality data was available for 32 compounds. The results of the internal QA statistical analysis for each pesticide are presented in Table 7.2. 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. Obviously, such data should be interpreted with caution. Considering all compounds the mean variation S_w was 0.005, S_b 0.011 and S_t was 0.013, levels that are considered very suitable when relating to the residue limit for pesticides (0.1 µg/L).

As a rule of thumb, the between-day standard deviation should be no more than double the within-day standard deviation. From Table 7.2 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, three out of 16 compounds had ratios above two, where the highest S_b/S_w ratio in this group was 4.7 and observed for FMC 65317 (degradation product of clomazon). The two other compounds were boscalid with a ratio of 2.4 and bifenox with a ratio of 2.3. These are rather low ratios compared to ratios in the previous report. The cause differs for the three compounds.

FMC 65317 is a degradation product from clomazone and is recently included in the program (it should be noted that only three sets of QA data were available for this compound). The number of analyzed samples is not yet sufficient to do a thorough statistical analysis and the statistical data should therefore be considered tentative.

For boscalid the ratio of 2.4 is still a little too high to meet the criteria but both S_b and S_w are small values. Compared to last years reporting period, where the ratio was 9.2 and it did not meet the normality criteria, the analytical procedure now seems to have improved and in good control. For bifenox it is apparent that the high S_b/S_w ratio is caused by the relatively high between-day deviation (S_b), but both S_w and S_b are still small values, actually indicating an analytical procedure in good control.

When all compounds are considered, high S_b/S_w ratio is also apparent for clomazone (6.8), propyzamide (4.9), RH-24580 (4.6), RH-24644 (4.2) and RH-24655 (4.5) (note normality criteria were not met for these compounds). The high S_b/S_w ratio is due to a relatively high between-day deviation (S_b) indicating that it may be possible to improve the analytical procedure for these compounds to bring down the this deviation. It should, however, be noted that only three sets of QA data were available for clomazone and the variation between days (S_b) for all five compounds is within the range of S_b values of all the other compounds analyzed.

In previous reports high S_b/S_w ratio was observed for diflufenican (3.2) CGA 108906 (5.3), and aclonifen (7.0). In the current reporting period the S_b/S_w ratio is still a little too high for diflufenican (2.3) but has improved since last year. Both CGA 108906 and aclonifen are now in good control with ratios of 1.0 and 0.6, respectively, and now meets the criteria for normality.

In last years report MNBA both had the highest total standard deviation (S_t) value and the highest S_b/S_w ratio of all included compounds. It was suggested that the high S_b/S_w ratio of MNBA seemed to be caused by a rather high S_b indicating that it may be possible to improve the analytical procedure for this compound to bring down the between-day deviation. In this reporting period all three standard deviations have been lowered significantly and the MNBA analysis is now in good control and now meets all the QA criteria.

The total standard deviation (S_t) of the various analyzes of pesticides and degradation products lie within the range 0.002-0.041 µg/L, the highest value being observed for aminopyralid. In general, the data suggest that the analytical procedure used for the quantification of the compounds with high S_b/S_w ratio and/or high S_t may benefit from a critical review and possible optimisation of within-day variation.

Table 7.2. Internal QA of pesticide analyzes carried out in the period 1 July 2012-30 June 2013. Results of the test for normality, one-way analysis of variance (ANOVA), the estimated values of standard deviations (w: within-day, b: between-day, t: total – see text for details), pesticide concentration in internal QA sample (Conc.) and number of duplicate samples (n) are given for each pesticide. For test the P value $\alpha=0.05$ was used.

Compound	Normal distribution $\alpha=0.05$	Significant S_b Between day contribution ANOVA $\alpha=0.05$	S_w (µg/L)	S_b (µg/L)	S_t (µg/L)	Ratio S_b/S_w	N	Conc. (µg/L)
Aclonifen	yes	yes	0.003	0.002	0.003	0.6	5	0.05
AE-05422291*	yes	-	0.002	0.004	0.005	2.0	30	0.05
AE-B107137*	-	-	0.015	0.022	0.026	1.5	30	0.10
AMBA*	yes	yes	0.009	0.009	0.013	1.0	9	0.10
Aminopyralid	-	-	0.015	0.038	0.041	2.6	30	0.10
AMPA*	yes	-	0.004	0.005	0.006	1.3	33	0.03
Azoxystrobin	-	-	0.003	0.011	0.012	3.9	32	0.05
Bentazone	-	-	0.004	0.009	0.010	2.1	38	0.05
Bifenox	yes	-	0.005	0.012	0.013	2.3	19	0.05
Bifenox acid*	-	-	0.006	0.029	0.029	4.8	19	0.10
Boscalid	yes	-	0.001	0.002	0.002	2.4	6	0.05
CGA108906*	yes	yes	0.011	0.011	0.016	1.0	9	0.10
CGA62826*	yes	-	0.007	0.012	0.014	1.6	9	0.10
Clomazone	-	-	0.004	0.027	0.028	6.8	3	0.05
CyPM*	-	-	0.004	0.014	0.015	3.5	32	0.05
Diflufenican	-	-	0.001	0.003	0.003	2.3	30	0.05
FMC 65317*	yes	-	0.006	0.028	0.028	4.7	3	0.05
Glyphosate	yes	yes	0.003	0.001	0.003	0.5	33	0.03
Mesotrione	yes	yes	0.009	0.007	0.011	0.7	9	0.10
Metalaxyl-M	-	-	0.002	0.005	0.005	2.5	12	0.05
Metrafenone	-	-	0.003	0.009	0.009	2.8	35	0.05
MNBA*	yes	yes	0.010	0.005	0.011	0.5	9	0.10
Nitrofen*	yes	-	0.004	0.007	0.008	2.0	21	0.05
Propyzamide	-	-	0.002	0.009	0.010	4.9	24	0.05
Prosulfocarb	yes	-	0.006	0.012	0.014	1.9	5	0.05
RH-24580*	-	-	0.002	0.009	0.009	4.6	24	0.05
RH-24644*	-	-	0.003	0.012	0.013	4.2	24	0.05
RH-24655*	-	-	0.002	0.011	0.011	4.5	24	0.05
Tebuconazole	yes	yes	0.004	0.002	0.005	0.5	16	0.05
TFMP*	-	-	0.005	0.011	0.012	2.3	42	0.05
Triazinamin-methyl*	yes	yes	0.003	0.002	0.004	0.9	3	0.05

**Degradation product.*

7.2.2 External QA

As described above the external QA program was based on samples spiked at the field sites. As part of the quality control a set of blanks made from HPLC water were also analyzed 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. A total of 32 blank samples made from HPLC water were analyzed and no compounds were detected in any of these analyzed blank samples. On the basis of this, samples analyzed in the monitoring program and found to contain pesticides or degradation products are regarded as true positive findings.

Table 7.3. Recovery of externally spiked samples carried out in the period 1.7.2012-30.6.2013. Average recovery (%) of the nominal concentration at low/high concentration level is indicated for each site. For each compound n_{low} and n_{high} refer to the number of samples recovered with the spiked compound at low and high concentrations, respectively. $n_{total\ analyzed}$ is the total number of spiked samples (including both low and high level samples). Bold font is used for recoveries outside the range of 70-120%.

	Tylstrup %		Jyndevad %		Silstrup %		Estrup %		Faardrup %		Average %	n_{low}/ n_{high}	$n_{total\ analyzed}$
	Low	High	Low	High	Low	High	Low	High	Low	High			
AMBA			**64**	**64**							64%	3/3	6
AMPA[*]					***26***	***18***		***15***			*18%*	*1/3*	*12*
Aminopyralid	78	**54**					86	75			73%	4/4	12
Bentazone			99	97			94	102	101	102	99%	7/7	14
Bifenox acid	112	94			114	111		102			106%	2/3	6
Boscalid	92	85									88%	1/1	2
CGA108906	**64**	**57**	73	70							66%	6/6	12
CyPM					117	**124**	**134**	**137**			129%	5/5	10
Diflufenican			91	94	89	87					90%	6/6	12
Glyphosate[*]					*100*	***65***	***61***	***62***			*72%*	*6/6*	*12*
Metrafenone							90	94	87	91	90%	6/6	12
RH-24644									96	102	99%	2/2	4
TFMP					84	**50**			**69**	**60**	66%	6/6	12
Tebuconazole					100	94					97%	1/1	2

[*] The concentrations of glyphosate and AMPA in ampule 2 Dr. Ehrenstorfer A/S were not correct.

Table 7.3 provides an overview of the recovery of all externally spiked samples. Since the results for each field site in Table 7.3 are based on only a few observations for each concentration level (high/low), the data should not be interpreted too rigorously.

A total of 42 samples were spiked in this reporting period. In general, the recovery of the spiked compounds in the samples is acceptable (i.e. in the range 70% to 120%), but the broad range of average recoveries indicates that for some compounds there may be reason for concern. Water used for making the spiked samples is taken on location from up-stream wells. For this reason minor background content may be present in some of the water used for spiking, and in particular for the low level QC samples, background content can cause an 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, especially AMPA data points to the need of keeping track on these particular compounds.

In previous reports the recoveries of AMPA at Estrup and Faardrup were good and within the acceptable range. However, in this present reporting period very low recoveries are observed both at low and high level at Silstrup and at Estrup AMPA was not recovered in any of the low level external QC samples and only at low recoveries in the high level samples. A total of 12 external QC samples were analyzed for the content of AMPA. From these, AMPA was only recovered in 4 samples (and with very low recoveries). Subsequent analysis of the initial ampoule 2 containing AMPA and glyphosate showed that the low recoveries and false negative samples are due to a failure in production of ampoule 2 (initial concentration of AMPA and glyphosate in the ampoule was to low - especially the AMPA concentration was to low). This flawed batch of ampoules was unfortuneately used in the external control program throughout the reporting period. In regard to reliability of the AMPA monitoring sample results, these data do not cause concern as the laboratory internal control samples show an analytical method in good control (refer Table 7.2 and Appendix 6 – laboratory internal control cards).

Previous reports have discussed the QA for glyphosate and the initiatives that have been taken to improve the analysis of this compound. In the previous reporting period the externally spiked samples showed a good recovery (ranging from 73-107%) indicating that a more robust analytical method has been implemented in the program. In the present reporting period slightly lower recoveries (61-65%) were observed both at Silstrup and Estrup, which is related to the incorrect concentrations in ampoule 2.

All the compounds included in the spiking procedure (Table 7.1) 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.

During the 2012/2013 monitoring period a total of eight pesticides (azoxystrobin, bentazone, bifenox, diflufenican, glyphosate, metalaxyl-M, metrafenone and tebuconazole) and nine degradation products (AE-B107137, AMPA, bifenox acid, CGA 108906, CGA 62826, CyPM, PPU, PPU-desamino and TFMP) 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. Control cards for all presented QA data 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 analyzes was good with total standard deviation (S_t) in the range 0.002-0.041 µg/L.

- As demonstrated by the external QA, recovery was generally good in externally spiked samples. The low recoveries of AMPA and glyphosate are related to the ampoules used for spiking in the external QA program in the reporting period. Therefore, the reliability of the AMPA and glyphosate analyzes in the monitoring program in general is not compromised.

- 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 8.1). 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 8.3). 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 2013 16 of the applied pesticides (or their degradation products) exhibited pronounced root zone leaching and 15 pesticides and degradation products 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 8.1 and 8.2). At both sites, leaching of azoxystrobin and CyPM has mostly been confined to the depth of the drainage system, and they have rarely been detected in groundwater, (Table 8.3 and 8.4). 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 4.7 and 2008/2012 at Estrup, Figure 5.6). In 2010 and 2011 CyPM continued to enter the drain water especially in Silstrup in high concentrations but in smaller concentrations in 2012. In this monitoring year azoxystrobine was not detected, while CyPM was detected in one drain water sample. Azoxystrobine was applied at Estrup in June 2012, and both azoxystrobine and CyPM leached in high concentrations to drain water in concentrations ≥ 0.1 µg/L. The degradation product CyPM was found in 7 groundwater samples from the two horizontal wells, and in one sample the concentration was ≥ 0.1 µg/L. There were no findings in groundwater monitoring wells. At the loamy Faardrup site azoxystrobin and CyPM were detected in four samples from the drainage water up till 2007, and in no samples from the sandy Jyndevad site in the period 2005-2007 (Appendix 5).

Table 8.1. 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 2013 are not included in the table.

Risk	Parent	Tylstrup	Jyndevad	Silstrup	Estrup	Faardrup
High	Azoxystrobin	⬛	⬛	🟥	🟥	🟦
	Bentazone	⬛	🟥	🟥	🟥	🟥
	Bifenox	⬛	⬛	🟥	🟥	🟥
	Ethofumesate			🟦	🟥	🟦
	Fluazifop-P-butyl	⬛	⬛	🟥		🟦
	Fluroxypyr	⬛	⬛	⬛	🟥	🟦
	Glyphosate		⬛	🟥	🟥	🟦
	Metalaxyl-M	🟥	🟥			
	Metamitron			🟦	🟥	🟦
	Metribuzin	🟥	🟥			
	Picolinafen		⬛		🟥	
	Pirimicarb	⬛	⬛	🟦	🟥	🟦
	Propyzamide	⬛		🟥		🟥
	Rimsulfuron	🟦	🟥	⬛		
	Tebuconazole	⬛	⬛	⬛	🟥	⬛
	Terbuthylazine	🟦	🟦	🟥	🟥	🟥
Low	Amidosulfuron		🟦	⬛	⬛	
	Bromoxynil	⬛	⬛	⬛	🟦	⬛
	Clomazone	⬛	⬛	⬛	⬛	🟦
	Diflufenican		⬛	🟦		
	Dimethoate	⬛	⬛	🟦	⬛	⬛
	Epoxiconazole	⬛	⬛	⬛	🟦	⬛
	Flamprop-M-isopropyl	⬛		🟦	🟦	⬛
	Ioxynil	⬛	⬛	⬛	🟦	⬛
	MCPA		⬛	⬛	🟦	🟦
	Mancozeb	🟦				
	Mesosulfuron-methyl		⬛		🟦	
	Metrafenone				🟦	⬛
	Pendimethalin	⬛	⬛	🟦	⬛	⬛
	Phenmedipham			⬛		🟦
	Propiconazole	⬛	⬛	🟦	🟦	⬛
	Prosulfocarb	⬛		🟦		⬛
	Pyridate		⬛	🟦		
	Triflusulfuron-methyl			🟦		⬛
None	Aclonifen	⬛	⬛			
	Aminopyralid	⬛			⬛	
	Boscalid	⬛				
	Chlormequat		⬛	⬛	⬛	
	Clopyralid	⬛		⬛	⬛	
	Cyazofamid	⬛	⬛			
	Desmedipham			⬛		⬛
	Fenpropimorph	⬛	⬛	⬛	⬛	⬛
	Florasulam		⬛		⬛	
	Iodosulfuron-methyl			⬛	⬛	
	Linuron	⬛				
	Mesotrione		⬛			
	Thiacloprid				⬛	
	Thiamethoxam	⬛				⬛
	Triasulfuron	⬛		⬛	⬛	
	Tribenuron-methyl	⬛	⬛	⬛	⬛	⬛

🟥 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 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 8.2. 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 degradation products are mentioned if analyzed under compound. Pesticides applied in spring 2013 are not included. N (number of samples with detections). M (maximum concentration).

Risk	Parent	Analyte	Tylstrup		Jyndevad		Silstrup		Estrup		Faardrup	
			N	M	N	M	N	M	N	M	N	M
High	Azoxystrobin	Azoxystrobin	0	-	0	-	10	0.03	125	1.40	0	.
		CyPM	0	-	0	-	79	0.34	261	2.10	4	0.06
	Bentazone	2-amino-N-isopropyl-benzamide	0	-	2	0.03	0	-	1	0.06	1	0.06
		Bentazone	1	0.01	54	1.90	45	6.40	161	20.00	21	43.00
	Bifenox	Bifenox	0	-	2	0.04	5	0.38	4	0.15	6	0.09
		Bifenox acid	0	-	1	0.10	20	4.80	16	1.90	18	8.60
		Nitrofen	0	-	0	-	5	0.34	0	.	6	0.16
	Ethofumesate	Ethofumesate					20	0.23	35	3.36	14	12.00
	Fluazifop-P-butyl	Fluazifop-P	0	-	0	-	0	-			9	3.80
		TFMP					51	0.64			0	-
	Fluroxypyr	Fluroxypyr	0	-	0	-	0	-	3	1.40	1	0.19
	Glyphosate	AMPA			1	0.01	138	0.35	414	1.60	15	0.11
		Glyphosate			0	-	83	4.70	291	31.00	5	0.09
	Metalaxyl-M	CGA 108906	61	4.80	54	3.70						
		CGA 62826	24	0.12	55	1.20						
		Metalaxyl-M	4	0.03	10	0.04						
	Metamitron	Desamino-metamitron					58	0.67	49	5.55	16	2.50
		Metamitron					45	0.55	42	26.37	12	1.70
	Metribuzin	Desamino-diketo-metribuzin	63	2.10	0	-						
		Diketo-metribuzin	184	0.62	3	0.09						
	Picolinafen	CL153815			0	-			31	0.50		
		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	1.60			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 (IN70941)	153	0.09	194	0.29	0	-				
		PPU-desamino (IN70942)	45	0.03	123	0.18	0	-				
	Tebuconazole	Tebuconazole	0	-	0	-	2	0.08	41	2.00	4	0.05
	Terbuthylazine	2-hydroxy-desethyl-terbuthylazine	5	0.02			28	0.11	87	6.30	8	1.00
		Desethyl-terbuthylazine	2	0.01	20	0.06	108	1.08	146	8.20	89	8.30
		Desisopropylatrazine	17	0.04			43	0.04	71	0.44	25	0.36
		Hydroxy-terbuthylazine	1	0.04			26	0.04	88	0.99	21	0.58
		Terbuthylazine	0	-	0	-	60	1.55	112	11.00	41	10.00
Low	Amidosulfuron	Amidosulfuron			3	0.11	0	-	0	-		
	Bromoxynil	Bromoxynil	0	-	0	-	0	-	3	0.60	0	-
	Clomazone	Clomazone	0	-	0	-	0	-	0	-	1	0.28
		FMC 65317	0	-	0	-	0	-	0	-	1	0.30
	Diflufenican	AE-B107137			0	-	5	0.13				
		Diflufenican			0	-	9	0.12				
	Dimethoate	Dimethoate	0	-	0	-	1	1.42	0	-	0	-
	Epoxiconazole	Epoxiconazole	0	-	0	-	0	-	14	0.39	0	-
	Flamprop-M-isopropyl	Flamprop	0	-			7	0.10	13	0.03	1	0.09
		Flamprop-M-isopropyl	0	-			12	0.11	20	0.07	1	0.04
	Ioxynil	Ioxynil	0	-	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		
	Metrafenone	Metrafenone							20	0.07	0	-
	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	0	-			5	0.18			0	-
	Pyridate	PHCP			0	-	4	2.69				
	Triflusulfuron-methyl	IN-E7710					5	0.01			0	-

