

The Danish Pesticide Leaching Assessment Programme

Monitoring results May 1999–June 2014

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Editor: Walter Brüsch

Cover photo: Henning C. Thomsen, AU.

Peas with pea aphids, Estrup (*Acyrtosiphon pisum* – sprayed with pirimicarb)

Cover: Henrik Klinge Pedersen

Layout and graphic production: Authors and Helle Winther

Printed: March 2016

Price: DKK 200

ISBN 978-87-7871-426-8

Available from:

Geological Survey of Denmark and Greenland

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The report is also available as a pdf file at www.pesticidvarsling.dk

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Preface

In 1998, the Danish Parliament initiated the Danish Pesticide Leaching Assessment Programme (PLAP), an intensive monitoring programme aimed at evaluating the leaching risk of pesticides under field conditions. The Danish Government funded the first phase of the programme from 1998 to 2001. The programme has now been prolonged three times, 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 2018.

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

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

This report presents the results for the period May 1999–June 2014. Results including part of the periode May 1999–June 2013 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, Brusch *et al.*, 2013a, Brusch *et al.*, 2013b, and Brusch *et al.*, 2015). 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 2012-2014.

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

Dansk sammendrag: Der er udarbejdet en dansk samlerapport for juni 2012 til juni 2014.

Walter Brusch
March 2016

Summary

In 1998, the Danish Parliament initiated the Pesticide Leaching Assessment Programme (PLAP), an intensive monitoring programme aimed at evaluating the leaching risk of pesticides under field conditions. The objective of the PLAP is to improve the scientific foundation for decision-making in the Danish regulation of pesticides. The specific aim is to analyse whether pesticides applied in accordance with current regulations will result in leaching of the pesticide and/or its degradation products to groundwater in unacceptable concentrations.

Throughout the monitoring period (1999-2014) 103 pesticides and/or degradation products (51 pesticides and 52 degradation products) have been analysed in PLAP, comprising five agricultural fields (1.2 to 2.4 ha) grown with different crop. The 15 most frequently analysed pesticides and/or degradation products represent in total 2.300–4.200 water samples collected from groundwater, drainage and suction cups. These numbers include 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.).

Table 0.1. The 15 most frequently analysed pesticides and/or degradation product in the period 1999-June 2014. All water samples including quality analysis (QA) samples, samples from groundwater wells, and samples from the variably-saturated zone (drainage and suction cups).

Pesticide or degradation products		All samples incl. QA	Pesticide/ Parent compound	Ground-water	Drainage + suction cups
Bentazone	P	4.197	Bentazone	2.603	1.051
Glyphosate	P	3.747	Glyphosate	2.216	1.091
AMPA	M	3.746	Glyphosate	2.217	1.092
Pirimicarb	P	3.432	Pirimicarb	2.120	887
Propiconazole	P	3.421	Propiconazole	2.084	899
Pirimicarb-desmethyl	M	3.078	Pirimicarb	1.911	780
CyPM	M	3.033	Azoxystrobin	1.910	740
Pendimethalin	P	2.881	Pendimethalin	1.811	694
Azoxystrobin	P	2.880	Azoxystrobin	1.798	717
Pirimicarb-desmethyl-formamido	M	2.678	Pirimicarb	1.638	707
Desethyl-terbuthylazine	M	2.619	Terbuthylazine	1.664	612
Fenpropimorph	P	2.494	Fenpropimorph	1.531	657
Triazinamin-methyl	M	2.386	Tribenuron-methyl	1.523	569
Fenpropimorph acid	M	2.341	Fenpropimorph	1.435	636
PPU	M	2.311	Rimsulfuron	1.519	502

P: Parent pesticide. M: Degradation product.

This report presents the results of the monitoring period July 2012–June 2014 comprising 7.378 single analyses 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 22 pesticides and 17 degradation products (Table 0.2) after applying the maximum allowed dose of the specific pesticide in connection with a specific crop (Table 0.3). The 39 substances include 4 substances not tested before June 2012, and 10 substances where the pesticides have not previously been used on crops and fields, but previously on other crops or fields.

Table 0.2. 22 pesticides and 17 degradation products have been analysed in PLAP in the period June 2012-June 2014. The number of water samples analysed, detections, and detections $\geq 0.1 \mu\text{g/L}$ in water samples from the variably-saturated zone (drainage and suction cups) and groundwater (vertical and horizontal groundwater wells).

Analyte	Parent pesticide	Groundwater	Drain + Suct.	Groundwater			Drain + suction cups		
		Samples	Samples	Det.	$\geq 0.1 \mu\text{g/L}$	Max conc.	Det.	$\geq 0.1 \mu\text{g/L}$	Max. conc.
Aclonifen	Aclonifen	36	11			ND			ND
Aminopyralid	Aminopyralid	237	123			ND			ND
Azoxystrobin	Azoxystrobin	189	85	1		0.02	22	1	0.13
CyPM	Azoxystrobin	189	85	26	4	0.19	76	29	0.4
Bentazone	Bentazone	307	113	17		0.049	76	13	2.8
Bifenox	Bifenox	88	53			ND	1		0.023
Bifenox acid	Bifenox	91	52	1		0.053	2	1	0.14
Nitrofen	Bifenox	88	53			ND			ND
Boscalid	Boscalid	33	16			ND			ND
Bromoxynil	Bromoxynil	89	23			ND			ND
Clomazone	Clomazon	84	38			ND			ND
FMC 65317	Clomazon	85	38			ND			ND
Diiflufenican	Diiflufenican	228	91	1	1	0.47	29	13	0.49
AE-05422291	Diiflufenican	228	91			ND			ND
AE-B107137	Diiflufenican	237	88	1		0.016	16		0.088
TFMP	Fluazifop-P-buthyl	216	75	32	3	0.12	24	4	0.41
CGA 192155	Fludioxonil	48	11			ND			ND
CGA 339833	Fludioxonil	48	11			ND			ND
Glyphosate	Glyphosat	226	100	23	1	0.13	63	11	0.66
AMPA	Glyphosat	225	100	9		0.028	73	9	0.16
Ioxynil	Ioxynil	89	23			ND			ND
EBIS	Mancozeb	25	7			ND			ND
Mesotrione	Mesotrione	140	44			ND			ND
AMBA	Mesotrione	140	44			ND			ND
MNBA	Mesotrione	140	44			ND			ND
Metalaxyl-M	Metalaxyl-M	320	107	53	9	0.33	1		0.014
CGA 108906	Metalaxyl-M	321	106	217	25	0.28	84	11	0.23
CGA 62826	Metalaxyl-M	321	106	103	4	0.24	45	4	0.12
Metrafenone	Metrafenone	195	98	1		0.04	2		0.011
Propyzamide	Propyzamide	82	35			ND			ND
RH-24580	Propyzamide	82	35			ND			ND
RH-24644	Propyzamide	82	35			ND			ND
RH-24655	Propyzamide	82	35			ND			ND
Prosulfocarb	Prosulfocarb	103	47	4		0.032	1		0.03
PPU	Rimsulfuron	66	28	47	5	0.23	28	5	0.16
PPU-desamino	Rimsulfuron	66	28	14		0.068	22		0.068
Tebuconazole	Tebuconazole	29	16			ND	2		0.084
1,2,4-triazol	Tebuconazole	16		7	1	0.17			
Triazinamin-methyl	Tribenuron-methyl	6	6			ND			ND

Max. conc.: Maximum concentration. ND: Pesticide not detected in the monitoring period 2012-2014. Suct.: Suction cups. Det.: Number of detections.

From these 39 substances, 21 were not detected in any of the water samples (Table 0.2).

Results covering the period May 1999–June 2013 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 Brüschi *et al.*, 2013a, Brüschi *et al.*, 2013b, Brüschi *et al.*, 2014, Brüschi *et al.*, 2015).

Table 0.3. Crops grown on the five PLAP-fields in 2012, 2013 and 2014.

	Tylstrup	Jyndeved	Silstrup	Estrup	Faardrup
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
2014	Potatoes	Potatoes	Winter wheat	Winter wheat	Winter wheat

*Spring barley replacing frost killed winter wheat on Silstrup.

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 2012-June 2014.

Highlights from the **monitoring period June 2012-June 2014:**

Bentazone

Bentazone was applied to peas at Jyndeved and Estrup in 2013, white clover at Faardrup in 2012 and 2013, and maize at Jyndeved in 2012.