Table 8.3. Detections of pesticides and their degradation products in water samples from the **groundwater monitoring screens** at the five PLAP sites (see Table 8.4 for details). Pesticides applied in spring 2013 are not included in the table. The substances in Table 8.3 are sorted as in Table 8.1

Risk	Parent	Tylstrup	Jyndevad	Silstrup	Estrup	Faardrup
High	Azoxystrobin	▨	▨	🟥	🟥	▨
	Bentazone	▨	▨	🟥	🟦	🟥
	Bifenox	▨	🟦	🟥	🟥	🟥
	Ethofumesate			🟦	▨	🟥
	Fluazifop-P-butyl	▨	▨	🟥		🟥
	Fluroxypyr	▨	▨	▨	🟦	🟦
	Glyphosate		🟦	🟦	🟥	🟦
	Metalaxyl-M	🟥	🟥			
	Metamitron			🟥	▨	🟥
	Metribuzin	🟥	🟥			
	Picolinafen		▨		▨	
	Pirimicarb	▨	▨	🟦	🟦	🟦
	Propyzamide	▨		🟥		🟦
	Rimsulfuron	🟦	🟥			
	Tebuconazole	🟦	🟦	▨	🟥	🟦
	Terbuthylazine	🟦	🟦	🟥	🟦	🟥
Low	Amidosulfuron		▨		▨	
	Bromoxynil	▨	▨		▨	▨
	Clomazone	▨	▨	▨	▨	▨
	Diflufenican		▨	🟥	▨	
	Dimethoate	▨	▨	🟦	▨	▨
	Epoxiconazole	▨	🟦	▨	▨	▨
	Flamprop-M-isopropyl	▨		🟦	▨	▨
	Ioxynil	▨	▨		▨	🟦
	MCPA		▨	▨	🟦	▨
	Mancozeb	🟦				
	Mesosulfuron-methyl		▨		▨	
	Metrafenone				▨	▨
	Pendimethalin	▨	▨	▨		▨
	Phenmedipham			▨		🟦
	Propiconazole	▨	▨	▨	🟦	🟦
	Prosulfocarb	▨		🟦		▨
	Pyridate		▨	🟥		
	Triflusulfuron-methyl			🟦		▨
None	Aclonifen	▨	▨			
	Aminopyralid	▨			▨	
	Boscalid	▨				
	Chlormequat		▨	▨	▨	
	Clopyralid	▨	▨			
	Cyazofamid	▨	▨			
	Desmedipham			🟦		▨
	Fenpropimorph	▨	🟦	▨	▨	▨
	Florasulam		▨		▨	
	Iodosulfuron-methyl			▨		
	Linuron	▨				
	Mesotrione		▨			
	Thiacloprid				▨	
	Metsulfuron-methyl			▨	🟦	
	Thiamethoxam	▨				▨
	Triasulfuron	▨		▨	▨	
	Tribenuron-methyl	▨	▨	▨		▨

🟥 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 8.4. 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). Only high and low risk included. The parent pesticide and degradation products are mentioned if analyzed under compound. Only pesticides/degradation products with more than two detections at one site are included. Pesticides applied in spring 2013 are not included. N (number of samples with detections). M (maximum concentration).

Risk	Parent	Analyte	Tylstrup		Jyndevad		Silstrup		Estrup		Faardrup	
			N	M	N	M	N	M	N	M	N	M
High	Azoxystrobin	Azoxystrobin	0	-	0	-	0	-	2	0.04	0	-
		CyPM	0		0		28	0.1	18	0.13	0	
	Bentazone	2-amino-N-isopropyl-benzamide	0	-	0	-	0	-	1	0.03	0	-
		Bentazone	0	-	1	0.01	29	0.44	16	0.02	13	0.60
	Bifenox	Bifenox	0	-	2	0.05	5	0.10	0	-	0	-
		Bifenox acid	0	-	0	-	27	3.10	1	0.11	1	0.19
	Ethofumesate	Ethofumesate					5	0.04	0	-	31	1.40
	Fluazifop-P-butyl	Fluazifop-P	0	-	0	-	1	0.07			6	0.17
		TFMP	0	-	0	-	87	0.29			0	-
	Fluroxypyr	Fluroxypyr	0	-	0	-	0	-	1	0.06	1	0.07
	Glyphosate	AMPA			2	0.02	20	0.08	8	0.07	2	0.03
		Glyphosate			0	-	17	0.04	47	0.67	5	0.03
	Metalaxyl-M	CGA 108906	184	1.50	174	2.70						
		CGA 62826	16	0.04	82	0.68						
		Metalaxyl-M	13	0.08	43	1.30						
	Metamitron	Desamino-metamitron					30	0.19	0	-	48	1.30
		Metamitron					29	0.17	0	-	24	0.63
	Metribuzin	Desamino-diketo-metribuzin	236	0.20	20	1.83						
		Diketo-metribuzin	453	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	-
	Rimsulfuron	PPU (IN70941)	58	0.05	374	0.23						
		PPU-desamino (IN70942)	9	0.03	98	0.09						
	Tebuconazole	Tebuconazole	1	0.01	1	0.01	0	-	5	0.12	1	0.01
	Terbuthylazine	2-hydroxy-desethyl-terbuthylazine	1	0.03			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			4	0.05	27	0.03	60	0.04
		Hydroxy-terbuthylazine	0	-			0	-	0	-	34	0.07
		Terbuthylazine	0	-	0	-	36	0.12	1	0.02	51	1.90
Low	Clomazone	Clomazone	0		0		0		0		0	
		FMC 65317	0		0		0		0		0	
	Diflufenican	Diflufenican			0	-	1	0.47				
	Dimethoate	Dimethoate	0	-	0	-	1	0.09	0	-	0	-
	Epoxiconazole	Epoxiconazole	0	-	1	0.01	0	-	0	-	0	-
	Flamprop-M-isopropyl	Flamprop-M-isopropyl	0	-			1	0.02	0	-	0	-
	Ioxynil	Ioxynil	0	-	0	-			0	-	1	0.01
	MCPA	MCPA			0	-	0	-	1	0.02	0	-
	Mancozeb	ETU	2	0.02								
	Metrafenone	Metrafenone							1	0.04	0	-
	Phenmedipham	MHPC					0	-			1	0.05
		Phenmedipham					0	-			2	0.03
	Propiconazole	Propiconazole	0	-	0	-	0	-	2	0.02	1	0.04
	Prosulfocarb	Prosulfocarb	0	-			1	0.03			0	-
	Pyridate	PHCP			0	-	14	0.31				
	Triflusulfuron-methyl	IN-M7222					1	0.05			0	-

- 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 8.3 and 8.4). At Estrup leaching was mostly confined to the depth of the drainage system and rarely detected in deeper monitoring screens (Appendix 5). On the sandy soils, bentazone leached at Jyndevad, but was only detected once 1 m b.g.s. at Tylstrup. At Jyndevad high concentrations (exceeding 0.1 µg/L) were detected in the soil water samples from suction cups 1 m b.g.s. four months after application. Thereafter, leaching diminished, and bentazone was not subsequently detected in the monitoring wells. Although leached in high average concentrations (>0.1 µg/L) at four sites, bentazone was generally leached within a short period of time. Initial concentrations of bentazone were usually very high, but then decreased rapidly. In general, concentrations exceeding 0.1 µg/L were only found within a period of one to four months following the application. The degradation product 2-amino-N-isopropyl-benzamide was detected twice in the vadose zone at Jyndevad, once in drainage water at Estrup and Faardrup (Table 8.2), and once in water from a horizontal well at Estrup (Table 8.4). Bentazone has up till 15 May 2013 been applied 17 times to the five tests fields. Bentazone has in the period 2001 to 2013 been found in eight groundwater samples in concentration ≥ 0.1 µg/L, while bentazone has been found in lower concentration in 58 groundwater samples. In total bentazone has been analyzed in 3.728 groundwater samples.

- 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 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 degradation product bifenox acid was found in very high concentrations in drain water from Faardrup, in a yearly average concentrations 2.54 µg/L (Table 6.2). In 2011/2012 bifenox acid leached, but in small concentrations, and bifenox was only found in few water samples. Another degradation product from bifenox and nitrofen, was found in drain water from Faardrup, often in low concentrations but 0.16 µg/L was found in one drainwater sample in November 2010. In Silstrup, 0.34 and 0.22 µg/L was found in two drainwater samples from October 2011. 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. Monitoring of bifenox stopped in December 2012.

- 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 8.1). 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 8.1 and 8.2) and groundwater monitoring screens (Table 8.3 and 8.4). 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 1,400 g/ha was used 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 0.1µg/L, neither ethofumesate nor metamitron was found in the analyzed water samples. The monitoring of ethofumesate and metamitrone stopped in June 2011.

- 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 samples exceeding 0.1 µg/L (four drain water samples, three soil water samples from the vadose zone and one groundwater sample), Table 8.2 and 8.4) 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 4.6, Table 8.3 and 8.4). 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 4.6). The average TFMP concentration in drainwater 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, but in 2012 after application in April 2012 TFMP was found in increasing concentrations in drain water, where 0.64 µg/L was measured in June 2012. In Silstrup TFMP was found in groundwater at the end of April, and it is possible that preferential flow caused the quick leaching. At Faardrup fluazifop-P-butyl was applied May 2011 in the new dose, and TFMP was not found in drain or groundwater. Up till now the pesticide has been applied ten times at four test fields.

- Glyphosate and AMPA were 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 seven times (in 2001, 2002, 2003, 2005, 2007, 2011 and 2012) within the monitoring period. All seven 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 5.7D). For the period June 2007 to July 2010 external quality assurance of the analytical methods indicates that the true concentration of glyphosate may have been 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 years after the application (Figure 5.7D). Numbers of detections exceeding 0.1 µg/L in groundwater monitoring wells is, 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). After application in September 2012 glyphosate and its degradation product AMPA have been found in concentrations up to 0,66 µg/L in drainage water from Silstrup, but not in concentrations exceeding 0,1 µg/L in groundwater. Glyphosate and its degradation product AMPA have been found frequently in high concentrations ≥ 0.1 µg/L in drain water from Estrup after application October 2011, and glyphosate was found in few groundwater samples in concentrations ≥ 0.1 µg/L. Monitoring at Faardrup stopped en August 2012.

- 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 8.3). 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). Metribuzine has been removed from the market in Denmark. The monitoring of metribuzine and degradation products stopped in February 2011.

- Metalaxyl-M was applied in June 2010 and found in low concentrations in few samples from the variably-saturated zone at Tylstrup. Two degradation products (CGA 62829 and CGA108906) however, were leached from the root zone (1 m b.g.s.), and CGA108906 in average concentrations exceeding 0.1 µg/L (Table 2.2, Figure 2.6, Table 8.1-8.4). CGA108906 was found in 95% of the analyzed groundwater samples and in 32% of the analyzed samples the concentration exceeded 0.1 µg/L. Similar to the other compounds CGA108906 was detected in samples from the upstream well of M1 and it was present in the groundwater before metalaxyl-M was applied to the test field. 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 2.2). During the second monitoring year CGA108906 was found more frequently and in higher concentrations at Tylstrup and Jyndevad in both the variably-saturated and the saturated zone. Both degradation products were found at Jyndevad in concentrations exceeding 0.1 µg/L and in increasing concentrations. In the third monitoring year the parent and degradation products were found in decreasing concentrations mostly < 0.1 µg/L. As a consequence of the monitoring results, the Danish EPA has withdrawn the approval of metalaxyl-M in August 2013. The monitoring of the parent and the two degradation products continues.

- At Estrup, CL153815 (degradation product of picolinafen) leached through the root zone and into the drainage water in average concentrations exceeding 0.1 µg/L (Appendix 5). CL153815 has not been detected in deeper monitoring screens (Table 8.3). Leaching of CL153815 has not been observed on the sandy soil at Jyndevad after application in October 2007 (Table 8.1, Table 8.3 and Appendix 5). The monitoring stopped in March 2010.

- 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 in average concentrations exceeding 0.1 µg/L through the root zone (1 m b.g.s.) entering the drainage system (Table 8.1) 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 8.1 and Kjær *et al.*, 2004). Both degradation products (pirimicarb-desmethyl and pirimicarb-desmethyl-formamido) have been detected in deeper monitoring screens at Faardrup (Table 8.3 and 8.4). The monitoring stopped in June 2007.

- 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 8.1 and 8.2) in 2005, 2006 and 2007. Propyzamide was also detected in the monitoring screens situated beneath the drainage system at Silstrup and Faardrup. 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 8.3 and 8.4). Propyzamide was applied white clover in January 2013 at Faardrup, and neither propyzamide nor the three degradation products (RH-24644, RH-24655, RH-24580) were found in drain or groundwater. The monitoring is still ongoing.

- 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 8.1 and 8.2). In groundwater PPU was occasionally detected and three samples exceeded 0.1 µg/L at Jyndevad in 2011/12, whereas it was detected in low concentration <0.1 µg/L at Tylstrup (Table 8.3 and 8.3). At both sites, PPU was relatively stable and persisted in the soil water for several years, with relatively little further degradation into PPU-desamino. 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 six samples at Jyndevad, never exceeded 0.1 µg/L. It should be noted that the concentration of PPU is underestimated by up to 22-47%. Results from the field-spiked samples indicate that PPU is unstable and may have degraded to PPU-desamino during analysis (Rosenbom *et al.*, 2010a). As a consequence of the monitoring results, the Danish EPA has withdrawn the approval of rimsulfuron. The monitoring stopped December 2012.

- 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 8.1 and 8.2). 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 8.3 and 8.4), at concentrations exceeding 0.1 µg/L during a two 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 8.4, 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. The monitoring of terbuthylazine stopped June 2009.

- Tebuconazole has been applied in autumn 2007 at Tylstrup, Jyndevad, Estrup and Faardrup. Only on the loamy soil of Estrup it leached 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 8.1 and 8.2). 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 8.3 and 8.4). 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 8.3 and 8.4). The monitoring stopped in December 2012.

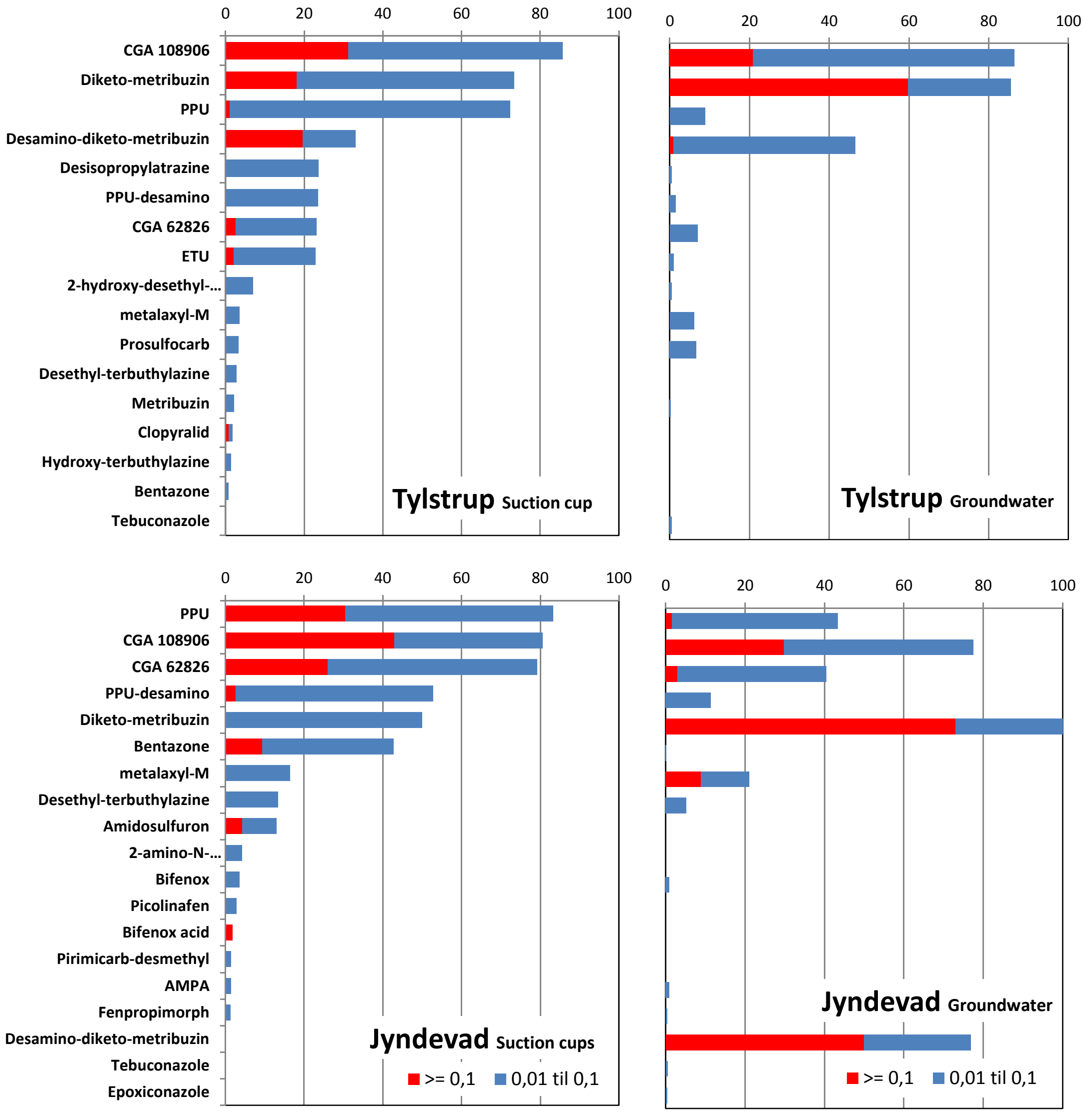

Figure 8.1. Frequency of detection in samples from the suction cups (left) and groundwater monitoring screens located deeper than the suction cups (right) at **the sandy soil sites: Tylstrup** and **Jyndevad.** Frequency is estimated for the entire monitoring period and the length of time that the different pesticides have been included in the programme and the number of analyzed 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 18 pesticides (or their degradation products), but mostly 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 8.1.

Table 8.2 shows 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 18 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.

16 of the 50 pesticides applied – about 32% – did not leach at all from 1 m b.g.s. during the monitoring period (Table 8.1). The group of 16 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.

The leaching patterns of the sandy and loamy sites are further illustrated in Figure 8.1 and 8.2, showing the frequency of detection in samples collected 1 m b.g.s. (suction cups on sandy soils and drainage systems on loamy soils) and the deeper located groundwater monitoring screens.