At the sandy field, Jyndeved, bentazone was found leaching through the variably-saturated zone (suction cups) after application on peas in 2013. Bentazone was found frequently in water from suction cups in 2013 and in concentrations up to 2 µg/L, but both bentazone concentrations and number of detections decreased in 2014. During the monitoring period bentazone was detected in 78% of the water samples from the suction cups, and in 22% ≥ 0.1 µg/L. Bentazone was, however, only detected once (0.01 µg/L) in a mixed groundwater sample (from the three screens) in the horizontal well at 2.5 m b.g.s. This confirms the leaching pattern detected after the application on maize in 2012, where bentazone 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 clover, at the clayey till field at Faardrup in 2012 and 2013, bentazone was detected in a drainage sample (0.02 µg/L) in January 2013. From January to March 2014 bentazone was detected in seven drainage water samples as well as in two mixed samples from a horizontal well. The findings from January to March 2014 were caused by snow melting. The approved amount of bentazone in 2013 on white clover was twice the amount of bentazone approved on clover today.

Bentazone leached after use on peas in May 2013 at the clayey till field Estrup, where bentazone was detected in 32 drainage water samples approx. 1.5 month after application. Bentazone was also detected in 14 groundwater samples in low concentrations ≤ 0.1 µg/L.

As of June 2014 bentazone has been applied on different crops 17 times in total onto the five PLAP-fields, amounts ranging between 375 g to 500 g L/ha. In the period May 2001-June 2014 bentazone has been detected in 82 groundwater samples, eight having concentrations above 0.1 µg/L. A total of 2.603 groundwater samples have been analysed for bentazone.

Metalaxyl-M

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 (Tylstrup and

Jyndevad) in the period June 2010 to June 2014. Metalaxyl-M was applied on potatoes in July 2010.

Metalaxyl-M was detected few times in low concentrations in water samples 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 three years after application. The degradation products were detected in low concentrations in 2014.

The highest concentrations of both compounds (up to 4.8 µg/L in January 2012) were detected in water collected from suction cups at 1 m depth.

In the period June 2011-June 2014 both degradation products were detected in 75-83% of the water samples taken from the variably-saturated zone (suction cups) and especially CGA 108906 was detected frequently in groundwater samples from both Tylstrup and Jyndevad (75 and 83% detections), where 17 and 26% of the analysed groundwater samples exceeded 0.1 µg/L.

Concentrations measured in water samples from the variably-saturated zone and from a horizontal well collecting groundwater just beneath the fluctuating groundwater table at Jyndevad, clearly indicated leaching of the compounds after metalaxyl-M had been applied to potatoes at the PLAP-field in 2010.

As a consequence of these monitoring results, the Danish EPA has withdrawn the approval of metalaxyl-M as of August 2013. The PLAP-monitoring of the parent and its two degradation products is still ongoing to evaluate their impact on the groundwater quality.

Fluazifop-P-butyl

Fluazifop-P-butyl was used in a new dose (50% lower than in past applications) in the spring of 2011 at the clayey till field Silstrup. Leaching of its degradation product TFMP was negligible in 2011. Before the regulation, TFMP had leached to both drainage and groundwater in concentrations above 0.1 µg/L at Silstrup (Badawi *et. al.* 2015).

Fluazifop-P-butyl had also been applied at Faardrup in May 2011. Here TFMP did not leach.

In April 2012 fluazifop-P-butyl was applied on red fescue at Silstrup (50% reduced dose). Here TFMP-concentrations exceeding 0.1 µg/L was measured in drainage and groundwater. In the monitoring year 2013 TFMP was detected in both drainage and groundwater. Concentrations, however, were below 0.1 µg/L. The TFMP was detected in a few drainage samples late 2013. Until June 2014 TFMP was not detected in drainage or groundwater.

Fluazifop-P-butyl was applied on red fescue at Faardrup in May 2011, but TFMP has not been detected in any water samples from within this monitoring period.

Given these different TFMP-leaching scenarios, the leaching risk of the compound and TFMP will be evaluated in PLAP in the years to come. Fluazifop-P-butyl has been

applied ten times in PLAP at four of the fields at potatoes, peas, red fescue and beets. Fluazifop-P-butyl was not approved by the EU commission in 2014, and fluazifop-P-butyl has not been reapplied in Denmark.

Glyphosate and AMPA

After application of glyphosate to kill the red fescue at the clayey till field Silstrup in September 2012, glyphosate and AMPA were detected 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 ten groundwater samples from vertical wells and in three groundwater samples from the new horizontal well.

Furthermore, glyphosate was applied on spring barley in August 2013 and were detected in drainage two month later in concentrations < 0.1 µg/L. Glyphosate or AMPA, or both, were detected (< 0.1 µg/L) in nine groundwater samples, in three different depths of a monitoring well.

At the clayey till field Estrup, concentrations of glyphosate and AMPA in drainage frequently exceeded 0.1 µg/L following the glyphosate application on winter wheat stubble in October 2011. AMPA was never detected in the groundwater. Glyphosate, however, was detected twice in groundwater samples in concentrations being 0.21 and 0.13 µg/L. Spraying in peas in August 2013 lead to detections of both glyphosate and AMPA in drainage, but not in groundwater. The concentrations in drainage were though lower than when spraying after the harvest of crops.

Azoxystrobin

After application of **azoxystrobin** on spring barley at Silstrup in 2013 the degradation product CyPM was detected in drainage (10 of 17 analysed samples > 0.1 µg/L) and in 22 groundwater samples (3 of 59 analysed samples > 0.1 µg/L). Azoxystrobin was detected in two drainage water samples and in one of the groundwater samples (< 0.1 µg/L).

Azoxystrobin was applied to spring barley at Estrup in June 2012. Here both azoxystrobin and CyPM leached in to drainage in concentrations ≥ 0.1 µg/L. The degradation product CyPM was detected in four groundwater samples from a horizontal well, and in one instance in concentration ≥ 0.1 µg/L. There were no detections in vertical groundwater monitoring wells.

Diflufenican

Diflufenican and AE-B107137 have been analysed after applications at Silstrup and Estrup in 2012 and 2013, where both diflufenican and the degradation product AE-B107137 were detected frequently in drainage.

Diflufenican was detected in one groundwater sample (0.47 µg/L) from Silstrup and AE-B107137 in one groundwater sample (0.016 µg/L) from Estrup. The degradation product AE-05422291 was never detected (Table 0.2).

Acclonifen, aminopyralid, boscalid, bromoxynil, clomazon, fludioxonil, ioxynil, mancozeb, mesotrione, propyzamid, tribenuron-methyl and degradation products thereof, were not detected in any water sample during the monitoring period.

Tebuconazole was detected in two drainage water samples and its degradation product, 1,2,4-triazole, was detected in seven groundwater samples - one detection being > 0.1 µg/L.

Metrafenone was detected in two drainage water samples and in one groundwater sample – all with concentrations <0.1 µg/L.

Prosulfocarb was detected in one drainage water sample and four groundwater samples - all detections >0.1 µg/L (Table 0.2).

The monitoring period 1999-2014:

The results of the entire period covering **51** pesticides and **52** degradation products show that from the 51 pesticides applied, 22 pesticides and/or their degradation product(s) were not detected in either drainage/water from suction cups or groundwater during the entire monitoring period. The lists also include parents detected in less than two samples in drainage/suction cups:

- Aclonifen, aminopyralid, boscalid, chlormequat, clopyralid, cyazofamid, desmedipham, fenpropimorph, florasulam, fludioxonil, iodosulfuron-methyl-natrium, linuron, mesotrione, thiacloprid, thiamethoxam, tribenuron-methyl and triasulfuron were not detected in drainage or in less than two samples. Amidosulfuron, bromoxynil, clomazone, mesosulfuron-methyl and picolinafen were not detected in groundwater.

The monitoring data indicate leaching of 17 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*
- *CL 153815* (degradation product of picolinafen)
- *AE-B107103* (degradation product of diflufenican)
- *Pirimicarb-desmethyl-formamido* (degradation product of pirimicarb)
- *Propyzamide*
- *Fluroxypyr*
- *Tebuconazole* and its degradation product *1,2,4-triazole*
- *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)
- *Metamitrone* and its degradation product **desamino-metamitrone**

- **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 detected. Apart from PPU, these were all frequently detected in groundwater in concentrations exceeding 0.1 µg/L more than six months after application.

The monitoring data also indicate leaching of an additional 17 pesticides, but in low concentrations. Although concentrations exceeded 0.1 µg/L in several 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.

One of the compounds (pyridate) was detected in the groundwater in concentrations exceeding 0.1 µg/L.

In order to describe the waterflow 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.

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 approx. 50% of all screens monitored and in approx. 60% of the screens placed in the upper shallow groundwater (Thorling, L. (ed.), 2015).

The detection of pesticides in groundwater over the past 20 years has fuelled the need of enhancing 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 transformation and 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, Rosenbom et al., 2015).

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, Annex VI (Council Directive 97/57/EC of 22 September 1997) enables field leaching study results to be included in the risk assessments.

1.1 Objective

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

used in arable farming and PLAP monitors leaching at five agricultural test sites representative of Danish conditions.

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

1.2 Structure of the PLAP

The pesticides included in the PLAP were selected by the Danish EPA on the basis of expert judgement. At present, 51 pesticides and 52 degradation products have been included in the PLAP. All the compounds analysed since 1999 are listed in Appendix 1.

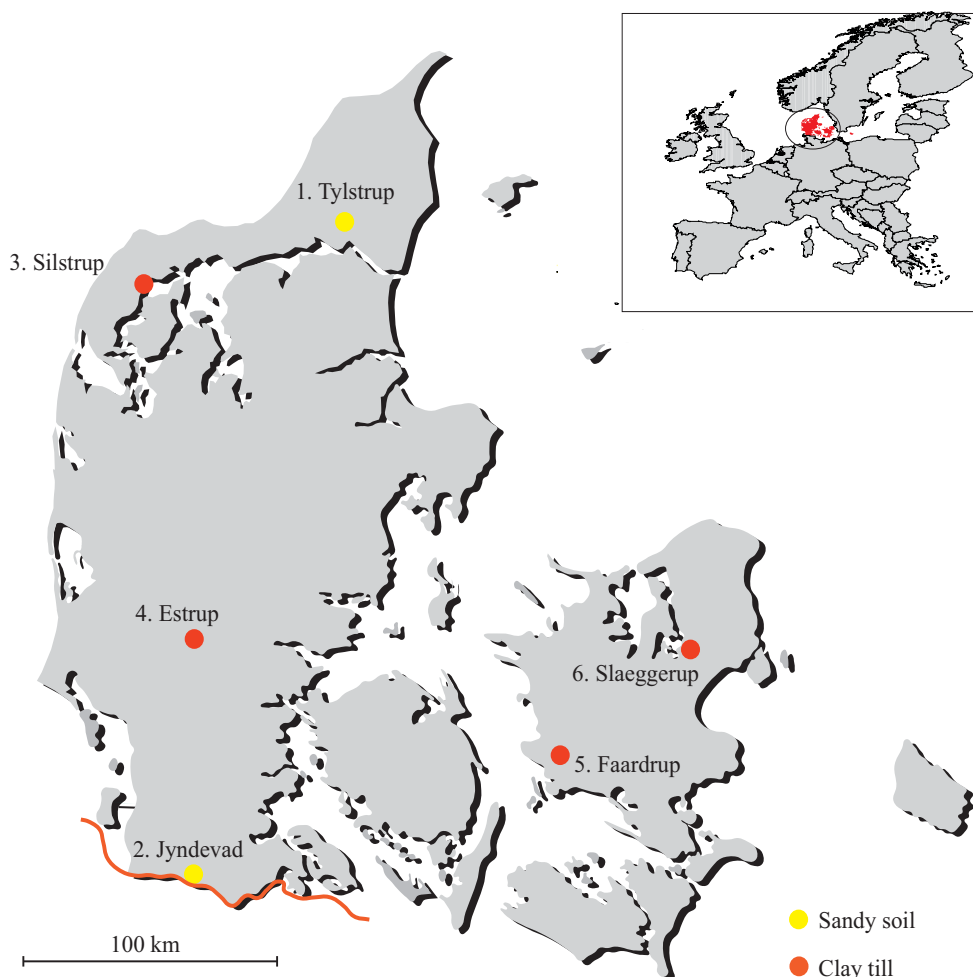


Figure 1.1. Location of the PLAP fields Tylstrup, Jydevad, Silstrup, Estrup, and Faardrup. Monitoring at Slaeggerup was terminated on 1 July 2003.

Soil type and climatic conditions are considered to be some of the most important parameters controlling pesticide leaching. The PLAP initially encompassed six fields representative of the dominant soil types and the climatic conditions in Denmark (Figure 1.1).

Monitoring at the Slaeggerup field 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 fields, thereby enabling pesticide leaching to groundwater to be rapidly detected (Table 1.1). Cultivation of the PLAP fields 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 fields can be related to the current approval conditions pertaining to the individual pesticides. The five test fields 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 fields (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 Length (m)	70 x 166	135 x 180	91 x 185	105 x 120	150 x 160
Area (ha)	1.1	2.4	1.7	1.3	2.3
Tile drain	No	No	Yes	Yes	Yes
Depths to tile drain (m b.g.s.)			1.1	1.1	1.2
Monitoring initiated	May 1999	Sep 1999	Apr 2000	Apr 2000	Sep 1999
Geological characteristics					
– Deposited by	Saltwater	Meltwater	Glacier	Glacier/meltwater	Glacier
– Sediment type	Fine sand	Coarse sand	Clayey till	Clayey till	Clayey till
– DGU symbol	YS	TS	ML	ML	ML
– Depth to the calcareous matrix (m b.g.s.)	6	5–9	1.3	1–4 ²⁾	1.5
– Depth to the reduced matrix (m b.g.s.)	>12	10–12	5	>5 ²⁾	4.2
– Max. fracture depth ³⁾ (m)	–	–	4	>6.5	8
– Fracture intensity 3–4 m depth (fractures/m)	–	–	<1	11	4
– Ks in C horizon (m/s)	2.0·10 ⁻⁵	1.3·10 ⁻⁴	3.4·10 ⁻⁶	8.0·10 ⁻⁸	7.2·10 ⁻⁶
Topsoil characteristics					
– DK classification	JB2	JB1	JB7	JB5/6	JB5/6
– Classification	Loamy sand	Sand	Sandy clay loam/ sandy loam	Sandy loam	Sandy loam
– Clay content (%)	6	5	18–26	10–20	14–15
– Silt content (%)	13	4	27	20–27	25
– Sand content (%)	78	88	8	50–65	57
– pH	4–4.5	5.6–6.2	6.7–7	6.5–7.8	6.4–6.6
– TOC (%)	2.0	1.8	2.2	1.7–7.3	1.4

¹⁾ Yearly normal based on a time series for the period 1961–90. The data refer to precipitation measured 1.5 m above ground 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 2014, but the main focus of this report is on the leaching risk of pesticides applied during 2012–2014. For a detailed description of the earlier part of the monitoring periods (May 1999–June 2013), see previous publications on http://pesticidvarsling.dk/-publ_result-/index.html. Within 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 field 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 field during the entire monitoring period from May 1999–June 2014. The five field models have been calibrated for the monitoring period May 1999–June 2004 and validated for the monitoring period July 2004–June 2014.

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

2 Pesticide leaching at Tylstrup

2.1 Materials and methods

2.1.1 Site description and monitoring design

Tylstrup is located in northern Jutland (Figure 1.1). 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 thick 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 approx. 2.6–4.8 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 field 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.

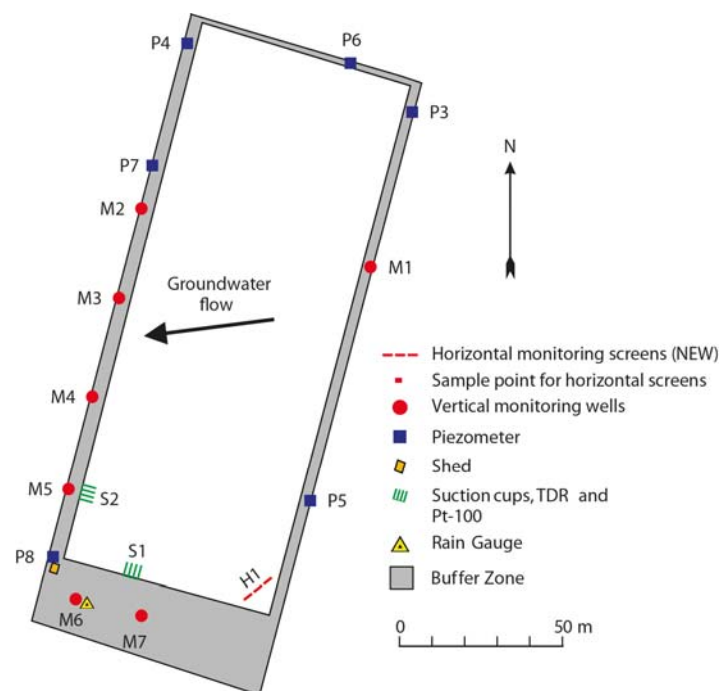


Figure 2.1. Overview of the **Tylstrup** site. The innermost white area indicates the cultivated land, while the grey area indicates the surrounding buffer zone. The positions of the various installations are indicated, as is the direction of groundwater flow (by an arrow). Pesticide monitoring is conducted 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 2013-2014 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.