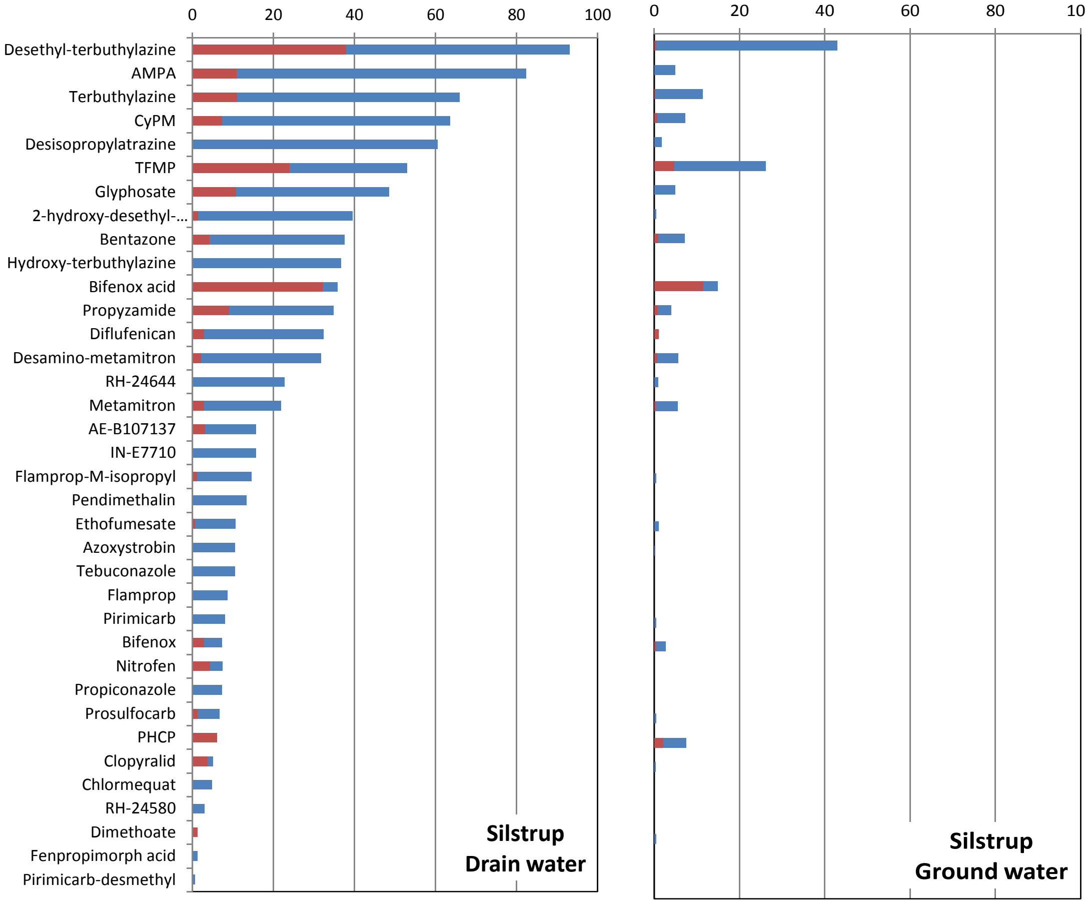

Figure 8.2. Frequency of detection in samples from the drainage system (left) and groundwater monitoring screens located deeper than the drainage system (right) **at the loamy soil sites**: **Estrup**, **Silstrup** and **Faardrup**. Frequency is estimated for the entire monitoring period and the time that the different pesticides have been included in the programme and the number of analyzed 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.

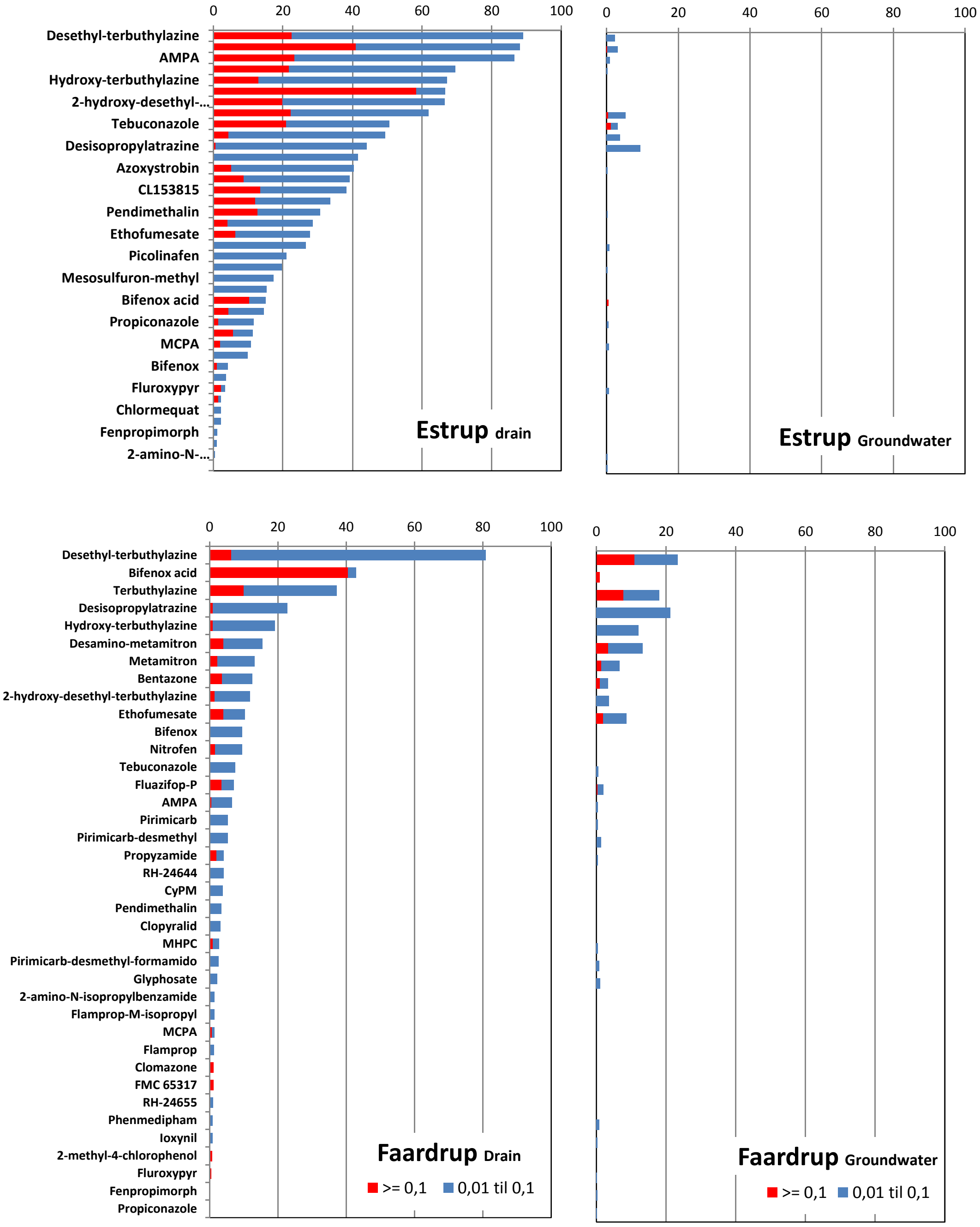

Figure 8.2 (continued). Frequency of detection in samples from the drainage system (left) and groundwater monitoring screens located deeper than the drainage system (right) **at the loamy soil sites**: **Estrup**, **Silstrup** and **Faardrup**. Frequency is estimated for the entire monitoring period and the time that the different pesticides have been included in the programme and the number of analyzsed 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.

On the sandy soils the number of leached pesticides as well as the frequency of detection was lower than on loamy soils (Figure 8.1 and 8.2), the exceptions being the mobile and persistent degradation products of metalaxyl-M, 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 provides good conditions for sorption and degradation. Pesticides being leached in the sandy soils were thus restricted to mobile as well as persistent pesticides. On the loamy soils pronounced macropore transport resulted in the pesticides moving very rapidly through the variably-saturated 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 8.2), and several pesticides were often detected in the drainage system, whereas the frequency of detection in the groundwater monitoring screens situated beneath the drainage system was lower and varied considerably between the three sites (Figure 8.2). These differences should be seen in relation to the different sampling procedures applied. Integrated water samples are sampled from the drainage systems, and the sample system 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 99, 91, 58 and 87 samples containing glyphosate and AMPA, desisopropyl-atrazine, bentazone and TFMP respectively, pesticides have only occasionally been detected in the screens beneath the drainage system (Appendix 5 and Figure 8.2).

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

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Appendixes

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

Appendix 2
Pesticide monitoring programme – Sampling procedure

Appendix 3
Agricultural management

Appendix 4
Precipitation data for the PLAP sites

Appendix 5
Pesticide detections in samples for drains, suction cups and groundwater monitoring wells

Appendix 6
Laboratory internal control cards

Appendix 7
Pesticides analyzed at five PLAP sites in the period up to 2007

Appendix 8
New horizontal wells

Appendix 9
Groundwater age from recharge modelling and tritium-helium analysis

Appendix 1

Chemical abstracts nomenclature for the pesticides encompassed by the PLAP

Table A1.1. Systematic chemical nomenclature for the pesticides and degradation products encompassed by the PLAP. P (parent). M (degradation product).

Parent pesticide	P/M	Analyte	Systematic name
Aclonifen	P	Aclonifen	2-chloro-6-nitro-3-phenoxyaniline
Amidosulfuron	P	Amidosulfuron	N-[[[[(4,6-dimethoxy-2-pyrimidinyl)amino]carbonyl]-amino]sulfonyl]-N-methylmethanesulfonamide
Amidosulfuron	M	Desmethyl-amidosulfuron	3-(4-hydroxy-6-methoxypyrimidin-2-yl)-1-(N-methyl-N-methylsulfonyl-aminosulfonyl)-urea
Aminopyralid	P	Aminopyralid	4-amino-3,6-dichloropyridine-2-carboxylic acid
Azoxystrobin	P	Azoxystrobin	Methyl (E)-2-{2-[(6-(2-cyanophenoxy)-4-pyrimidin-4-yloxy]phenyl}-3-methoxyacrylate
Azoxystrobin	M	CyPM	E-2-(2-[6-cyanophenoxy)-pyrimidin-4-yloxy]-phenyl) – 3-methoxyacrylic acid
Bentazone	M	2-amino-N-isopropylbenzamid	2-amino-N-isopropylbenzamide
Bentazone	P	Bentazone	3-(1-methylethyl)-1H-2,1,3-benzothiadiazin-4(3H)-one 2,2 dioxide
Bifenox	P	Bifenox	methyl 5-(2,4-dichlorophenoxy)-2-nitrobenzoate
Bifenox	M	Bifenox acid	5-(2,4-dichlorophenoxy)-2-nitrobenzoic acid
Bifenox	M	Nitrofen	2,4-dichlorophenyl 4'-nitrophenyl ether
Boscalid	P	Boscalid	2-chloro-N-(4'-chlorobiphenyl-2-yl)nicotinamide
Bromoxynil	P	Bromoxynil	3,5-dibromo-4-hydroxybenzonitrile
Chlormequat	P	Chlormequat	2-chloroethyltrimethylammonium chloride
Clomazon	P	Clomazon	2-[(2-chlorphenyl)methyl]-4,4-dimethyl-3-isoxazolidione
Clomazon	M	FMC65317	(N-[2- chlorophenol)methyl] -3-hydroxy-2,2- dimethyl propanamide (Propanamide-clomazone)
Clopyralid	P	Clopyralid	3,6-Dichloropyridine-2-carboxylic acid
Cyazofamid	P	Cyazofamid	4-chloro-2-cyano-N,N-dimethyl-5-p-tolylimidazole-1-sulfonamide
Desmedipham	P	Desmedipham	Ethyl 3-(phenylcarbamoyloxy)phenylcarbamate
Desmedipham	M	EHPC	Carbamic acid, (3-hydroxyphenyl)-ethyl ester
Diflufenican	M	AE-05422291	2-[3-(trifluoromethyl)phenoxy]pyridine-3-carboxamide
Diflufenican	M	AE-B107137	2-[3-(trifluoromethyl)phenoxy]pyridine-3-carboxylic acid
Diflufenican	P	Diflufenican	2',4'-difluoro-2-(a,a,a-trifluoro-m-tolyloxy)nicotinanilide
Dimethoat	P	Dimethoat	O,O-dimethyl S-methylcarbamoylmethyl-phosphorodithioate
Epoxiconazole	P	Epoxiconazole	(2RS, 3SR)-1-(2-(2-chlorophenyl)-2,3-epoxy-2-(4-fluorophenyl)propyl)-1H-1,2,4-triazol
Ethofumesat	P	Ethofumesat	(±)-2-ethoxy-2,3-dihydro-3,3-dimethylbenzofuran-5-yl-methanesulfonate
Fenpropimorph	P	Fenpropimorph	Cis-4-[3-[4-(1,1-dimethylethyl)-phenyl]-2-methylpropyl]-2,6-imethylmorpholine
Fenpropimorph	M	Fenpropimorph-acid	Cis-4-[3-[4-(2-carboxypropyl)-phenyl]-2-methylpropyl]-2,6-dimethylmorpholine
Flamprop-M-isopropyl	M	Flamprop (free acid)	N-benzoyl-N-(3-chloro-4-flourophenyl)-D-alanine
Flamprop-M-isopropyl	P	Flamprop-M-isopropyl	Isopropyl N-benzoyl-N-(3-chloro-4-flourophenyl)-D-alaninate
Florasulam	P	Florasulam	2',6',8-Trifluoro-5-methoxy-s-triazolo [1,5-c]pyrimidine-2-sulfonanilide
Florasulam	M	Florasulam-desmethyl	N-(2,6-difluorophenyl)-8-fluro-5-hydroxy[1,2,4]triazolo[1,5-c]pyrimidine-2-sulfonamide
Fluazifop-P-buthyl	M	Fluazifop-P (free acid)	(R)-2-(4-((5-(trifluoromethyl)-2-pyridinyl)oxy)phenoxy-propanoic acid
Fluazifop-P-buthyl	P	Fluazifop-P-buthyl	butyl (R)-2-{4-[5-(trifluoromethyl)-2-pyridyloxy]phenoxy}propionate
Fluazifop-P-buthyl	M	TFMP	5-trifluoromethyl-pyridin-2-ol
Fluroxypyr	P	Fluroxypyr	(4-amino-3,5-dichloro-6-fluro-2-pyridinyl)oxy]acetic acid
Glyphosate	M	AMPA	Amino-methylphosphonic acid
Glyphosate	P	Glyphosate	N-(phosphonomethyl)glycine
Iodosulfuron-methyl-natrium	P	Iodosulfuron-methyl-natrium	sodium salt of methyl 4-iodo-2-[[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl]amino]sulfonyl]benzoate
Iodosulfuron-methyl-natrium	P	Metsulfuron methyl	methyl 2-(4-methoxy-6-methyl-1,3,5-triazin-2-ylcarbamoylsulfamoyl)benzoate
Ioxynil	P	Ioxynil	4-hydroxy-3,5-diiodobenzonitrile
Linuron	P	Linuron	3-(3,4-dichlorophenyl)-1-methoxy-1-methylurea
Mancozeb	M	ETU	Ethylenethiourea
MCPA	M	4-chlor-2-methylphenol	2-methyl-4-chlorophenol
MCPA	P	MCPA	(4-chloro-2-methylphenoxy)acetic acid
Mesosulfuron-methyl	M	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. P (parent). M (degradation product).

Parent pesticide	P/M	Analyte	Systematic name
Mesosulfuron-methyl	P	Mesosulfuron-methyl	Methyl 2-[3-(4,6-dimethoxypyrimidin-2-yl)ureidosulfonyl]-4-methanesulfonamidomethylbenzoate
Mesotrione	M	AMBA	2-amino-4-methylsulfonylbenzoic acid
Mesotrione	P	Mesotrione	2-(4-mesyl-2-nitrobenzoyl)cyclohexane-1,3-dione
Mesotrione	M	MNBA	methylsulfonyl-2-nitrobenzoic acid
Metalaxyl-M	M	CGA 108906	2-[(1-carboxyethyl)(methoxyacetyl)amino]-3-methylbenzoic acid
Metalaxyl-M	M	CGA 62826	2-[(2,6-dimethylphenyl)(methoxyacetyl)amino]propanoic acid
Metalaxyl-M	P	Metalaxyl-M	methyl N-(methoxyacetyl)-N-(2,6-xylyl)-D-alaninate
Metamitron	P	Metamitron	4-amino-4,5-dihydro-3-methyl-6-phenyl-1,2,4-triazin-5-one
Metamitron	M	Metamitron-desamino	4,5-dihydro-3-methyl-6-phenyl-1,2,4-triazine-5-one
Metrafenone	P	Metrafenone	3'-bromo-2,3,4,6'-tetramethoxy-2',6-dimethylbenzophenone
Metribuzin	P	Metribuzin	4-amino-6-tert-butyl-4,5-dihydro-3-methylthio-1,2,4-triazine-5-one
Metribuzin	M	Metribuzin-desamino	6-(1,1-dimethylethyl)-3-(methylthio)- 1,2,4-triazin-5-(4H)-one
Metribuzin	M	Metribuzin-desamino-diketo	6-tert-butyl-4,5-dihydro-3-methylthio-1,2,4-triazine-3,5-dione
Metribuzin	M	Metribuzin-diketo	4-amino-6-tert-butyl-4,5-dihydro-1,2,4-triazine-3,5-dione
Pendimethalin	P	Pendimethalin	N-(1-ethyl)-2,6-dinitro-3,4-xynile
Phenmedipham	M	3-aminophenol	1-amino-3-hydroxybenzene
Phenmedipham	M	MHPC	Methyl-N-(3-hydoxyphenyl)-carbamate
Phenmedipham	P	Phenmedipham	3-[(methoxycarbonyl)amino]phenyl (3-methylphenyl)carbamate
Picolinafen	M	CL153815	6-(3-trifluoromethylphenoxy)-2-pyridine carboxylic acid
Picolinafen	P	Picolinafen	4'-fluoro-6-(a,a,a-trifluoro-m-tolyloxy)pyridine-2-carboxanilide
Pirimicarb	P	Pirimicarb	2-(dimethylamino)-5,6-dimethyl-4-pyrimidinyldimethylcarbamate
Pirimicarb	M	Pirimicarb-desmethyl	2-(dimethylamino)-5,6-dimethyl-4-pyrimidinylmethylcarbamate
Pirimicarb	M	Pirimicarb-desmethyl-formamido	2-methylformamido-5,6-dimethylpyrimidine-4-yl dimethylcarbamate
Propiconazol	P	Propiconazol	1-[[2-(2,4-dichlorophenyl)-4-propyl-1,3-dioxolan-2-yl]methyl]-1H-1,2,4-triazole
Propyzamid	P	Propyzamid	3,5-dichloro-N-(1,1-dimethylprop-2-ynyl)benzamide
Propyzamid	M	RH24580	N-(1,1-dimethylacetonyl)-3,5-dichlorobenzamide
Propyzamid	M	RH24644	2-(3,5-dichlorophenyl)-4,4-dimethyl-5-methylene-oxalzoline
Propyzamid	M	RH24655	3,5-dichloro-N-(1,1-dimethylpropenyl)benzamide
Prosulfocarb	P	Prosulfocarb	N-[[3-(4-methoxy-6-methyl-1,3,5-triazin-2-yl)-3-[2-(3,3,3,-trifluro=propyl)phenylsulfonyl]urea
Pyridat	M	PHCP	3-phenyl-4-hydroxy-6-chloropyridazine
Pyridat	P	Pyridat	O-6-chloro-3-phenylpyridazin-4-yl S-octyl thiocarbonate
Rimsulfuron	M	IN70941 (PPU)	N-(4,6-dimethoxy-2-pyrimidinyl-N-((3-ethylsulfonyl)-2-pyridinyl)urea (IN70941)
Rimsulfuron	M	IN70942 (PPU-desamino)	N-((3-(ethylsulfonyl)-2-pyridyl)-4,6 dimethoxy-2 pyrimidinamine (IN70942)
Rimsulfuron	P	Rimsulfuron	N-[[(4,6-dimethoxy-2-pyrimidinyl)amino]carbonyl]-3-(ethylsulfonyl)-2-pyridinesulfonamide
Tebuconazole	P	Tebuconazole	a-[2-(4-chlorophenyl)ethyl]-a-(1,1-dimethylethyl)-1H-1,2,4-triazole-1-ethanol
Terbuthylazin	M	2-hydroxy-desethyl-terbuthylazine	6-hydroxy-N-(1,1-dimethylethyl)-1,3,5,triazine-2,4-diamine
Terbuthylazin	M	2-hydroxy-terbuthylazin	6-hydroxy-N-(1,1-dimethylethyl)-N´-ethyl-1,3,5,triazine-2,4-diamine
Terbuthylazin	M	Desethylterbuthylazin	6-chloro-N-(1,1-dimethylethyl)-1,3,5,triazine-2,4-diamine
Terbuthylazin	M	Desisopropylatrazin	6-chloro-N-ethyl-1,3,5-triazine-2,4-diamine
Terbuthylazin	P	Terbuthylazin	6-chloro-N-(1,1-dimethylethyl)-N-ethyl-1,3,5,triazine-2,4-diamine
Thiacloprid	M	Thiacloprid-amide	(3-[(6-chloro-3-pyridinyl)methyl]-2-thiazolidinylidene) urea
Thiacloprid	M	Thiacloprid sulfonic acid	sodium 2-[[[(aminocarbonyl)amino]-carbonyl][(6-chloro-3-pyridinyl)-methyl]amino]ethanesulfonate
Thiacloprid	M	M34	2-{carbamoyl[(6-chloropyridin-3-yl)methyl]amino}etanesulfonic acid
Thiacloprid	P	Thiacloprid	(Z)-3-(6-chloro-3-pyridylmethyl)-1,3-thiazolidin-2-ylidenecyanamide
Thiamethoxam	M	CGA 322704	[C(E)]-N-[(2-chloro-5-thiazolyl)methyl]-N'-methyl-N'-nitroguanidine
Thiamethoxam	P	Thiamethoxam	3-(2-cholro-thiazol-5-ylmethyl)-5-methyl[1,3,5]oxadiazinan-4ylidene-N-nitroamine
Triasulfuron	P	Triasulfuron	1-[2-(2-chloroethoxy)phenylsulfonyl]-2-(4-methoxy-6-methyl-1,3,5-triazine-2-yl)-urea
Triasulfuron	M	Triazinamin	2-amino-4-methoxy-6-methyl-1,3,5-triazine
Tribenuron-methyl	M	Triazinamin-methyl	4-methoxy-6-methyl-1,3,5-triazin-methylamine
Tribenuron-methyl	P	Tribenuron-methyl	methyl 2-[4-methoxy-6-methyl-1,3,5-triazin-2-yl(methyl)carbamoylsulfamoyl]benzoate
Triflusulfuron-methyl	M	IN-D8526	N,N-dimethyl-6-(2,2,2-trifluoroethoxy)-1,3,5-triazine-2,4-diamine
Triflusulfuron-methyl	M	IN-E7710	N-methyl-6-(2,2,2-trifluoroethoxy)-1,3,5-triazine-2,4-diamine
Triflusulfuron-methyl	M	IN-M7222	6-(2,2,2-trifluoroethoxy)-1,3,5-triazine-2,4-diamine
Triflusulfuron-methyl	P	Triflusulfuron-methyl	methyl 2-[4-dimethylamino-6-(2,2,2-trifluoroethoxy)-1,3,5-triazin-2-ylcarbamoylsulfamoyl]-m-toluate

Appendix 2

Pesticide monitoring programme – Sampling procedure

From each of the PLAP sites, samples were collected of groundwater, drainage water and soil water in the variably-saturated 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 analyzes 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).

Table A2.1. Pesticide monitoring programme in suction cups (S), horizontal monitoring wells (H) and vertical monitoring wells (M) 2012-13. 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, H1 ^{m}	M1, M3, M4, M5, S1a, S2a, S1b*, S2b*	M2, **M6**, M7
Jyndevad	M1, M4, S1a, S2a, H1 ^{m}	M2, M5, M7	M3, **M6**, S1b, S2b
Silstrup	M5, H1.2, H2 ^{m}	M9, M10. M12, H1.1, H1.3	M1, M2, M4, **M6**, M8, M7, M11, **M13**, **H2.1, H2.2, H2.3**
Estrup	M4, H1.2, H2 ^{m}	M1, M5, M6, H1.1 H1.3	M2, **M3, M7**
Faardrup	M4, M5, H2.3, H2 ^{m}	M6, H2.1, 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. ^{m}*- Mixed water samples from three screens.*

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

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).

From 2012 five new horizontal monitoring wells at the five PLAP sites were sampeled monthly. Each horizontal well contain three screens and water sampels form the screens are mixed to one sample.

Until July 2004, pesticide analyzes 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 analyzed for pesticides. In June 2004 the drainage monitoring programme was revised. From July 2004 and onwards pesticide analyzes 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). ND are included as 0 µg/L calculating average concentrations.

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 2.2, 3.2, 4.2, 5.2 and 6.2 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 2.2 and 3.2 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 2.2 and 3.2 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.

Appendix 3

Agricultural management

Table A3.1. Management practice at **Tylstrup** during the 2009 to 2013 growing seasons. The active ingredients of the various pesticides are indicated in parentheses.

Date	Management practice
08-07-2009	Irrigation 27 mm. Started 08/07 23.00 Ended 09/07 07.00
08-07-2009	Mavrik 2F (tau-fluvalinate) - pests - 0.1 l/ha (not analyzed)
20-08-2009	Harvest of spring barley. Stubleheight 16 cm, grainyield 53.4 hkg/ha 85% DM
28-08-2009	Straw removed, yield 17.4 hkg/ha 100% DM
04-04-2010	Ploughed - depth 24 cm
26-04-2010	Rolled with concrete roller
04-05-2010	Seed bed preparation, 10.0 cm depth (across)
06-05-2010	Planting of potatoes. cv. Kuras rowdistance 75 cm, plantdistance 25 cm, depth 17 cm, final plantnumber 4,0/m^2
17-05-2010	Ridging
26-05-2010	Fenix (aclonifen) - weeds - 1.0 l/ha + Titus WSB (rimsulfuron) - weeds - 10 g/ha
08-06-2010	Titus WSB (rimsulfuron) - weeds - 20 g/ha
15-06-2010	Ranman (cyazofamid) - fungi - 0.2 l/ha
24-06-2010	Ranman (cyazofamid) - fungi - 0.2 l/ha
01-07-2010	Ranman (cyazofamid) - fungi - 0.2 l/ha
06-07-2010	Irrigation 29 mm. Started 06/07 22:00 Ended 07/07 07:00
09-07-2010	Ridomil Gold MZ Pepite (mancozeb - metalaxyl) - fungi - 2.0 kg/ha
16-07-2010	Ranman (cyazofamid) - fungi - 0.2 l/ha
23-07-2010	Ranman (cyazofamid) - fungi - 0.2 l/ha
27-07-2010	Irrigation 28 mm. Started 27/07 22:00 Ended 28/07 07:00
02-08-2010	Ranman (cyazofamid) - fungi - 0.2 l/ha
09-08-2010	Dithane NT (mancozeb) - fungi - 2.0 kg/ha
17-08-2010	Dithane NT (mancozeb) - fungi - 2.0 kg/ha
23-08-2010	Dithane NT (mancozeb) - fungi - 2.0 kg/ha
20-10-2010	Harvest of potatoes. Tuber yield 128,02 hkg/ha - 100% DM
17-04-2011	Ploughed - depth 24 cm.
18-04-2011	Rolled with concrete roller
19-04-2011	Spring barley sown, cv.TamTam, seeding rate 180 kg/ha, sowing depth 3.3 cm, row distance 12.5 cm. Final plantnumber 365/m^2
19-04-2011	Seed bed preparation, 8 cm depth
10-05-2011	Oxitril CM (ioxynil + bromoxynil) - weeds - 0.4 l/ha (not analyzed)
16-08-2011	Harvest of spring barley. Stubble height 14 cm, grain yield 75.7 hkg/ha - 85% DM
18-08-2011	Straw removed, yield 34.6 hkg/ha - 100% DM
22-03-2012	Ploughed - depth 24 cm.
22-03-2012	Spring barley
24-03-2012	Spring barley sown, cv. TamTam, seeding rate 185 kg/ha, sowing depth 2.75 cm, row distance 12.5 cm. Using combine driller with a tubular packer roller, Final plant number 344 /m2 Sown with rotor harrow combine sowing machine
29-04-2012	Fertilisation - 123.9 N, 17.7 P, 59 K, kg/ha
21-05-2012	Fox 480 SC (bifenox) - weeds - 1.2 l/ha
25-05-2012	Mustang forte (aminopyralid/florasulam/2,4-D) - weeds - 0.75 l/ha
31-05-2012	Irrigation 24 mm. Started 31/5 ended 31/5
28-06-2012	Bell (boscalid + epoxiconazol) - fungi - 1.5 l/ha (epoxiconazol not analyzed)
13-08-2012	Glyfonova 450 Plus (glyphosate) - weeds - 2.4 l/ha (not analyzed)
27-08-2012	Harvest of spring barley. Tubbleheight 15 cm, grain yield 62.0 hkg/ha - 85% DM. Straw removed, yield 37.3 hkg/ha - 100% DM
31-08-2012	Tracer (potasium bromide), 30 kg/ha
20-09-2012	Ploughed - depth 22 cm
23-09-2012	Winter rye sown, cv. Magnifico, seeding rate 64.0 kg/ha, sowing depth 3.5 cm, row distance 13.0 cm. Finalplant number 125/m2 Sown with rotorharrow combine sowing machine
12-10-2012	Boxer (prosulfocarb) - weeds - 4.0 l/ha
04-04-2013	Fertilisation - 56.7 N, 8.1 P, 27 K, kg/ha
02-05-2013	Fertilisation - 71.4 N, 10.2 P, 34 K, kg/ha
08-05-2013	Starane XL (fluroxypyr) - weeds - 1.2 l/ha

Date	Management practice
20-08-2013	Harvest of winter rye. Stubleheight 15 cm, grainyield 77.4 hkg/ha - 85% DM, Straw remowed, yield 33.8 hkg/ha - 100% DM

Table A3.2. Management practice at **Jyndevad** during the 2009 to 2013 growing seasons. The active ingredients of the various pesticides are indicated in parentheses.

Date	Management practice
07-08-2009	Harvest of spring barley. Seed yield 63.96 hkg/ha 85% DM, strawyield 19.5 hkg/ha 100% DM, stubbleheight 15 cm
14-04-2010	Ploughed. Depth 24 cm
15-04-2010	Rolled with concrete roller
22-04-2010	Seed bed preparation. 9.0 cm depth
04-05-2010	Planting of potatoes. cv. Kuras rowdistance 75 cm, plantdistance 33 cm, depth 8 cm, final plantnumber $4,0/m^2$
04-05-2010	Ridging
27-05-2010	Fenix (aclonifen) - weeds - 1.0 l/ha + Titus WSB (rimsulfuron) - weeds - 10 g/ha
08-06-2010	Titus WSB (rimsulfuron) - weeds - 20 g/ha
24-06-2010	Irrigation - 25 mm/ha started on 24/6 ended on 25/6
28-06-2010	Ranman (cyazofamid) - fungi - 0.2 l/ha
30-06-2010	Irrigation - 25 mm/ha started on 30/6 ended on 1/7
06-07-2010	Amistar (azoxystrobin) - fungi - 0.5 l/ha
07-07-2010	Ranman (cyazofamid) - fungi - 0.2 l/ha
08-07-2010	Irrigation - 30 mm/ha started on 8/7 ended on 9/7
14-07-2010	Ranman (cyazofamid) - fungi - 0.2 l/ha
16-07-2010	Karate 2,5 WG (Lambda-cyhalothrin) - 0.3 kg/ha (not analyzed)
25-07-2010	Ridomil Gold MZ Pepite (mancozeb - metalaxyl-M) - fungi - 2.0 kg/ha
01-08-2010	Ranman (cyazofamid) - fungi - 0.2 l/ha
09-08-2010	Ranman (cyazofamid) - fungi - 0.2 l/ha
16-08-2010	Ranman (cyazofamid) - fungi - 0.2 l/ha
23-08-2010	Tyfon (propamocarb+fenamidone) - fungi - 2 l/ha (not analyzed)
31-08-2010	Dithane NT (mancozeb) - fungi - 2.0 kg/ha (not analyzed)
10-09-2010	Dithane NT (mancozeb) - fungi - 2.0 kg/ha (not analyzed)
23-09-2010	Shirlan (fluazinam) - fungi - 0.4 l/ha (not analyzed)
19-10-2010	Harvest of potatoes Yield in tubers 120.6 hkg/ha, 100% DM
22-03-2011	Ploughed. Depth 24 cm
23-03-2011	Sowing spring barley cv. Quench, depth 4.0 cm, rowdistance 12 cm, seed rate 164 kg/ha, final plantnumber 301 m^2 - using a combine drill
24-03-2011	Rolled with concrete roller
26-04-2011	Oxitril CM (bromoxynil + ioxynil) - 0.5 l/ha (not analyzed) + DFF (diflufenican) - 0.25 l/ha- weeds
02-05-2011	Irrigation - 30 mm/ha started on 02/05 ended on 03/05
23-05-2011	Irrigation - 32 mm/ha started on 23/05 ended on 24/05
04-07-2011	Irrigation - 30 mm/ha started on 4/7 ended on 5/7
23-08-2011	Harvest of spring barley. Seed yield 72.4 hkg/ha 85% DM, stubble height 15 cm
25-08-2011	Remowal of straw, straw yield 30.2 hkg/ha 100% DM,
30-03-2012	Ploughed. Depth 22 cm
30-03-2012	Maize
02-04-2012	Rolled with a concrete roller
30-04-2012	Fertilization 140 N, 17.7 P, 65.3 K, kg/ha
30-04-2012	Fertilization 120 K, kg/ha
03-05-2012	Fertilization 29.4 N, 14.7 P, kg/ha
03-05-2012	Sowing maize - cv. Atrium - seed distance 12 cm, row distance 75 cm, depth 6 cm - Seed rate 111.000 seeds/ha, final plant number $12.8/m^2$
07-05-2012	Tracer (potasium bromide), 30,54 kg/ha
26-05-2012	Fighter 480 (bentazone) - weeds - 1.0 l/ha
05-06-2012	Callisto (mesotrion) - weeds - 1.5 l/ha
15-06-2012	Catch (florasulam + 2,4 D) - 0.06 l/ha - weeds - (not analyzed)
15-06-2012	Tomahawk 180 EC (fluroxypyr) - 1.5 l/ha weeds - (not analyzed)
08-10-2012	Harvest of maize.Whole crop yield 151.41 hkg/ha 100% DM. Stubble height 25 cm
06-04-2013	Ploughing - 22 cm depth
06-04-2013	Pea
12-04-2013	Rolled with concrete roller
14-04-2013	Sowing pea cultivare Alvestra, depth 5 cm, rowdistance 12 cm, seed rate 235 kg/ha,using a combine drill, final plant number $92/m^2$
07-05-2013	Fighter 480 (bentazon) + Stomp (pendimethalin) 0.4 l/ha + 0.6 l/ha - weeds (pendimethalin not analyzed)
16-05-2013	Bentazon 480 (bentazon) + Stomp (pendimethalin) 0.5 l/ha + 0.6 l/ha - weeds (pendimethalin not analyzed)
17-05-2013	Fertilization 16.0 P, 83.2 K, kg/ha
06-06-2013	Irrigation - 30 mm/ha started on eastside 06/06 ended on westside 07/06
09-07-2013	Irrigation - 30 mm/ha started on eastside 09/07 ended on westside10/07
16-07-2013	Pirimor G (pirimicarb) - pests - 0.25 kg/ha (not analyzed)

Date	Management practice
07-08-2013	Harvest of pea - western half of the field - interrupted by rain. Seed yield 38.8 hkg/ha 86% DM.Strawyield 30.1 hkg/ha 100% DM, stubble height 10 cm. Straw shreddet at harvest
14-08-2013	Harvest of the eastern half of the field - straw shreddet at harvest
20-08-2013	Stuble cultivation - 8,0 cm depth
22-08-2013	Rotor harrowed - 7 cm depth

Table A3.3. Management practice at **Silstrup** during the 2009 to 2013 growing seasons. The active ingredients of the various pesticides are indicated in parentheses.