The field was ploughed on 20 September 2012 and 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 the leaching of prosulfocarb was monitored. The winter rye was harvested on 20 August 2013 yielding 77.4 hkg/ha (85% dry matter) as well as 33.8 hkg/ha of straw (100% dry matter).

Having been ploughed on 26 February 2014, a crop of potatoes (cv. Kuras) was planted on 15 April 2014. The tubers had been treated with fludioxonil prior to the planting. Two degradation products of fludioxonil, CGA 339833 and CGA 192155, were included in the monitoring programme. The final ridges were formed during planting. The herbicide clomazone was sprayed the following day, it was however not included in the monitoring. The herbicide rimsulfuron was sprayed twice, on 15 May and 22 May, but was not included in the monitoring programme. Within this monitoring year the field was irrigated twice using 24 mm/ha on 13 June and 20 June 2014. The potatoes was sprayed several times with the fungicide mancozeb from June to August. This will be elaborated in next year's report, 1999-2015.

2.1.3 Model setup and calibration

The numerical model MACRO (version 5.2 Larsbo *et al.*, 2005) was applied to the Tylstrup field 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 2014 and to establish an annual water balance.

Compared to Brusch *et al.* (2015), one additional year of validation was added to the MACRO-setup for the Tylstrup field. The setup was hereby calibrated for the monitoring period May 1999-June 2004 and “validated” for the monitoring period July 2004-June 2014.

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 all 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⁾
01.05.99–30.06.99 ¹⁾	120	269	0	112	156
01.07.99–30.06.00	773	1.073	33	498	608
01.07.00–30.06.01	773	914	75	487	502
01.07.01–30.06.02	773	906	80	570	416
01.07.02–30.06.03	773	918	23	502	439
01.07.03–30.06.04	773	758	0	472	287
01.07.04–30.06.05	773	854	57	477	434
01.07.05–30.06.06	773	725	67	488	304
01.07.06–30.06.07	773	1.147	59	591	615
01.07.07–30.06.08	773	913	126	572	467
01.07.08–30.06.09	773	1.269	26	600	695
01.07.09–30.06.10	773	867	27	424	470
01.07.10–30.06.11	773	950	57	506	501
01.07.11–30.06.12	773	923	24	501	446
01.07.12–30.06.13	773	803	0	528	275
01.07.13–30.06.14	773	852	48	440	460

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 2.2C-E). During the last seven hydraulic years, excluding the latest spring period, the level of 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 to some extent captured even though the groundwater table rose earlier from a lower level and with higher amplitude than predicted (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 2013–June 2014, precipitation and the actual evapotranspiration were in the low end of the range observed since the monitoring began at the field, leaving the groundwater recharge/percolation being medium size compared to the other hydraulic years (Figure 2.2B). The monthly precipitation pattern for this year was low to medium expect for October, December and May if compared with earlier years. July 2013 was the driest month ever monitored with only 16 mm of precipitation (Appendix 4). Artificial irrigation was, however, not needed on the winter rye, whereas the requirement of the potatoes planted in April 2014 was 48 mm in June 2014.

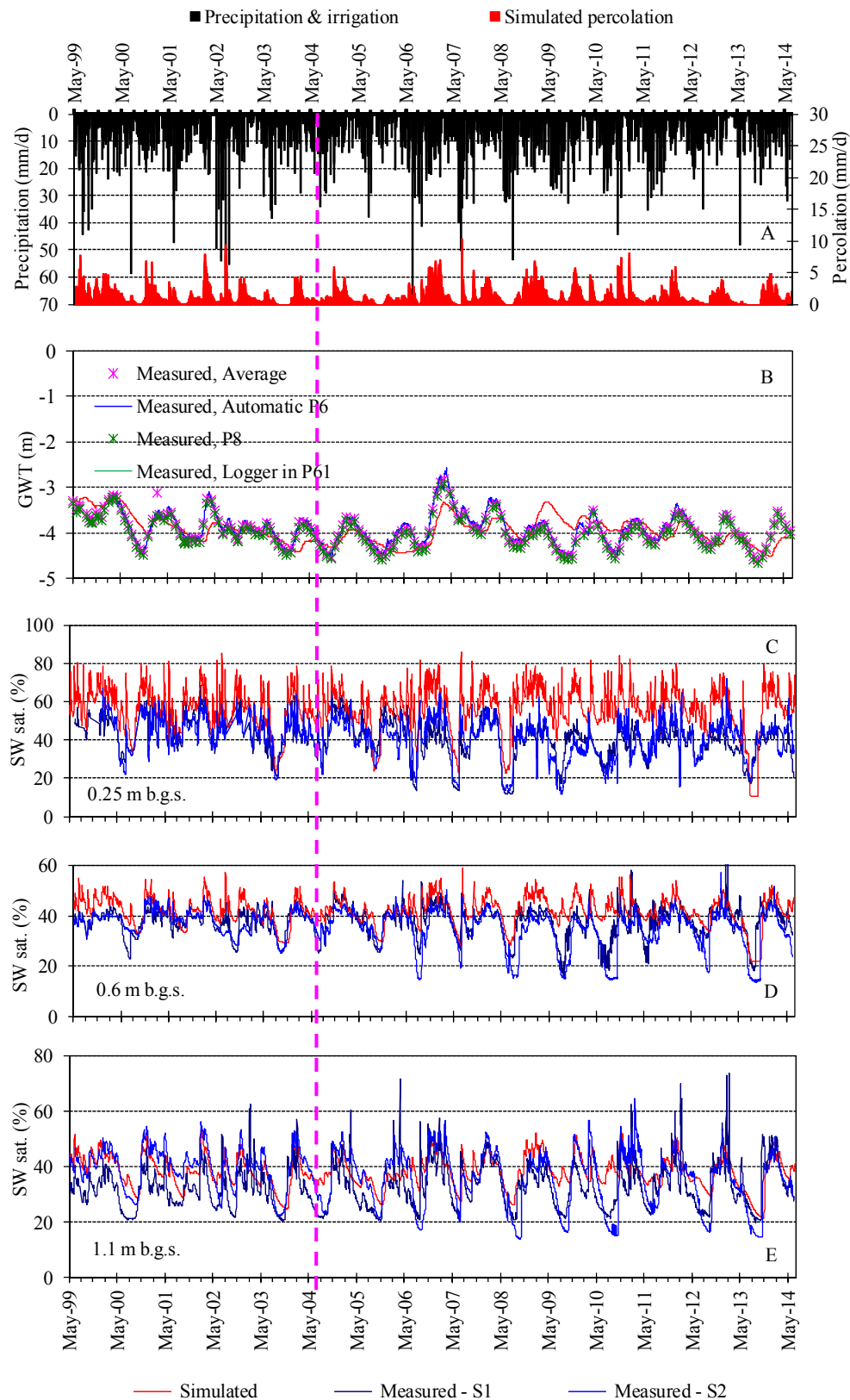


Figure 2.2. Soil water dynamics at Tylstrup: Measured precipitation, irrigation and simulated percolation 1 m b.g.s. (A), simulated and measured groundwater table GWT (B), and simulated and measured soil water saturation (SW sat.) at three different soil depths (C, D and E). The measured data in B derive 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 2014).

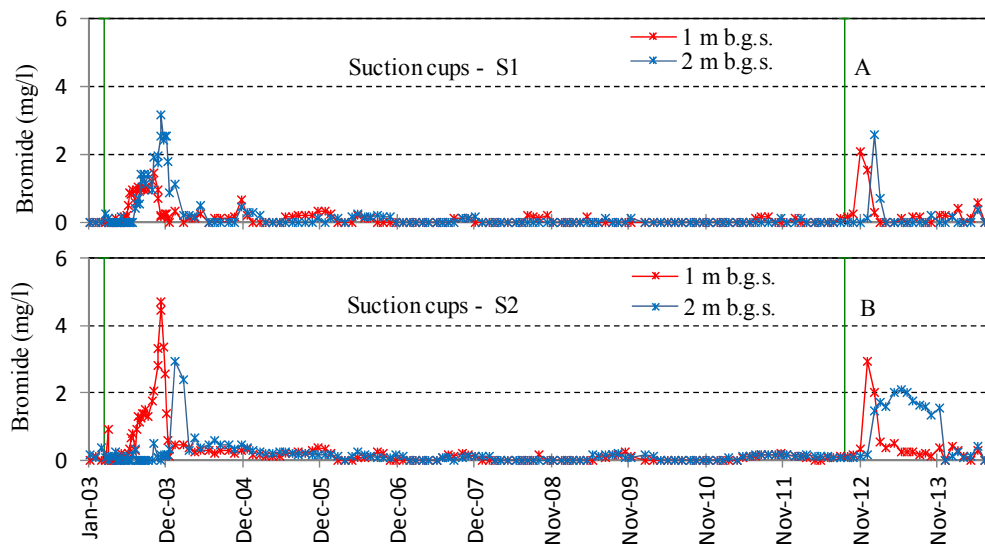


Figure 2.3. Measured bromide concentration in the variably-saturated zone at **Tylstrup**. The measured data derive from suction cups installed 1 m b.g.s. and 2 m b.g.s. at locations S1 (A) and S2 (B) indicated in Figure 2.1. The green vertical lines indicate the dates of bromide applications.