Date	Management practice
30-03-2009	Harrowed 2 times across - depth 5 cm
02-04-2009	Tracer (potasium bromide). 31.5 kg/ha
11-04-2009	Sowing spring barley cv. Keops depth 3.5 cm, row distance 15 cm, seeding rate 120 kg/ha, final plantnumber 263/m^2. Undersown red fescue cv. Jasperina, broadcast, seeding rate 8.8 kg/ha
11-04-2009	Rolled with Cambridge roller
19-05-2009	Fighter 480 (bentazone) - weeds - 1.25 l/ha
24-06-2009	Amistar (azoxystrobin) - fungi - 1.0 l/ha
16-07-2009	Whole crop harvest, 94.6 hkg/ha 100% DM stubble height 15 cm
24-08-2009	Hussar OD (iodosulfuron-methyl) - weeds - 0.020 l/ha
09-09-2009	Fox 480 SC (bifenox) - weeds - 1.5 l/ha
02-05-2010	Fusilade Max (fluazifop-P-butyl) - weeds - 1.5 l/ha
05-05-2010	Hussar OD (iodosulfuron) + SweDane MCPA 750 - weeds - 0.1 l/ha + 0.7 l/ha
20-07-2010	Harvest of grass seed. Yield 16.5 hkg/ha 87% DM, stubble height 12 cm,
21-07-2010	Straw burned, 69.3 hkg/ha 100% DM
21-07-2010	Harvest of grass seed. Yield 15.2 hkg/ha 87% DM, stubble height 5 cm.
15-04-2011	Hussar OD (iodosulfuron) - weeds - 0.05 l/ha (not analyzed)
26-04-2011	Fusilade Max (fluazifop-P-butyl) - weeds - 1.5 l/ha
21-07-2011	Harvest of grass seed. Yield 15.2 hkg/ha 87% DM.
30-07-2011	Straw removed - straw yield 45.8 hkg/ha 100% DM, stubble height 12 cm
31-07-2011	Red fescue
16-09-2011	Fox 480 SC (bifenox) - weeds - 1.5 l/ha
05-10-2011	Pig slurry application -surface applied - 29.0 t/ha - 122,1 Total-N, 72.8 NH4-N,30.2 P, 52.2 K, 14,9 Mg, kg/ha, 908 g/ha CU, (VAP nr 36552)
15-03-2012	Fertilization 60 N, 32 S kg/ha
13-04-2012	DFF (diflufenican) - weeds - 0.15 l/ha
19-04-2012	Fusilade Max (fluazifop-P-butyl) - weeds - 1.5 l/ha
18-05-2012	Folicur (tebuconazol) - fungi - 1.0 l/ha
25-07-2012	Straw removed - straw yield 48.3 hkg/ha 100% DM, stubble height 12 cm
25-07-2012	Harvest of grass seed. Yield 14.16 hkg/ha 87% DM.
10-09-2012	Tracer (potasium bromide) 30.0 kg/ha
10-09-2012	Glyfonova 450 Plus (glyphosate) - weeds (killing the red fescue) - 4.8 l/ha
10-09-2012	Winter wheat
08-10-2012	Ploughed - depth 24 cm -packed
09-10-2012	Sowing winter wheat cv. Hereford. Depth 2.4 cm, seeding rate 200 kg/ha, row distance 15.0 cm using a Horch Pronto 6 DC
09-11-2012	DFF (diflufenican) + Oxitril CM (ioxynil+bromoxynil - not analyzed) - weeds - 0.12 g/ha + 0.2 l/ha
22-02-2013	Fertilization 52.5 N, 7.5 P, 25.0 K kg/ha
03-05-2013	Sowing spring barlye cv. Quenc, replacing winter wheat injured by frost. Depth 3.8 cm, seeding rate 175 kg/ha, row distance 15 cm, Horch Pronto 6 DC, final plant number 303 m^2
03-05-2013	Spring barley
04-05-2013	Fertilization 67.2 N, 9.6 P, 32.0 K kg/ha
30-05-2013	Duotril 400 EC (ioxynil+bromoxynil - not analyzed) - weeds - 0.6 l/ha
25-06-2013	Amistar (azoxystrobin) - fungi - 1.0 l/ha
01-07-2013	Folicur 250 EC (tebuconazol) - fungi - 1.0 l/ha
20-08-2013	Glyfonova 450 Plus (glyphosate) - weeds (killing the grass) - 2.4 l/ha
06-09-2013	Harvest of spring barley. Grain yield 59.8 hkg/ha 85% DM, straw yield 46.0 hkg/ha 100% DM, stubbleheight 14 cm. Straw shredded at harvest.
20-09-2013	Liming 3.2 t/ha
24-09-2013	Ploughed - depth 24 cm - packed

Table A3.4. Management practice at **Estrup** during the 2009 to 2013 growing seasons. The active ingredients of the various pesticides are indicated in parentheses.

Date	Management practice
12-03-2009	Ploughed - depth 18 cm - packed with a ring roller
02-04-2009	Seed bed preparation depth 5 cm
06-04-2009	Tracer (potasium bromide) 30 kg/ha
08-04-2009	Spring barley sown, cv. Keops, seeding rate 182 kg/ha, sowing depth 4.0 cm, row distance 12 cm. Final plantnumber 350/m^2
08-04-2009	Rolled with a cam roller
01-05-2009	Fox 480 SC (bifenox) - weeds - 1.2 l/ha
14-05-2009	Basagran M75 (bentazone+MCPA) - weeds - 1.5 l/ha
04-06-2009	Amistar (azoxystrobin) - fungi - 1.0 l/ha
07-08-2009	Harvest of spring barley. Stuble height 12 cm, grainyield 71.4 hkg/ha 85% DM,
07-08-2009	Straw shredded. Amount 39.9 hkg/ha 100% DM
24-08-2009	Sowing winter rape. Cv. Cabernet, sowing depth 3.0 cm, seeding rate 4 kg/ha, row distance 12.5 cm final plantnumber 86/m^2
24-08-2009	Ploughed - depth 20 cm - packed with a ring roller
24-08-2009	Rotor harrowed - depth 4 cm
25-08-2009	Command CS (Clomazone) - weeds - 0.33 l/ha
30-09-2009	Fox 480 SC (bifenox) - weeds - 0.75 l/ha
09-10-2009	Cyperb (cypermethrin) - pests - 0.15 l/ha
20-04-2010	Due to outwintering field partially sown withspring rape. Cv. Pluto, sowing depth 3.0 cm and 0.5 cm, seeding rate 5,0 kg/ha, row distance 12.0 cm
10-05-2010	Biscaya OD 240 (thiacloprid) - pests- 0.3 l/ha
20-08-2010	Harwest of winter rape. Seed yield 38.3 hkg/ha 91% DM. Straw shredded 41.8 hkg/ha 100% DM. Stubble height 30 cm
23-08-2010	Spring rape shredded 11.64 hkg/ha 100% DM. Stubble height 8 cm
06-09-2010	Rotor harrowed - depth 5 cm
14-09-2010	Winter wheat sown cv. Frument. depth 4.0 cm rowdistance 12 cm seeding rate 210 kg/ha, final plantnumber 370/m^2
14-09-2010	Ploughed - depth 20 cm - packed with a ring roller
14-09-2010	Seedbed preparation - depth 5 cm
30-09-2010	Express ST (tribenuron-methyl) - weeds - 1 tablet/ha
26-04-2011	Fox 480 SC (bifenox) - weeds - 1.2 L/ha
09-05-2011	Flexity (metrafenon) - fungi - 0.5 L/ha
07-06-2011	Flexity (metrafenon) - fungi - 0.5 L/ha
22-08-2011	Straw shredded at harvest - 53.8 hkg/ha 100% DM
22-08-2011	Harvest of winter wheat. Stubble height 12 cm, grain yield 66.3 hkg/ha 85% DM
03-10-2011	Roundup Max (glyphosate) - weeds - 2.0 kg/ha
03-10-2011	spring barley
22-03-2012	Fertilization 117 N, 15 P, 55 K, kg/ha
29-03-2012	Rotor harrowed - depth 4 cm
30-03-2012	Spring barley sown, cv. Keops, seeding rate 159 kg/ha, sowing depth 4.3 cm, row distance 12 cm. Final plant number 330/m^2
03-04-2012	Rolled with a Cambridge roller
15-05-2012	Fox 480 SC (bifenox) - weeds - 1.2 l/ha
18-05-2012	Mustang forte (aminopyralid/florasulam/2,4-D) - weeds - 0.75 l/ha
21-05-2012	Fertilization manganes nitrate (23,5%) - 2.0 l/ha
29-05-2012	Fertilization manganes nitrate (23,5%) - 2.0 l/ha
13-06-2012	Amistar (azoxystrobin) - fungi - 1.0 l/ha
13-08-2012	Harvest of spring barley. stubble height 12 cm, grain yield 62,9 hkg/ha 85% DM.
13-08-2012	Straw shredded at harvest - 41.0 hkg/ha 100% DM
26-09-2012	Tracer (potasium bromide) - 30 kg/ha
09-11-2012	Ploughed - depth 20 cm - packed with a Dalbo ring roller
08-03-2013	Ploughed - depth 20 cm - packed with a Dalbo ring roller
08-03-2013	Peas
05-04-2013	Fertilization 16 P, 84 K, kg/ha
23-04-2013	Rolled with a Cambridge roller
23-04-2013	Sowing peas - cultivare Alvesta - depth 5 cm rowdistance 12 cm seeding rate 230 kg/ha. Final plantnumber 82/m^2
23-04-2013	Seedbed preparation - depth 5 cm
25-04-2013	Command CS (Clomazone) - weeds - 0.25 l/ha
16-05-2013	Cyperb (cypermethrin) - pests - 0.3 l/ha (not analyzed)
16-05-2013	Fighter 480 (bentazone) - weeds - 1.0 l/ha
13-07-2013	Pirimor G (pirimicarb) - pests - 0.25 kg/ha
21-08-2013	Glyphonova 450 Plus (glyphosate) - weeds - 2.4 l/ha
06-09-2013	Straw shedded at harvest - 24.38 hkg/ha 100% DM

Table A3.5. Management practice at **Faardrup** during the 2009 to 2013 growing seasons. The active ingredients of the various pesticides are indicated in parentheses.

Date	Management practice
05-04-2009	Sowing sugar beet cv. Palace. depth 3.0 cm row distance 50.0 cm plant distance 20 cm seeding rate 100000 seeds/ha. Final plantnumber 8.5/m^2
05-04-2009	Seed bed preparation - depth 6 cm
24-04-2009	1.5 l/ha Betanal (phenmedipham) + 1.0 l/ha Goliath (metamitron) - weeds
30-04-2009	10 g/ha Safari (triflusulfuron-methyl) + 1.5 l/ha Betanal (phenmedipham) + 1.0 l/ha Goliath (metamitron) + 0.07 l/ha Ethosan (ethofumesate) - weeds
11-05-2009	10 g/ha Safari (triflusulfuron-methyl) + 1.5 l/ha Betanal (phenmedipham) + 1.0 l/ha Goliath (metamitron) + 0.07 l/ha Ethosan (ethofumesate) - weeds
14-05-2009	Focus Ultra (cycloxydim) - weeds -1.0 l/ha
17-06-2009	Focus Ultra (cycloxydim) - weeds -1.0 l/ha
06-10-2009	Harvest of sugar beet. 147.9 hkg/ha 100% root dry matter and 40.1 hkg/ha 100% top dry matter
01-11-2009	Ploughing - depth 20 cm
07-04-2010	Seed bed preparation - depth 6 cm
22-04-2010	Sowing spring barley using a mixture of varieties. Depth 4.5 cm, row distance 12 cm seeding rate 150 kg/ha. Undersown red fescue cv. Maximum, seeding rate 7,0 kg/ha. Depth 2.0 cm row distance 13 cm
01-06-2010	Fighter 480 (bentazone) - weeds - 1.25 l/ha
02-07-2010	Amistar (azoxystrobin) - fungi - 1.0 l/ha (not analyzed)
21-08-2010	Harvest of spring barley. Grain yield 58.5 hkg 85% DM.
21-08-2010	Straw removed. Straw yield 27.5 hkg/ha 100% DM. Stubbleheight 10 cm
25-10-2010	Fox 480 SC (bifenox) - weeds - 1.5 l/ha
21-05-2011	Fusilade Max (fluazifop-P-butyl) - weeds - 1.5 l/ha
05-07-2011	Windrowing. Stubble hight 5 cm
20-07-2011	Threshing of grass seed. Yield 7.2 hkg/ha 87% DM, stubble height 5 cm.
20-07-2011	Straw removed. Straw yield 21.1 hkg/ha
03-10-2011	Spring barley and white clover
03-10-2011	Glyphogan (glyphosate) - weeds - 5.0 l/ha
08-11-2011	Ploughing - depth 20 cm
26-03-2012	Fertilization 112 N, 9 P, 30 K, kg/ha
04-04-2012	Seed bed preparation - depth 7 cm
04-04-2012	Sowing spring barley using a mixture of varieties. Depth 3-4 cm, row distance 13 cm seeding rate 98 kg/ha. Final plant number 200/m^2. Under-sown white clover cv. Liflex, seeding rate 2.0 kg/ha, depth 2-3 cm, row distance 13 cm
04-04-2012	Tracer (potasium bromide), 30 kg/ha
18-05-2012	Fighter 480 (bentazone) - weeds - 1.25 l/ha
06-06-2012	Flexity (metrafenon) - fungi - 0.5 l/ha
12-08-2012	Harvest of spring barley stubble height 15 cm. Grain yield 67.51 hkg/ha, 85% DM
12-08-2012	Straw removed. Straw yield 27.62 hkg/ha, 100% DM
27-08-2012	White clover
26-01-2013	Kerb 400 SC (propyzamid) - fungi - 1.0 l/ha
14-05-2013	Fighter 480 (bentazone) - weeds - 3.0 l/ha
22-05-2013	Rolled with a concrete roller
31-05-2013	Karate (Lambda-cyhalothrin) - pest - 0.3 l/ha (not analyzed)
12-06-2013	Karate (Lambda-cyhalothrin) - pest - 0.3 l/ha (not analyzed)
28-07-2013	Threshing of white clover. Seed yield fresh 1.560 hkg/ha, Straw yield fresh 0.96 hkg/ha

Appendix 4

Precipitation data for the PLAP sites

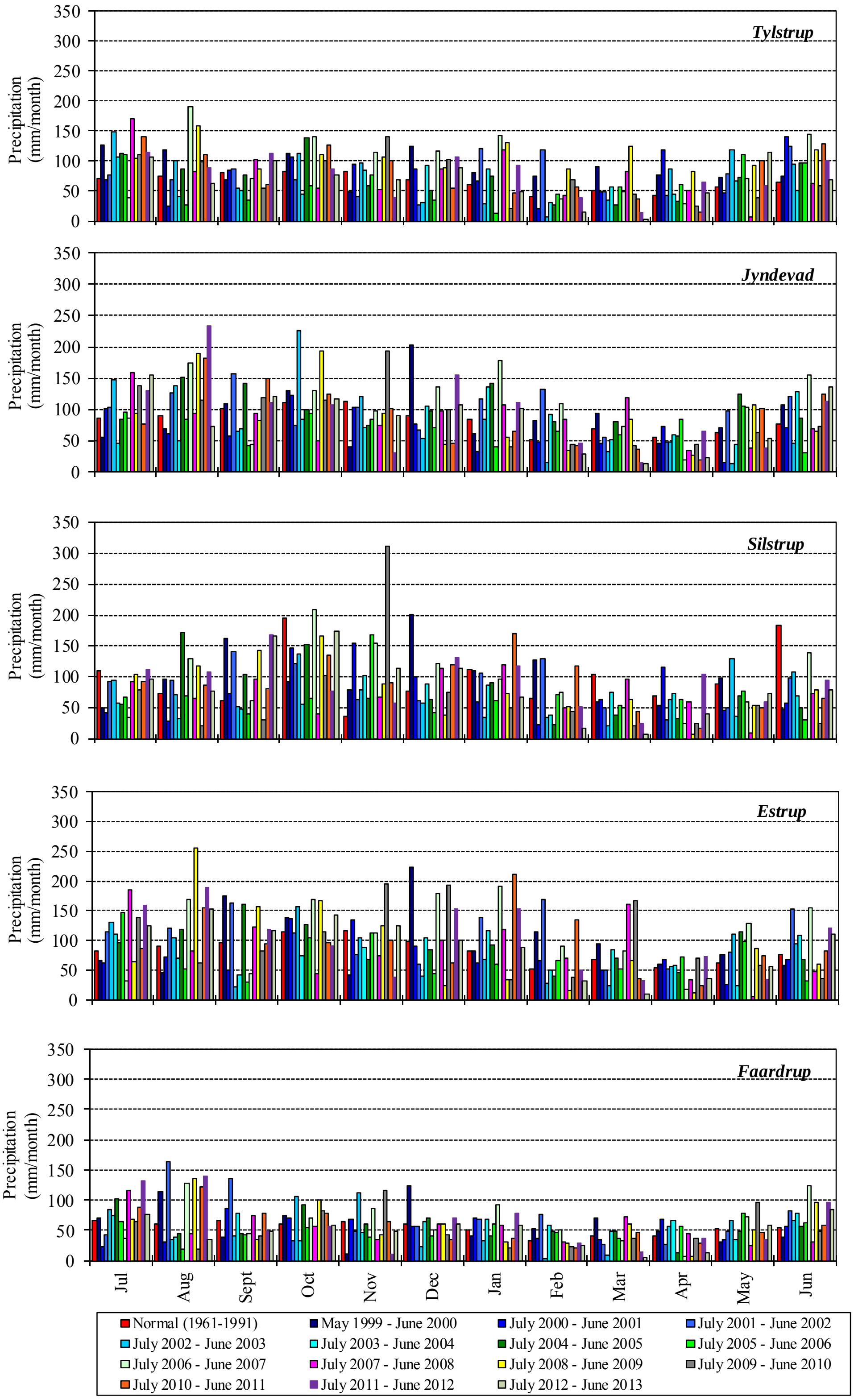

Figure A4.1. Monthly precipitation at all localities for the monitoring period July 2000–June 2013. Normal values (1961–1990) are included for comparison.

Appendix 5

Pesticide detections in samples for drains, suction cups and groundwater monitoring wells

Table A5.1. Number of samples where pesticides were not detected (nd), detected in concentrations below 0.1 µg/L (≤0.1 µg/L) or detected in concentrations above 0.1 µg/L (> 0.1 µg/L) at **Tylstrup**. Numbers are accumulated for the entire monitoring period, and pesticides monitored for less than one year are not included. All samples included.

		Horizontal			Vertical			Suction cups		
Parent	Compound	nd	<0.1	≥0.1	nd	<0.1	≥0.1	nd	<0.1	≥0.1
Aclonifen	Aclonifen	4			123			68		
Aminopyralid	Aminopyralid	14	-	-	70	-	-	37	-	-
Azoxystrobin	Azoxystrobin				216	-	-	95	-	-
	CyPM				216	-	-	95	-	-
Bentazone	2-amino-N-isopropyl-benzamide				191	-	-	72	-	-
	Bentazone				330	-	-	136	1	-
Bifenox	Bifenox	8	-	-	41	-	-	22	-	-
	Bifenox acid	8	-	-	41	-	-	22	-	-
	Nitrofen	8	-	-	41	-	-	22	-	-
Boscalid	Boscalid	9	-	-	102	-	-	56	-	-
Bromoxynil	Bromoxynil				192	-	-	72	-	-
Clomazone	Clomazone				230	-	-	82	-	-
	FMC 65317				208	-	-	74	-	-
Clopyralid	Clopyralid				83	-	-	81	-	-
Cyazofamid	Cyazofamid	4	-	-	123	-	-	68	-	-
Dimethoate	Dimethoate				176	-	-	65	-	-
Epoxiconazole	Epoxiconazole				199	-	-	74	-	-
Fenpropimorph	Fenpropimorph				313	-	-	89	-	-
	Fenpropimorph acid				276	-	-	75	-	-
Flamprop-M-isopropyl	Flamprop				176	-	-	65	-	-
	Flamprop-M-isopropyl				176	-	-	65	-	-
Fluazifop-P-butyl	Fluazifop-P				178	-	-	65	-	-
	TFMP				3	-	-			
Fluroxypyr	Fluroxypyr				194	-	-	70	-	-
Ioxynil	Ioxynil				198	-	-	72	-	-
Linuron	Linuron				271	-	-	67	-	-
Mancozeb	ETU				198	2	-	37	7	-
Metalaxyl-M	CGA 108906	2	13	-	26	130	41	16	53	29
	CGA 62826	14	1	-	182	15	-	74	21	3
	Metalaxyl-M	15	-	-	184	13	-	96	4	-
Metribuzin	Desamino-diketo-metribuzin				289	231	5	168	30	51
	Desamino-metribuzin				366	-	-	87	-	-
	Diketo-metribuzin				73	138	315	81	192	61
	Metribuzin				387	1	-	89	2	-
Pendimethalin	Pendimethalin				436	-	-	144	-	-
Pirimicarb	Pirimicarb				301	-	-	82	-	-
	Pirimicarb-desmethyl				301	-	-	81	-	-
	Pirimicarb-desmethyl-formamido				173	-	-	52	-	-
Propiconazole	Propiconazole				313	-	-	89	-	-
Propyzamide	Propyzamide				221	-	-	82	-	-
	RH-24580				221	-	-	82	-	-

Parent	Compound	Horizontal			Vertical			Suction cups		
		nd	<0.1	≥0.1	nd	<0.1	≥0.1	nd	<0.1	≥0.1
	RH-24644				221	-	-	82	-	-
	RH-24655				157	-	-	58	-	-
Prosulfocarb	Prosulfocarb	7	-	-	33	-	-	18	-	-
Rimsulfuron	PPU	9	-	-	589	58	-	74	191	3
	PPU-desamino	9	-	-	638	9	-	205	63	-
	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				301	-	-	82	-	-
	Triazinamin				291	-	-	76	-	-
Tribenuron-methyl	Triazinamin-methyl				446	-	-	138	-	-

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 (>0.1 µg/L) at **Jyndevad**. Numbers are accumulated for the entire monitoring period, and pesticides monitored for less than one year are not included. All samples included.

		Horizontal			Vertical			Suction cups		
Parent	Compound	nd	<0.1	≥0.1	nd	<0.1	≥0.1	nd	<0.1	≥0.1
Aclonifen	Aclonifen	9			162			42		
Amidosulfuron	Amidosulfuron				88	-	-	20	2	1
	Desmethyl-amidosulfuron				88	-	-	23	-	-
Azoxystrobin	Azoxystrobin				233	-	-	65	-	-
	CyPM				233	-	-	65	-	-
Bentazone	2-amino-N-isopropyl-benzamide				178	-	-	45	2	-
	Bentazone	10	1	-	510	-	-	91	45	10
Bifenox	Bifenox	4	-	-	216	2	-	54	2	-
	Bifenox acid	4	-	-	166	-	-	52	1	-
	Nitrofen	4	-	-	218	-	-	56	-	-
Bromoxynil	Bromoxynil				218	-	-	61	-	-
Chlormequat	Chlormequat				14	-	-	28	-	-
Clomazone	Clomazone	1			6			2		
	FMC 65317	1			7			2		
Cyazofamid	Cyazofamid	4	-	-	131	-	-	32	-	-
Diflufenican	AE-05422291	12	-	-	140	-	-	37	-	-
	AE-B107137	12	-	-	140	-	-	52	-	-
	Diflufenican	12	-	-	140	-	-	37	-	-
Dimethoate	Dimethoate				190	-	-	52	-	-
Epoxiconazole	Epoxiconazole				323	1	-	90	-	-
Fenpropimorph	Fenpropimorph				257	1	-	78	1	-
	Fenpropimorph acid				264	-	-	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	-	71	1	-
	Glyphosate				223	-	-	72	-	-
Ioxynil	Ioxynil				218	-	-	61	-	-
MCPA	2-methyl-4-chlorophenol				210	-	-	56	-	-
	MCPA				210	-	-	56	-	-
Mesosulfuron-methyl	Mesosulfuron				12	-	-	45	-	-
	Mesosulfuron-methyl				285	-	-	78	-	-
Mesotrione	AMBA	11	-	-	74	-	-	28	-	-
	MNBA	11	-	-	74	-	-	28	-	-
	Mesotrione	11	-	-	74	-	-	28	-	-
Metalaxyl-M	CGA 108906	-	7	5	45	101	61	12	21	33
	CGA 62826	-	4	8	137	70	.	11	35	20
	Metalaxyl-M	-	7	5	175	14	17	44	10	-
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	-	-

		Horizontal			Vertical			Suction cups		
Parent	Compound	nd	<0.1	≥0.1	nd	<0.1	≥0.1	nd	<0.1	≥0.1
	Pirimicarb-desmethyl				251	-	-	68	1	-
	Pirimicarb-desmethyl-formamido				251	-	-	69	-	-
Propiconazole	Propiconazole				291	-	-	87	-	-
Pyridate	PHCP				184	-	-	59	-	-
	Pyridate				116	-	-	39	-	-
Rimsulfuron	PPU	-	1	6	489	361	6	39	130	64
	PPU-desamino	-	7	-	765	91	-	110	117	6
	Rimsulfuron				189	-	-	52	-	-
Tebuconazole	Tebuconazole				213	1	-	58	-	-
Terbuthylazine	Desethyl-terbuthylazine				490	27	-	130	20	-
	Terbuthylazine				260	-	-	79	-	-
Tribenuron-methyl	Triazinamin-methyl				252	-	-	77	-	-

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

		Drainage			Horizontal			Vertical			Suction cups		
Parent	Compound	nd	<0.1	≥0.1	nd	<0.1	≥0.1	nd	<0.1	≥0.1	nd	<0.1	≥0.1
Amidosulfuron	Amidosulfuron	1											
	Desmethyl-amidosulfuron	1	-	-									
Azoxystrobin	Azoxystrobin	95	10	-	133	-	-	253	-	-			
	CyPM	49	75	4	162	8	-	308	20	-			
Bentazone	2-amino-N-isopropyl-benzamide	65	-	-	74	-	-	131	-	-			
	Bentazone	75	40	5	133	8	1	244	18	2			
Bifenox	Bifenox	63	3	2	62	-	-	116	5	-			
	Bifenox acid	36	2	18	52	4	6	103	3	14			
	Nitrofen	63	2	3	62	-	-	121	-	-			
Bromoxynil	Bromoxynil	7	-	-									
Chlormequat	Chlormequat	20	1	-	36	-	-	66	-	-			
Clopyralid	Clopyralid	44	-	-	67	-	-	124	-	-			
Clomazone	Clomazone	19	-	-	17	-	-	32	-	-			
	FMC 65317	19	-	-	17	-	-	32	-	-			
Desmedipham	Desmedipham	101	-	-	107	1	-	240	-	-	58	-	-
	EHPC	74	-	-	68	-	-	139	-	-	26	-	-
Diflufenican	AE-05422291	25	-	-	28	-	-	44	-	-			
	AE-B107137	18	4	1	28	-	-	44	-	-			
	Diflufenican	16	8	1	28	-	-	43	-	1			
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	-	-	148	-	-	27	-	-
Flamprop-M-isopropyl	Flamprop	74	7	-	74	-	-	148	-	-	27	-	-
	Flamprop-M-isopropyl	70	11	1	73	1	-	148	-	-	27	-	-
Fluazifop-P-butyl	Fluazifop-P	116	-	-	140	1	-	301	-	-	59	-	-
	TFMP	40	28	23	84	23	2	141	48	14			
Fluroxypyr	Fluroxypyr	50	-	-	74	-	-	142	-	-			
Glyphosate	AMPA	28	121	17	140	8	-	257	12	-	8	-	-
	Glyphosate	82	64	19	145	3	-	255	14	-	8	-	-
Iodosulfuron-methyl	Iodosulfuron-methyl	60	-	-	85	-	-	165	-	-			
	Metsulfuron-methyl	60	-	-	85	-	-	165	-	-			
Ioxynil	Ioxynil	7	-	-									
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	8
Pendimethalin	Pendimethalin	91	14	-	122	-	-	222	-	-			
Phenmedipham	3-aminophenol	56	-	-	72	-	-	173	-	-	53	-	-
	MHPC	101	-	-	108	-	-	240	-	-	59	-	-
	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	-	-

		Drainage			Horizontal			Vertical			Suction cups		
Parent	Compound	nd	<0.1	≥0.1	nd	<0.1	≥0.1	nd	<0.1	≥0.1	nd	<0.1	≥0.1
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	-	-									
Tebuconazole	Tebuconazole	17	2	-	15	-	-	23	-	-			
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			
Triasulfuron	Triazinamin	46	-	-	77	-	-	146	-	-			
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 (>=0.1 µg/L) at **Estrup**. Numbers are accumulated for the entire monitoring period, and pesticides monitored for less than one year are not included. All samples included.

		Drainage			Horizontal			Vertical			Suction cups		
Parent	Compound	nd	<0.1	≥0.1	nd	<0.1	≥0.1	nd	<0.1	≥ 0.1	nd	<0.1	≥0.1
Amidosulfuron	Amidosulfuron	100	-	-	34	-	-	109	-	-			
Aminopyralid	Aminopyralid	35	-	-	23	-	-	37	-	-			
Azoxystrobin	Azoxystrobin	172	110	15	148	1	-	418	1	-			
	CyPM	36	138	123	136	12	1	414	5	-			
Bentazone	2-amino-N-isopropyl-benzamide	237	1	-	79	1	-	271	-	-	5	-	-
	Bentazone	177	145	12	127	15	-	445	1	-	3	2	2
Bifenox	Bifenox	91	3	1	61	-	-	132	-	-			
	Bifenox acid	89	6	10	63	-	-	133	-	1			
	Nitrofen	95	-	-	61	-	-	132	-	-			
Bromoxynil	Bromoxynil	136	1	2	41	-	-	125	-	-	3	-	-
Chlormequat	Chlormequat	45	1	-	18	-	-	56	-	-			
Clomazone	Clomazone	0*			5	-	-	6	-	-			
	FMC 65317	0*			5	-	-	6	-	-			
Clopyralid	Clopyralid	1	-	-									
Dimethoate	Dimethoate	88	-	-	42	-	-	158	-	-	23	-	-
Epoxiconazole	Epoxiconazole	35	12	2	19	-	-	69	-	-			
Ethofumesate	Ethofumesate	91	27	8	46	-	-	158	-	-			
Fenpropimorph	Fenpropimorph	82	1	-	39	-	-	150	-	-	23	-	-
	Fenpropimorph acid	83	-	-	34	-	-	124	-	-	20	-	-
Flamprop-M-isopropyl	Flamprop	119	13	-	55	-	-	208	-	-	23	-	-
	Flamprop-M-isopropyl	112	20	-	55	-	-	208	-	-	23	-	-
Florasulam	Florasulam	92	-	-	35	-	-	125	-	-			
	Florasulam-desmethyl	81	-	-	30	-	-	100	-	-			
Fluroxypyr	Fluroxypyr	87	1	2	34	-	-	120	1	-			
Glyphosate	AMPA	66	307	107	216	1	-	642	7	-	23	-	-
	Glyphosate	189	191	100	211	4	1	606	38	4	23	-	-
Iodosulfuron-methyl	Metsulfuron-methyl	131	-	-	55	-	-	208	-	-	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	-	-	157	-	-			
	Metamitron	81	27	15	46	-	-	158	-	-			
Metrafenone	Metrafenone	40	20	-	40	-	-	74	1	-			
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	192	-	-	66	-	-	223	-	-	6	-	-
	Pirimicarb-desmethyl-formamido	199	13	13	76	-	-	261	-	-	5	-	-
Propiconazole	Propiconazole	192	23	3	86	-	-	309	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	-			

Parent	Compound	Drainage			Horizontal			Vertical			Suction cups		
		nd	<0.1	≥0.1	nd	<0.1	≥0.1	nd	<0.1	≥ 0.1	nd	<0.1	≥0.1
	Hydroxy-terbuthylazine	43	72	16	50	-	-	180	-	-			
	Terbuthylazine	49	78	34	63	-	-	222	1	-			
Thiacloprid	M34	55	-	-	34	-	-	66	-	-			
	Thiacloprid	47	-	-	34	-	-	66	-	-			
	Thiacloprid sulfonic acid	56	-	-	34	-	-	66	-	-			
	Thiacloprid-amide	46	1	-	34	-	-	66	-	-			
Triasulfuron	Triazinamin	131	-	-	56	-	-	203	1	-	22	-	-
Tribenuron-methyl	Triazinamin-methyl	52	2	-	37	-	-	70	-	-	1	-	-

**No samples from drainage.*

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. All samples included.

		Drainage			Horizontal			Vertical			Suction cups		
Parent	Compound	Nd	<0.1	≥ 0.1	nd	<0.1	≥ 0.1	Nd	<0.1	≥ 0.1	nd	<0.1	≥ 0.1
Azoxystrobin	Azoxystrobin	106	-	-	92	-	-	194	-	-			
	CyPM	102	4	-	92	-	-	194	-	-			
Bentazone	2-amino-N-isopropyl-benzamide	67	1	-	61	-	-	132	-	-			
	Bentazone	144	15	6	110	5	1	252	4	3			
Bifenox	Bifenox	56	6	-	30	-	-	74	-	-			
	Bifenox acid	24	1	17	30	-	1	73	-	-			
	Nitrofen	56	5	1	30	-	-	74	-	-			
Bromoxynil	Bromoxynil	101	-	-	81	-	-	225	-	-	73	-	-
Clomazone	Clomazone	84	-	1	69	-	-	166	-	-			
	FMC 65317	84	-	1	69	-	-	166	-	-			
Desmedipham	Desmedipham	99	-	-	66	-	-	166	-	-	29	-	-
	EHPC	83	-	-	52	-	-	124	-	-	16	-	-
Dimethoate	Dimethoate	77	-	-	58	-	-	149	-	-			
Epoxiconazole	Epoxiconazole	81	-	-	66	-	-	143	-	-			
Ethofumesate	Ethofumesate	150	7	6	104	-	-	227	25	6	27	2	-
Fenpropimorph	Fenpropimorph	101	-	-	80	1	-	225	-	-	73	-	-
	Fenpropimorph acid	101	-	-	81	-	-	225	-	-	73	-	-
Flamprop-M-isopropyl	Flamprop	76	1	-	58	-	-	149	-	-			
	Flamprop-M-isopropyl	70	1	-	56	-	-	143	-	-			
Fluazifop-P-butyl	Fluazifop-P	123	5	3	87	-	-	206	5	1	26	3	-
	Fluazifop-P-butyl	99	-	-	66	-	-	166	-	-	29	-	-
	TFMP	64	-	-	43	-	-	94	-	-			
Fluroxypyr	Fluroxypyr	182	-	1	146	1	-	368	-	-	73	-	-
Glyphosate	AMPA	163	9	1	128	-	-	321	2	-	58	5	-
	Glyphosate	169	4	-	127	1	-	319	4	-	62	1	-
Ioxynil	Ioxynil	99	1	-	81	-	-	224	1	-	73	-	-
MCPA	2-methyl-4-chlorophenol	142	-	1	109	-	-	256	-	-			
	MCPA	141	1	1	109	-	-	256	-	-			
Metamitron	Desamino-metamitron	147	12	4	104	-	-	210	36	12	29	-	-
	Metamitron	151	10	2	104	-	-	234	20	4	29	-	-
Metrafenone	Metrafenone	32	-	-	21	-	-	46	-	-			
Pendimethalin	Pendimethalin	55	2	-	55	-	-	125	-	-			
Phenmedipham	MHPC	97	1	1	66	-	-	165	1	-	29	-	-
	Phenmedipham	99	-	-	66	-	-	164	2	-	29	-	-
Pirimicarb	Pirimicarb	148	7	-	116	-	-	319	2	-	73	-	-
	Pirimicarb-desmethyl	94	6	-	66	-	-	163	3	-	29	-	-
	Pirimicarb-desmethyl-formamido	97	3	-	66	-	-	164	2	-	29	-	-
Propiconazole	Propiconazole	178	-	-	138	-	-	372	1	-	73	-	-
Propyzamide	Propyzamide	93	2	2	80	1	-	178	-	-			
	RH-24580	97	-	-	81	-	-	178	-	-			
	RH-24644	93	4	-	81	-	-	178	-	-			
	RH-24655	96	1	-	81	-	-	178	-	-			
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			

		Drainage			Horizontal			Vertical			Suction cups		
Parent	Compound	Nd	<0.1	≥ 0.1	nd	<0.1	≥ 0.1	Nd	<0.1	≥ 0.1	nd	<0.1	≥ 0.1
	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	-	-			
Tribenuron-methyl	Triazinamin-methyl	77	-	-	57	-	-	148	-	-			
Triflusulfuron-methyl	IN-D8526	63	-	-	38	-	-	92	-	-			
	IN-E7710	63	-	-	38	-	-	92	-	-			
	IN-M7222	63	-	-	38	-	-	92	-	-			
	Triflusulfuron-methyl	63	-	-	38	-	-	92	-	-			