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). Leaching of the bromide applied in March 2003 is evaluated in Barlebo *et al.* (2007). Bromide applied late August 2012 show an expected time delay from the suction cups 1 m b.g.s. to 2 m b.g.s. (Figure 2.3) and in the monitoring wells M3, M4 and M5 (Figure 2.4).

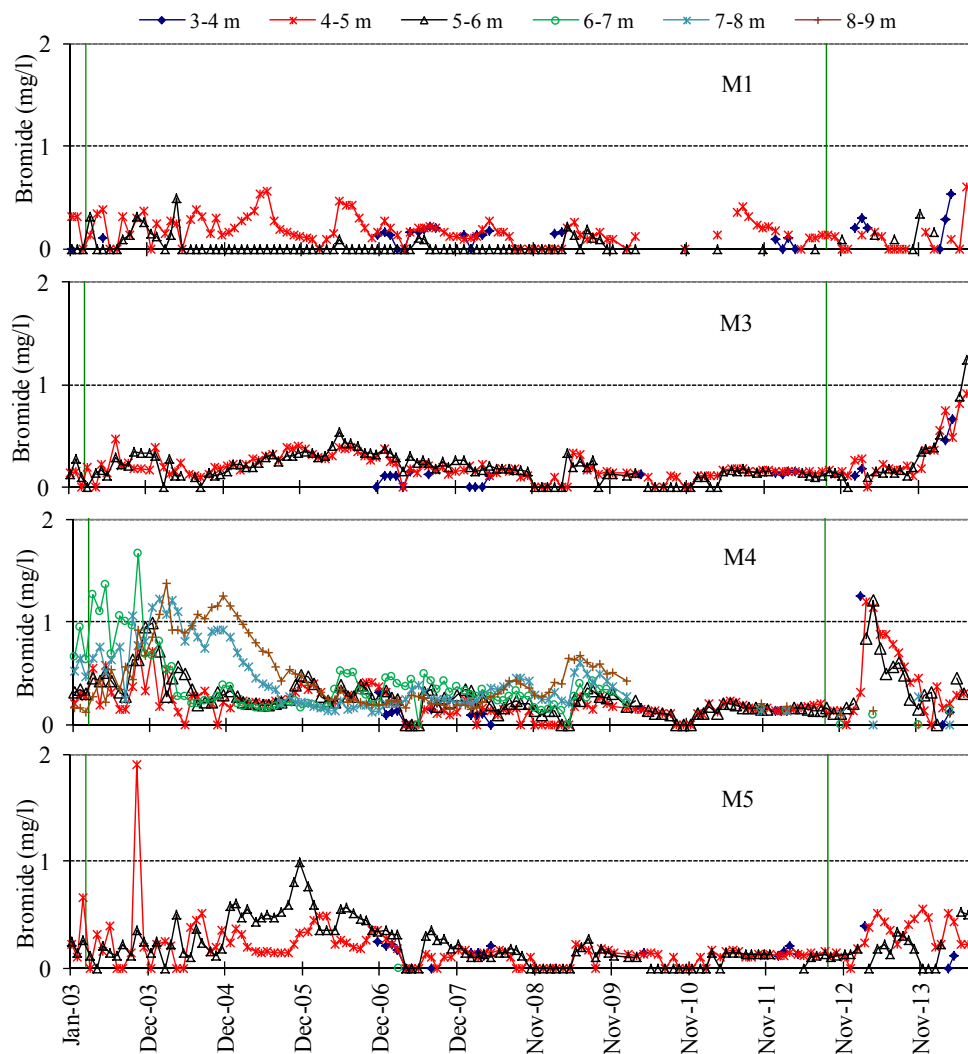


Figure 2.4. Bromide concentration in the groundwater at **Tylstrup**. The data derive from monitoring wells M1 and M3–M5. Screen depth is indicated in m b.g.s. The green vertical lines indicate the dates of bromide applications.

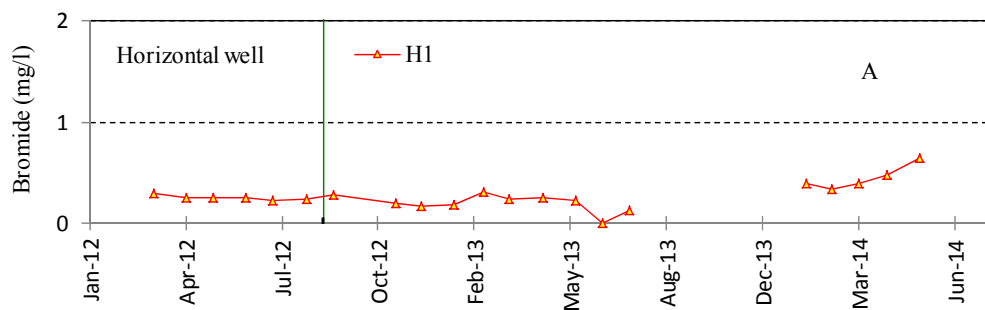


Figure 2.5. Bromide concentration in the groundwater at **Tylstrup**. The data derive from the horizontal monitoring well H1. The green vertical line indicate the date of bromide application.

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, together with precipitation and simulated precipitation, shown 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 2014 are not evaluated in this report and they are not included in Figure 2.6, but the pesticides are shown in Table 2.2

The current report focuses on the pesticide applied from 2012 and onwards, while leaching risk of pesticides applied before 2012 has been evaluated in previous monitoring reports (see http://pesticidvarsling.dk/publ_result/index.html).

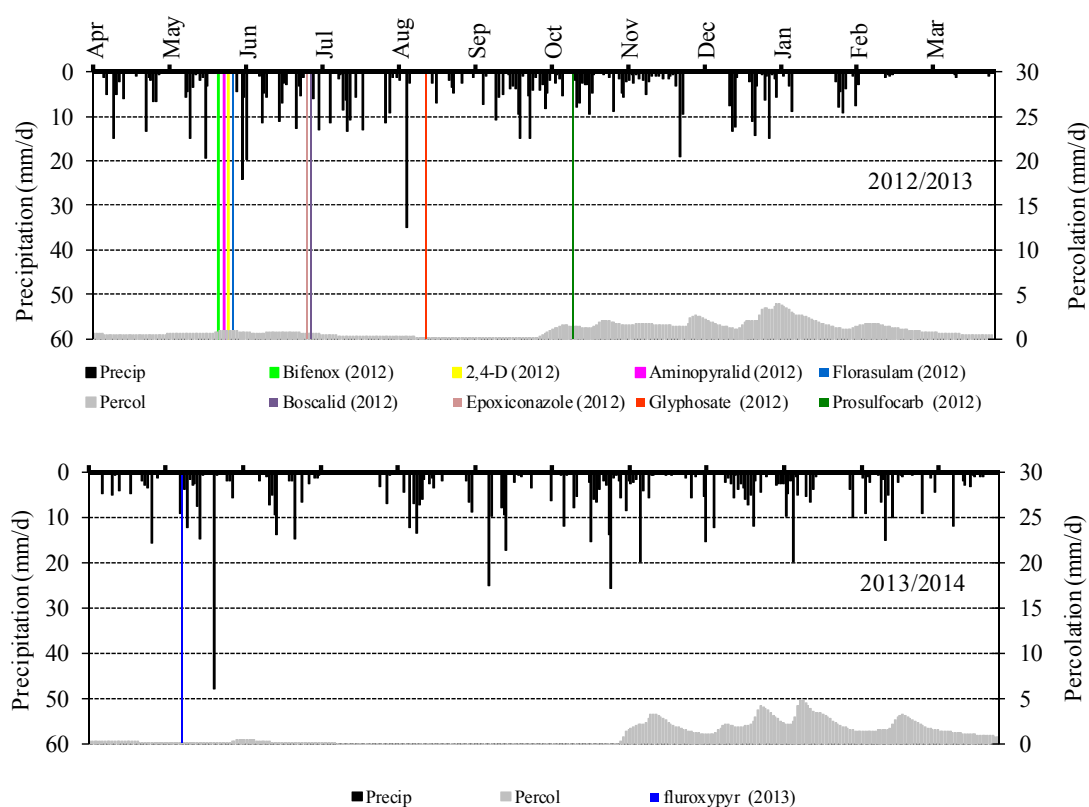


Figure 2.6. Application of pesticides included in the monitoring programme, precipitation and irrigation (primary axis) together with simulated percolation 1 m b.g.s. (secondary axis) at **Tylstrup** in 2012/2013 (upper) and 2013/2014 (lower).