Appendix 6

Laboratory internal control cards

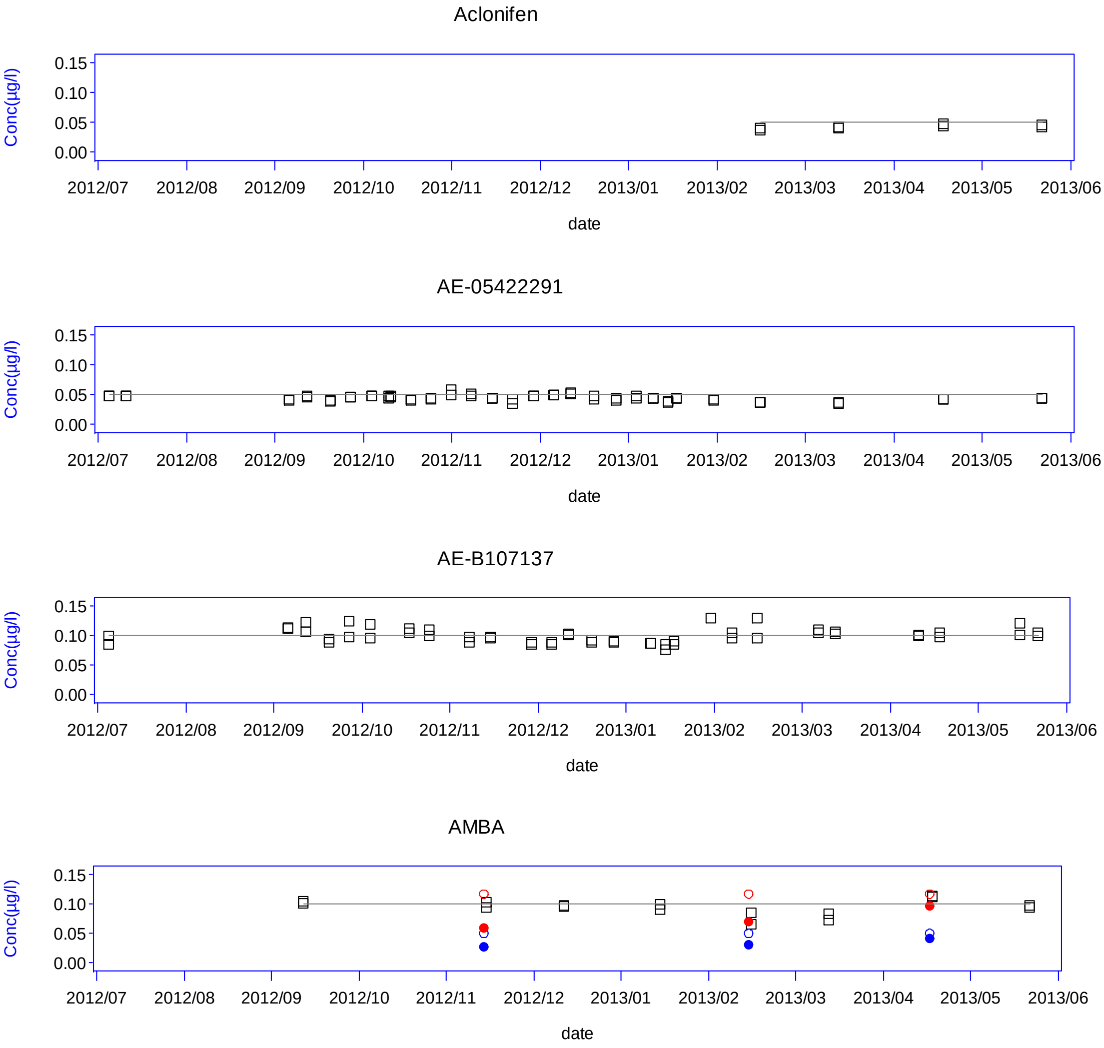

Figure A6.1. Quality control data for pesticide analysis by laboratory 1. Internal laboratory control (IQ) samples are indicated by square symbols and the nominal level is indicated by the solid grey line (□ IQ measured, — IQ nominal concentration). External control (EQ) samples are indicated by circles.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

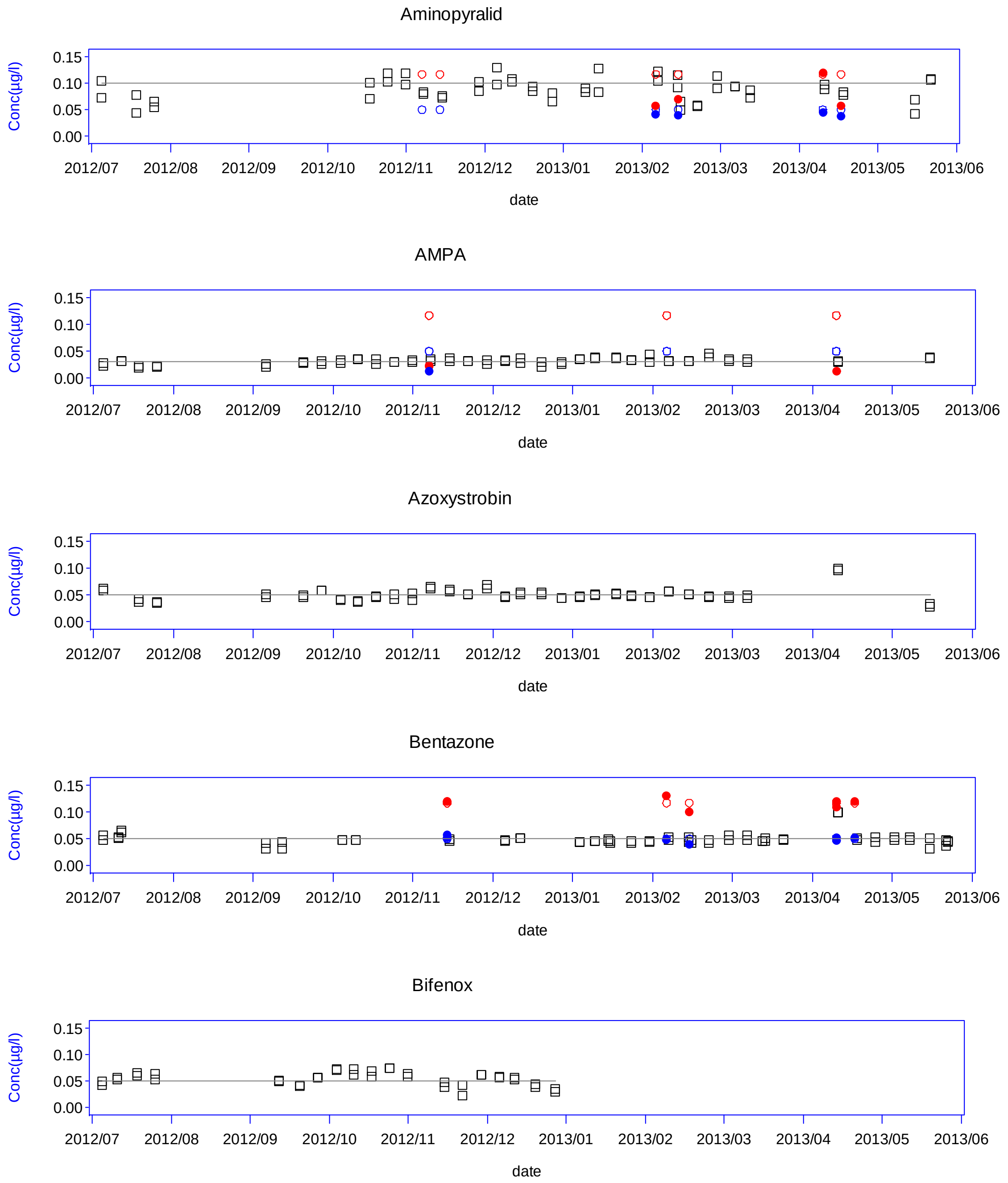

Figure A6.1 continued. Quality control data for pesticide analysis by laboratory 1. Internal laboratory control (IQ) samples are indicated by square symbols and the nominal level is indicated by the solid grey line (□ IQ measured, — IQ nominal concentration). External control (EQ) samples are indicated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

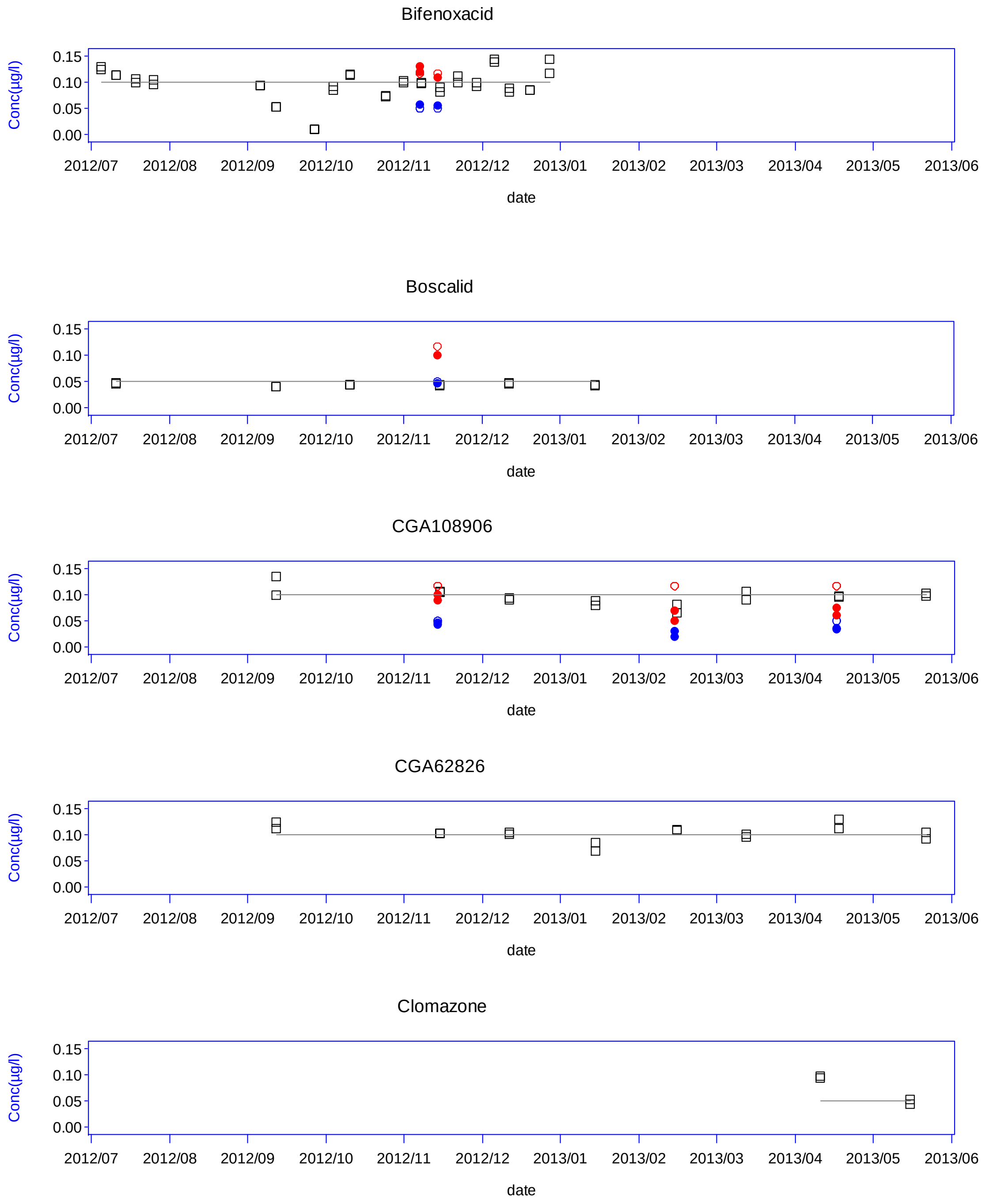

Figure A6.1 continued. Quality control data for pesticide analysis by laboratory 1. Internal laboratory control (IQ) samples are indicated by square symbols and the nominal level is indicated by the solid grey line (□ IQ measured, — IQ nominal concentration). External control (EQ) samples are indicated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

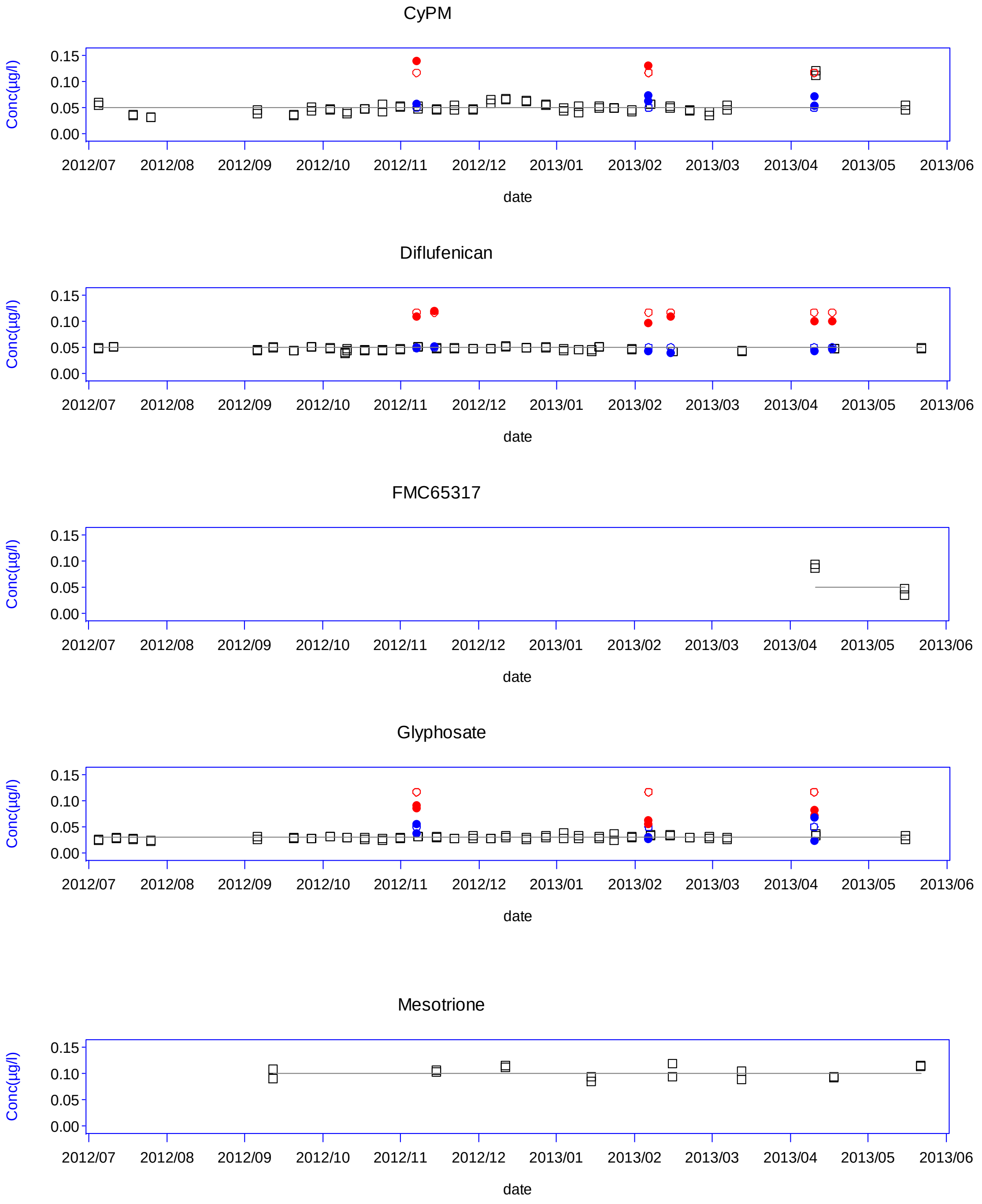

Figure A6.1 continued. Quality control data for pesticide analysis by laboratory 1. Internal laboratory control (IQ) samples are indicated by square symbols and the nominal level is indicated by the solid grey line (□ IQ measured, — IQ nominal concentration). External control (EQ) samples are indicated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

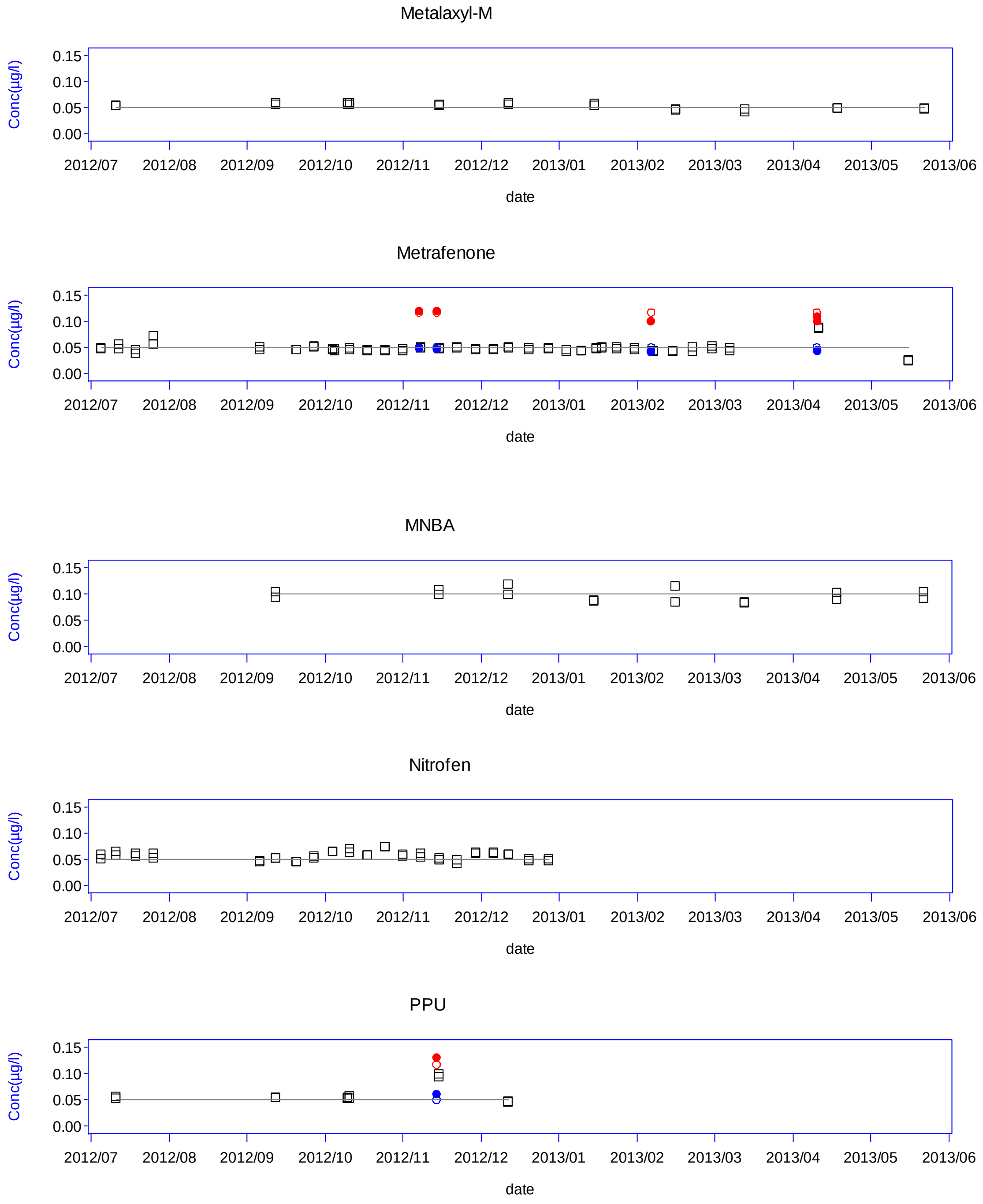

Figure A6.1 continued. Quality control data for pesticide analysis by laboratory 1. Internal laboratory control (IQ) samples are indicated by square symbols and the nominal level is indicated by the solid grey line (□ IQ measured, — IQ nominal concentration). External control (EQ) samples are indicated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

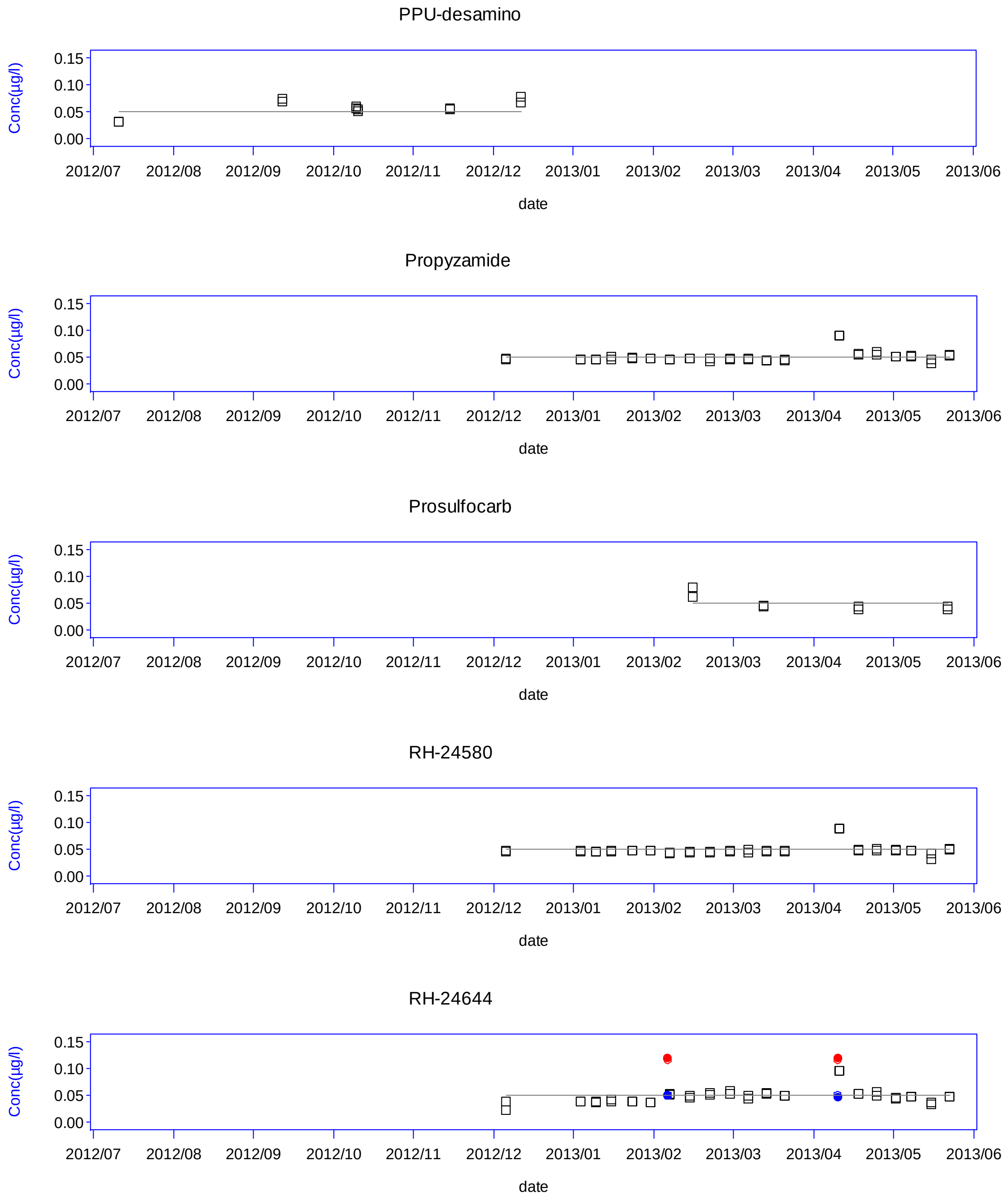

Figure A6.1 continued. Quality control data for pesticide analysis by laboratory 1. Internal laboratory control (IQ) samples are indicated by square symbols and the nominal level is indicated by the solid grey line (□ IQ measured, — IQ nominal concentration). External control (EQ) samples are indicated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

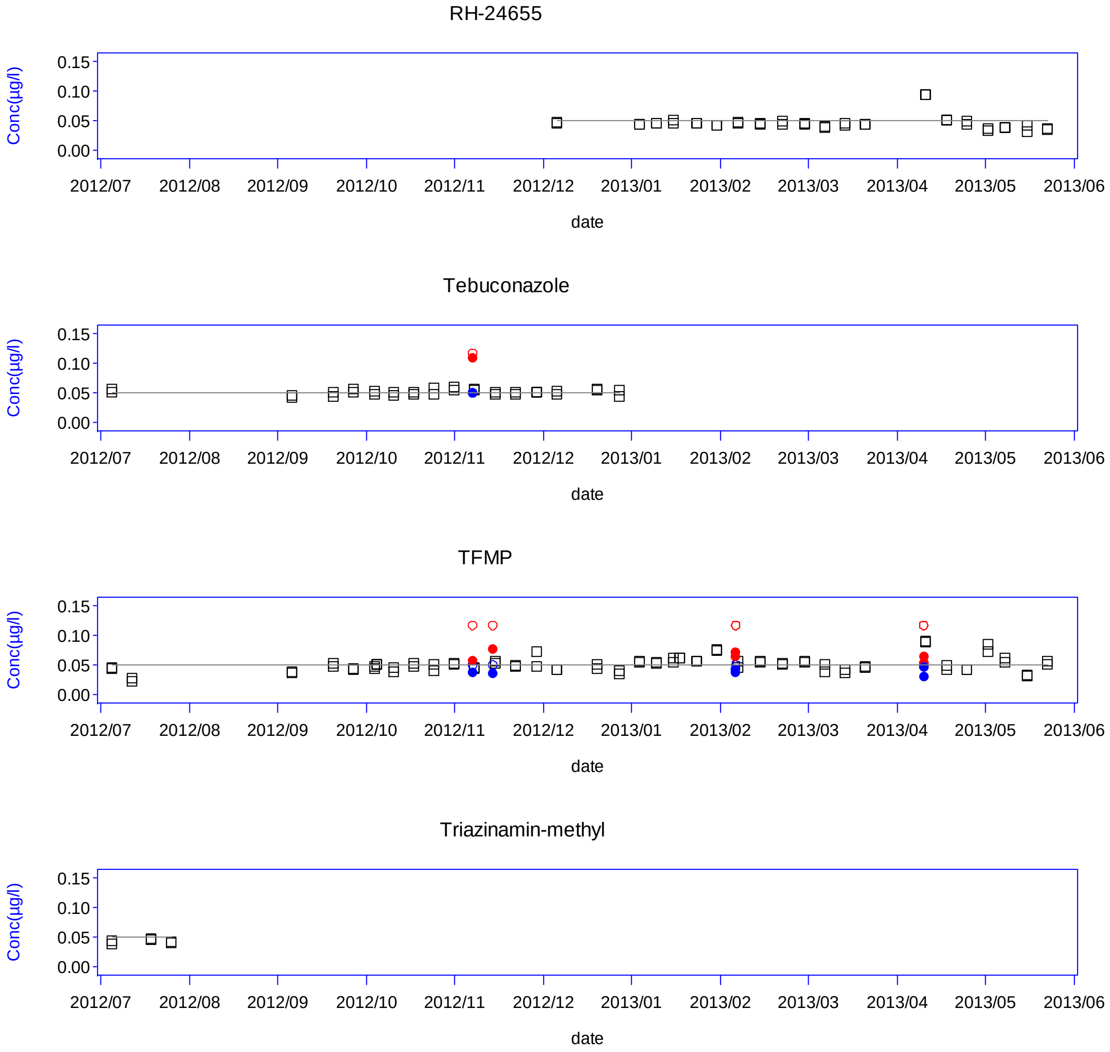

Figure A6.1 continued. Quality control data for pesticide analysis by laboratory 1. Internal laboratory control (IQ) samples are indicated by square symbols and the nominal level is indicated by the solid grey line (□ IQ measured, — IQ nominal concentration). External control (EQ) samples are indicated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

Appendix 7

Pesticides analyzed at five PLAP sites in the period up to 2007

Table A7.1. Pesticides analyzed 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 analyzed 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	<0.015)
- *PPU-desamino*4) (Titus)	Jun 04	Jul 10†	6211	3008	13	<0.015)
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*						<0.016)
-*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 analyzed 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 A7.2. Pesticides analyzed 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 analyzed 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-*						<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 analyzed 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 A7.3. Pesticides analyzed 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 analyzed 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 A7.3 continued. Pesticides analyzed 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 analyzed 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	0.22[4)]
- *RH-24644*						0.01[4)]
- *RH-24580*						<0.01[4)]
- *RH-24655*						<0.01[4)]
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 A7.4. Pesticides analyzed 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 analyzed 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 analyzed 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 A7.5. Pesticides analyzed 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 analyzed 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 analyzed 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.

Appendix 8

New horizontal wells

New horizontal wells at each PLAP-site, with three new horizontal screens were established at each PLAP-site in 2011.

A horizontal well with three PE-screens (3 m long, separated by 1 m packer-section attached 0.8 m bentonite, slits of 0.1 mm, Figure A8.1) was installed September 2011 at all five PLAP-sites to optimize monitoring of the sites both in time and space.

The aim of the optimization was:

- at the sandy sites (Tylstrup and Jyndevad) to improve the early warning regarding pesticides and/or their degradation products leaching to the upper fluctuating groundwater by sampling a spatially representative sample of the porewater, which has just reaching the groundwater zone. The well was hence installed at 4.5 m depth at Tylstrup and 2.5 m depth at Jyndevad,

- at the loamy sites (Silstrup, Estrup and Faardrup) to improve spatial representativity of the water sampled in the variably-saturated zone below drain-depth. To ensure this, the wells are (i) installated at 2 m depth, (ii) oriented such as it is as orthogonal to the orientation of the dominating fracture system as possible and at the same time crossing underneath a drain-line with one of its three filtersections/screens, and (iii) not affected by or affecting sampling from the vertical monitoring wells.

The location of the wells on the PLAP-fields is illustrated in Figure 2.1, 3.1, 4.1, 5.1 and 6.1. The wells/screens/filtersections are installed in boreholes of 9 cm in diameter. These boreholes are drilled by applying the directional drilling system RotamoleTM, which uses a dry percussion-hammer air pressure technique causing minimal disturbances of the soil medium.

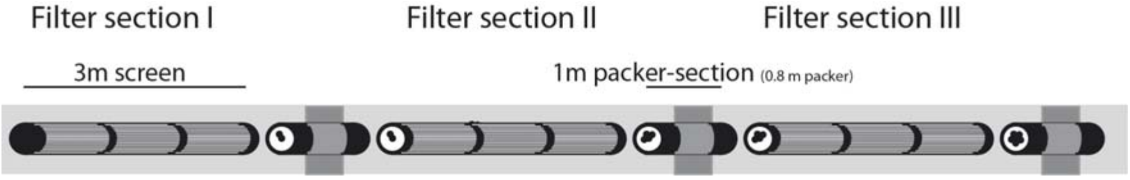

Figure A8.1. Design of horizontal well with three filter sections of 3 m (inner diameter 25 mm; outer diameter 32 mm) each separated by 1m packer-section attached 0.8 m bentonite (thickness at installation 1 cm; expand to a thickness of 3.5 cm). Water can be sampled through two PE-tubes (inner diameter 4 mm; outer diameter 6 mm) ending 1 and 2 meters into each section, repectively.

Water sampling for pesticide analysis from these new horizontal screens started April 2012 (half a year after installation) and is only conducted when the soil media surrounding the screens is saturated. Water samples are, hence, collected at the:

- **Sandy sites** monthly. 3 liters are sampled from each filter via applying suction onto the two tubes. A half liter of the 3 liters, is passed through cells in a flow box measuring pH, temperature, and conductivity. The remaining 2½ liters is pooled with the equal volumes from the two other filters. Subsamples for analysis are then taken from the 7½ liter pooled sample.

- **Loamy sites** monthly if the groundwater table in the nearest vertical monitoring well is situated more than 20 cm above the screens. Having saturated conditions, one liter of water sample is collected from each screen via the two tubes during approximately 10 minutes. The liter sample is passed through cells in a flow box measuring pH, temperature, and conductivity. The samples from each screens are then pooled and send for analysis.

The design of the wells facilitates the possibility of collecting water from six points along the 12 m long well. This option is not utilised yet.

Appendix 9

Groundwater age from recharge modelling and tritium-helium analysis

The site investigations carried out at the various PLAP sites offer good opportunity to model the groundwater age from soil porosity and netprecipitation assuming simple piston flow for groundwater.

For obvious reasons it would be advantageous to be able to compare groundwater age obtained by recharge modelling and soil porosities with groundwater age obtained by other methods.

Other methods for agedating of young groundwater are based on natural or anthropogenic tracers include tritium-helium ($^3H/^3He$), chlorofluorocarbons (CFCs) and sulphurhexafluoride (SF_6). Preliminary studies using the latter two methods were, however, unable to produce sufficiently accurate results to permit direct comparison, due to:

- Decline in atmospheric CFCs over the last two decades and
- Difficulties in determining the amount of excess air entering groundwater due to dynamic change in groundwater table.

The tritium-helium method was tested in 2010 at Jyndevad and Tylstrup.

The other sites were discounted becauce of:

- Low pumping rate excluded sampling for dissolved gases in clamped copper tubes and
- the piston flow model cannot be expected to be valid for the glacial till sites, making direct comparison of the two methods impossible.

Age from recharge modelling

Recharge data obtained by the MACRO model for the 2000-2009 (Rosenbom et al., 2010) were used to estimate water velocity and groundwater age from the deepest screens at the Jyndevad and Tylstrup sites, Table 9.1. The deeper wells are normally only used for water level monitoring, and the wells were included to be able to extend the age interval. Porosity obtained from bulk density of 10 cm cores indicates a soil porosity of 0.43 at 0.5 m and deeper (Lindhardt et al., 2001).

The average water velocities during the last 2-3 years (prior to age-dating in 2010), which are probably more realistic for estimating groundwater age for the shallower filters were 1.42–1.60 m/yr for Jyndevad and 1.35–1.38 m/yr for Tylstrup. A water velocity of 1.4 m/yr appears reasonable for estimating groundwater age at both sites based on recharge data. Groundwater age estimates using a water velocity of 1.4 m/yr for all filters, except for the deep one at Tylstrup (1.1 m/yr) are compared with groundwater age estimated by the tritium-helium method, Figure A9.1.

Table A9.1. Average recharge 2000-2009, water velocity and groundwater age. Yr- year.

Location	Recharge mm/yr	Porosity	Velocity m/yr	Water Table m b.s.	Fiter depth m b.s.	Age yr
Jyndevad	613	0.43	1.43	2.5	11.5	6.3
Tylstrup	477	0.43	1.11	4.5	11.5	6.3

Age from tritium-helium analysis

Samples for tritium and helium collected in one liter plastic bottles and clamped copper tubes respectively were shipped to the University of Bremen and analyzed according to Sültenfuß et al. (2009). The age of water was determined from the ratio between tritium (^{3}H), half-life 12.5 yr., and its daughter product helium-3 (^{3}He) in the water.

The tritium-helium age and the recharge model age differ less than one year for most wells over the entire depth interval and no systematic difference in age can be observed (Figure A9.1). Wells including both sites are shown with increasing depth from left to right in Figure A9.1. The depths are meters below water table to the mid-screen. The length of each screen is 1 m, meaning that the water table was 10 cm below top-screen for the shallowest depth indicated in the figure. Depth of water table checked during pumping did not indicate problems with intake of air, and no bubbles were observed during sampling.

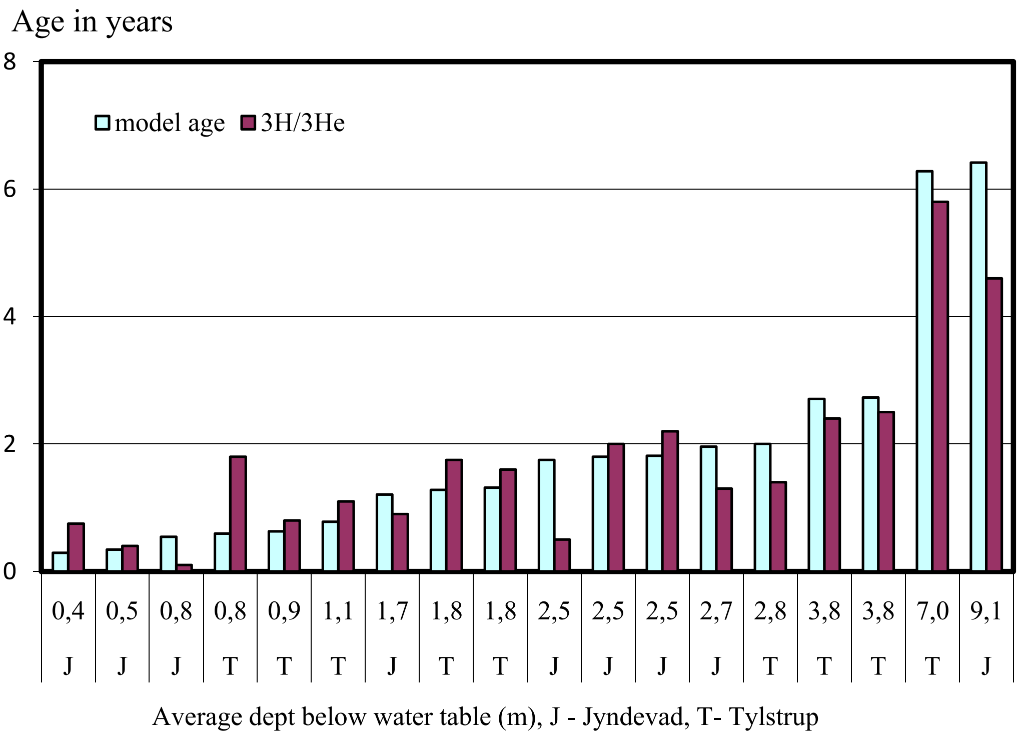

Figure A9.1. Groundwater age at Jyndevad and Tylstrup. Recharge model age assumes water velocity of 1.4 m/yr, except for the Tylstrup deep filter (1.1 m/yr).

Minor difference in groundwater age determined by recharge modelling and tritium-helium analyzes is expected due to the analytical uncertainty regarding tritium and helium. Furthermore, groundwater velocity may vary due to local variations in porosity and permeability affecting the depth of iso-age lines below water table. Given these uncertainties it is concluded that the model age and the tritium-helium age are consistens.