Table 2.2. Pesticides analysed at **Tylstrup**. Precipitation (precip.) and percolation (percol.) are accumulated within the first year (Precip 1st year, Percol 1st year) and first month (Precip 1st month, Percol 1st 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).

Crop	Applied product	Analysed pesticide	Applica. date	End monito.	Y 1 st precip.	Y 1 st percol.	M 1 st precip.	M 1 st 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	Dec 12	958	491	62	12	0.01-0.02**
		PPU-desamino(M)	May 10	Dec 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 14*	934	514	127	43	<0.01
		CGA 108906(M)	Jul 10	Jun 14*	934	514	127	43	0.03-0.12**
		CGA 62826(M)	Jul 10	Jun 14*	934	514	127	43	<0.01-0.02**
	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 14*	852	335	121	22	<0.02
Winter rye 2013	Boxer	Prosulfocarb(P)	Oct 12	Jun 14*	507	285	79	49	<0.01
Potatoes 2014	Maxim 100 FS	CGA 339833(M)	Apr 14	Jun 14*					<0.03
	Fludioxonil (P)	CGA 192155(M)	Apr 14	Jun 14*					<0.01
	Dithane NT Mancozeb (P)	EBIS*** (M)	Jun 14	Jun 14*					<0.02

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

* monitoring continues the following year.

** If difference between S1 and S2.

*** EBIS will be reported in next report.

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 (CGA 62826 and CGA 108906) leached from the root zone (1 m b.g.s.), the latter in average concentrations exceeding 0.1 µg/L (Table 2.2 and Figure 2.7). Both compounds were detected in suction cups 1 m b.g.s. in 2010, 2011, 2012, 2013 and 2014, and the leaching of CGA 108906 slowly ceased in 2014. In the second monitoring year, CGA 108906 was detected 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 2012-2014 the concentrations have fallen below 0.1 µg/L (Figure 2.7).

In the saturated zone, before spraying, neither metalaxyl-M nor CGA 62826 was detected in any samples collected from the wells situated downstream the field.

However, both compounds were detected in samples collected from M1 situated upstream of the field (Figure 2.8). As the tracer test suggested that water sampled in M1 had not infiltrated at the PLAP field, but originated from the upstream neighbouring fields, detections in M1 show that these compounds have leached from previous application occurring at the upstream neighbouring fields, where both metalaxyl and metalaxyl-M have been applied (Brüsch *et al.*, 2013, Appendix 7).

In the period April 2010 to June 2014, CGA 108906 was detected in 81% of the analysed groundwater samples. In 16% of the analysed samples concentrations exceed 0.1 µg/L. Similar to the other compounds, CGA 108906 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, detected 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 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 CGA 108906 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 H1 (Figure 2.7 and 2.8) clearly indicate that the findings originate from the test field.

Metalaxyl-M, CGA 62826 and CGA 108906 were detected in up to 70% of the groundwater samples in 2012-2014, and one of the degradation products, CGA 108906, was detected in 98% of the water samples from the variably-saturated zone.

CGA 108906 was detected 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 market in 2007 as metalaxyl-M with a maximum allowed dosage of 77.6 g a.i./ha.

Since 2006 metalaxyl-M has been applied to 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.

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.

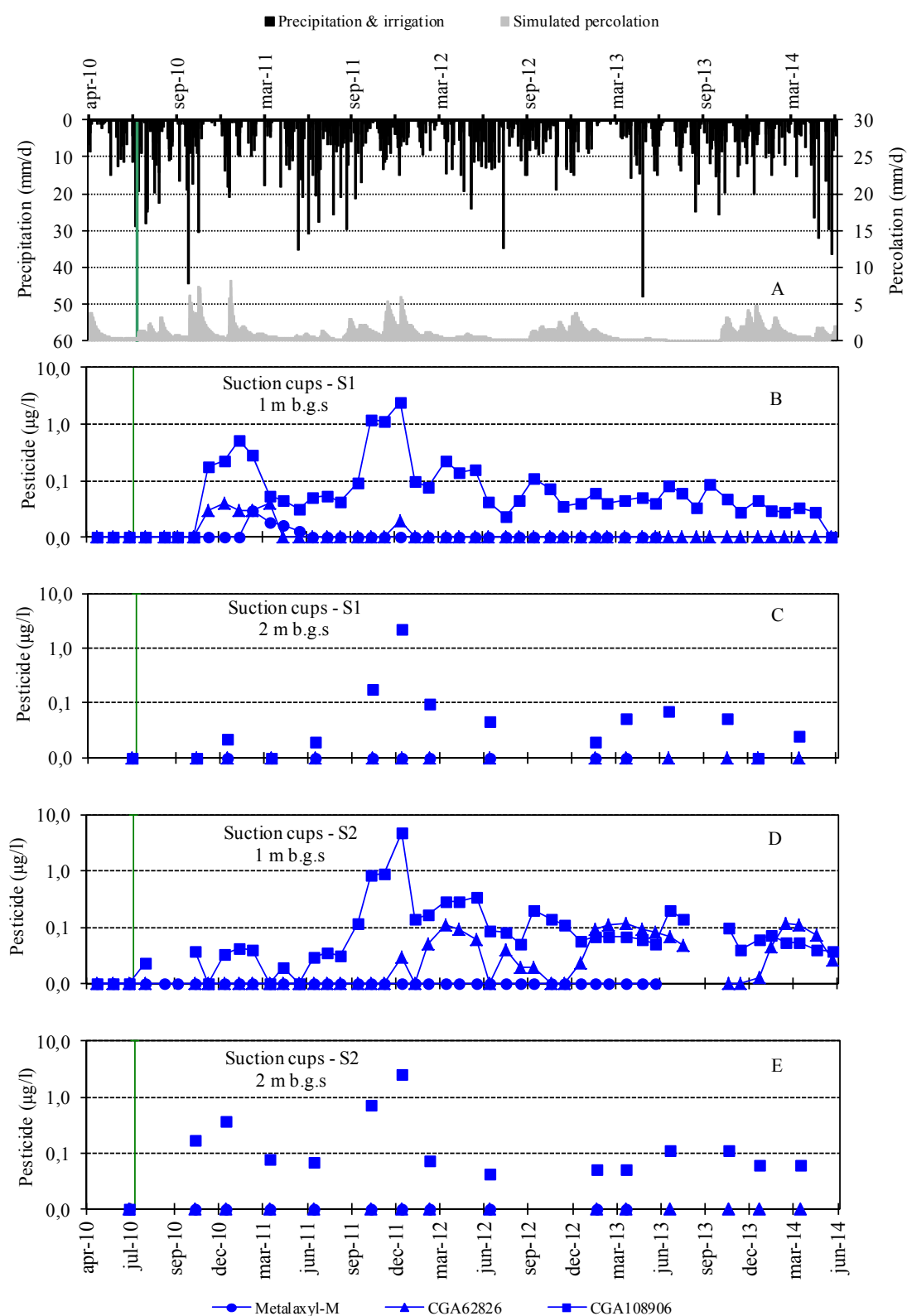


Figure 2.7. Precipitation, irrigation and simulated percolation 1 m b.g.s. (A) together with measured concentration of metalaxyl-M, CGA 62826 and CGA 108906 (µg/L) in suction cups installed at location S1 at 1 m b.g.s. (B) and 2 m b.g.s. (C) and location S2 at 1 m b.g.s. (D) and 2 m b.g.s. (E) at **Tylstrup**. The green vertical line indicates the date of pesticide application.

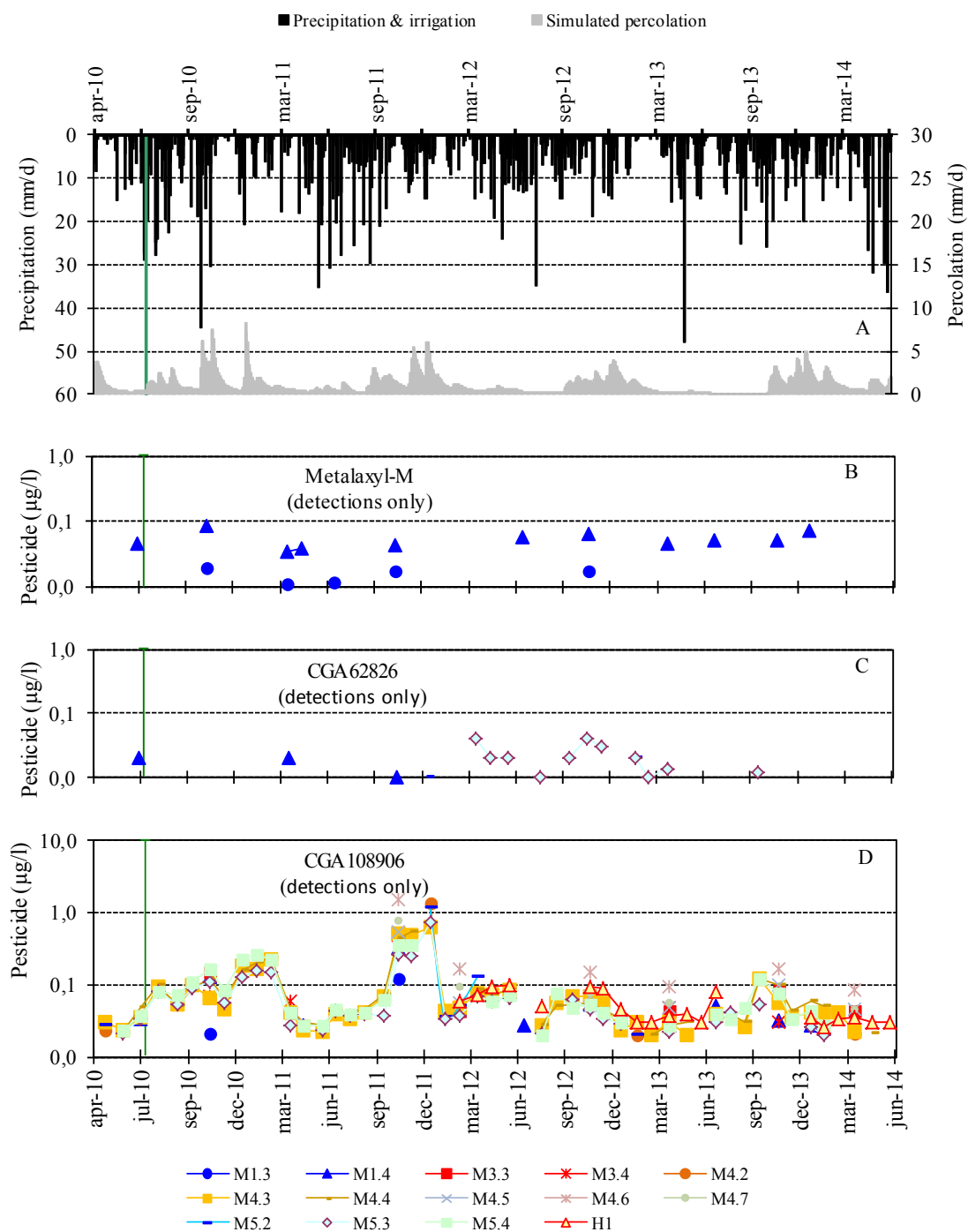


Figure 2.8. Precipitation, irrigation and simulated percolation 1 m b.g.s. (A) together with measured concentration of metalaxyl-M (B), CGA 62826 (C) and CGA 108906 (D) ($\mu\text{g/L}$) in horizontal and monitoring wells at **Tylstrup**. The green vertical line indicates the date of pesticide application.

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 had been no findings in groundwater or in the variably-saturated zone in Tylstrup when 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 detected in one sample (0.03 µg/l) in the variably-saturated zone.

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

Fludioxonil was applied on potatoes in April 2014. Fludioxonil and the two degradation products were not detected in this monitoring period.

Mancozeb was applied on potatoes in June 2014. The degradation product from mancozeb, EBIS, will be reported in the next report.

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 3.1). The field covers a cultivated area of 2.4 ha (135 x 180 m) and is practically flat. A windbreak borders the eastern side of the field. 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 field 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 2013-2014 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.

The field was ploughed on 6 April 2013. A crop of pea (cv. Alvesta) was sown on 14 April and emerged on 26 April. The herbicides pendimethalin and bentazone were applied twice (on 7 and 16 May 2013) followed by pirimicarb on 16 July. Only bentazone was included in the monitoring programme. Irrigation of the pea was done twice using 30 mm on 6 June and 9 July. Due to the weather conditions the western half of the field was harvested on 7 August and the eastern half on 14 August. The total yield of peas was 38.8 hkg/ha of peas (86% dry matter). A total amount of 30.1 hkg/ha of straw (100% dry matter) was shredded at the days of harvest.

The field was ploughed on 26 March. Planting of potatoes took place on 15 April 2015. At deliverance the tubers had been treated with the fungicide imazalil. Yet the leaching of imazalil was not monitored. Fludioxonil, a fungicide, was sprayed onto the potato seed tubers during planting. Here it was chosen to include its degradation products CGA 339833 and CGA 192155 in the monitoring programme. Final ridges were formed during the planting. Glyphosate and clomazone, both herbicides, were applied on 30 April. Only clomazone and its degradation product FMC 65317 were included in the monitoring programme. An additional herbicide, rimsulfuron, was used on 6 May and 27 May, but not added to the monitoring programme. Fungicides applied from June to August will be detailed in next years report. The field was irrigated 20 mm on 14 June as well as 25 mm on 19 June.

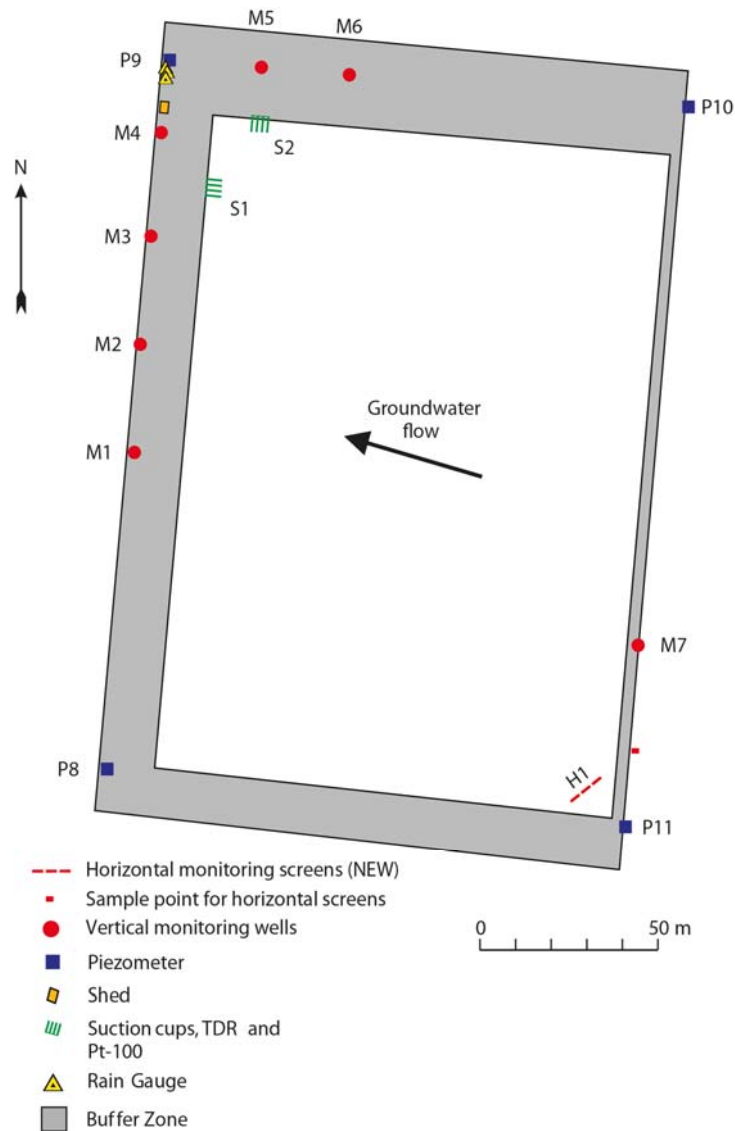


Figure 3.1. Overview of the **Jyndevad** field. The innermost white area indicates the cultivated land, while the grey area indicates the surrounding buffer zone. The positions of the various installations are indicated, as is the direction of groundwater flow (by an arrow). Pesticide monitoring is conducted monthly and half-yearly from selected horizontal and vertical monitoring screens and suction 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 field 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 2014 and to establish an annual water balance.

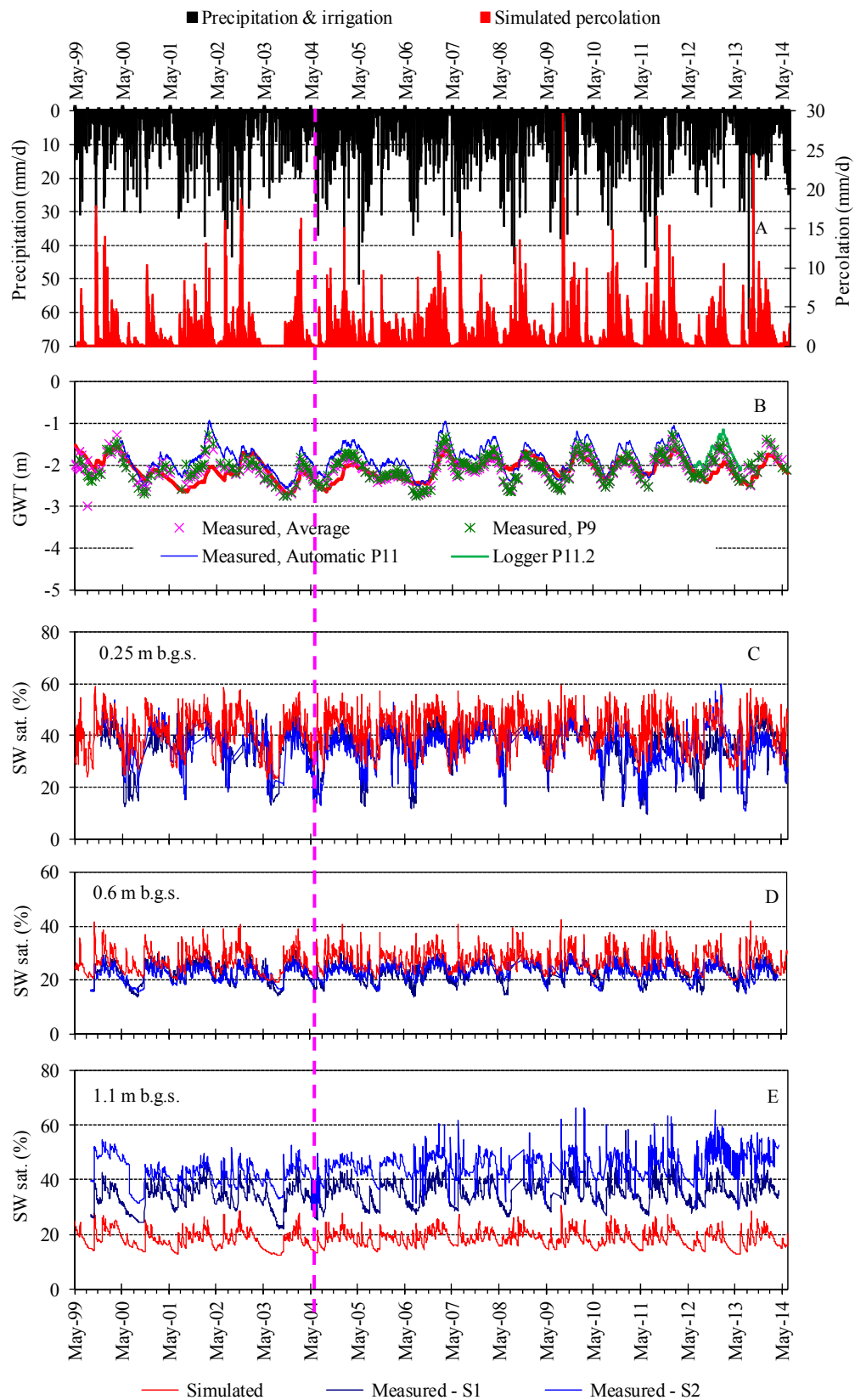


Figure 3.2. Soil water dynamics at **Jynde vad**: Measured precipitation, irrigation and simulated percolation 1 m b.g.s. (A), simulated and measured groundwater table, GWT) (B), and simulated and measured soil water saturation (SW sat.) at three different soil depths (C, D and E). The measured data 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 3.1). The broken vertical line indicates the beginning of the validation period (July 2004-June 2014).

Compared with the setup in Brüsich *et al.* (2013b), a year of validation was added to the MACRO-setup for the Jyndevad field. The setup was hereby calibrated for the monitoring period May 1999-June 2004, and validated for the monitoring period July 2004-June 2014. 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 failure 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 2013-June 2014, was characterised by having high precipitation, low-medium simulated actual evapotranspiration, low irrigation values and high groundwater recharge. Monthly precipitation in the latest hydraulic year was characterised as being medium to high with September having the highest precipitation measured for this month since the monitoring began. The month of July, however, turn out to have the lowest precipitation ever monitored for this month with only 26 mm of precipitation (Appendix 4) why artificial irrigation (30 mm) was needed with pea. Like at Tylstrup artificial irrigation was also needed on potatoes twice (20 mm and 25 mm) in June 2014. Continuous percolation 1 m b.g.s. was simulated for this hydraulic year.

Table 3.1. Annual water balance for **Jynde vad** (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⁾
01.07.99–30.06.00	995	1.073	29	500	602
01.07.00–30.06.01	995	810	0	461	349
01.07.01–30.06.02	995	1.204	81	545	740
01.07.02–30.06.03	995	991	51	415	627
01.07.03–30.06.04	995	937	27	432	531
01.07.04–30.06.05	995	1.218	87	578	727
01.07.05–30.06.06	995	857	117	490	484
01.07.06–30.06.07	995	1.304	114	571	847
01.07.07–30.06.08	995	1.023	196	613	605
01.07.08–30.06.09	995	1.078	84	551	610
01.07.09–30.06.10	995	1.059	80	530	610
01.07.10–30.06.11	995	1.070	92	554	607
01.07.11–30.06.12	995	1.159	30	490	699
01.07.12–30.06.13	995	991	60	478	572
01.07.13–30.06.14	995	1.104	75	485	693

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 Jynde vad. 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). The bromide applied in May 2012 showed the same response time in the temporary saturated zone as in April 2003 (Figure 3.3), but the response time was quicker in the downstream wells M1, M2 and M4 (Figure 3.4). In the upstream wells M5 and M7 no bromide response was observed (Figure 3.1 and 3.4). The bromide concentration in the horizontal well decreased from 1.98 mg/l in October 2012 to approx. 0.1 mg/l in June 2014 (Figure 3.5).

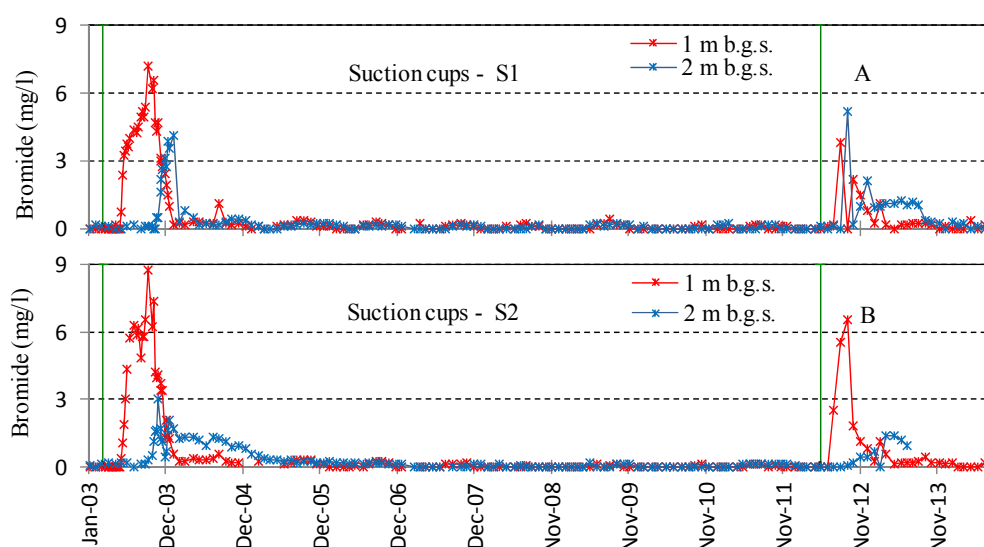


Figure 3.3. Bromide concentration in the variably-saturated zone at **Jynde vad**. The measured data derive from suction cups installed 1 m b.g.s. (upper) and 2 m b.g.s. (lower) at locations S1 and S2 (Figure 3.1). The green vertical lines indicate the dates of bromide applications.

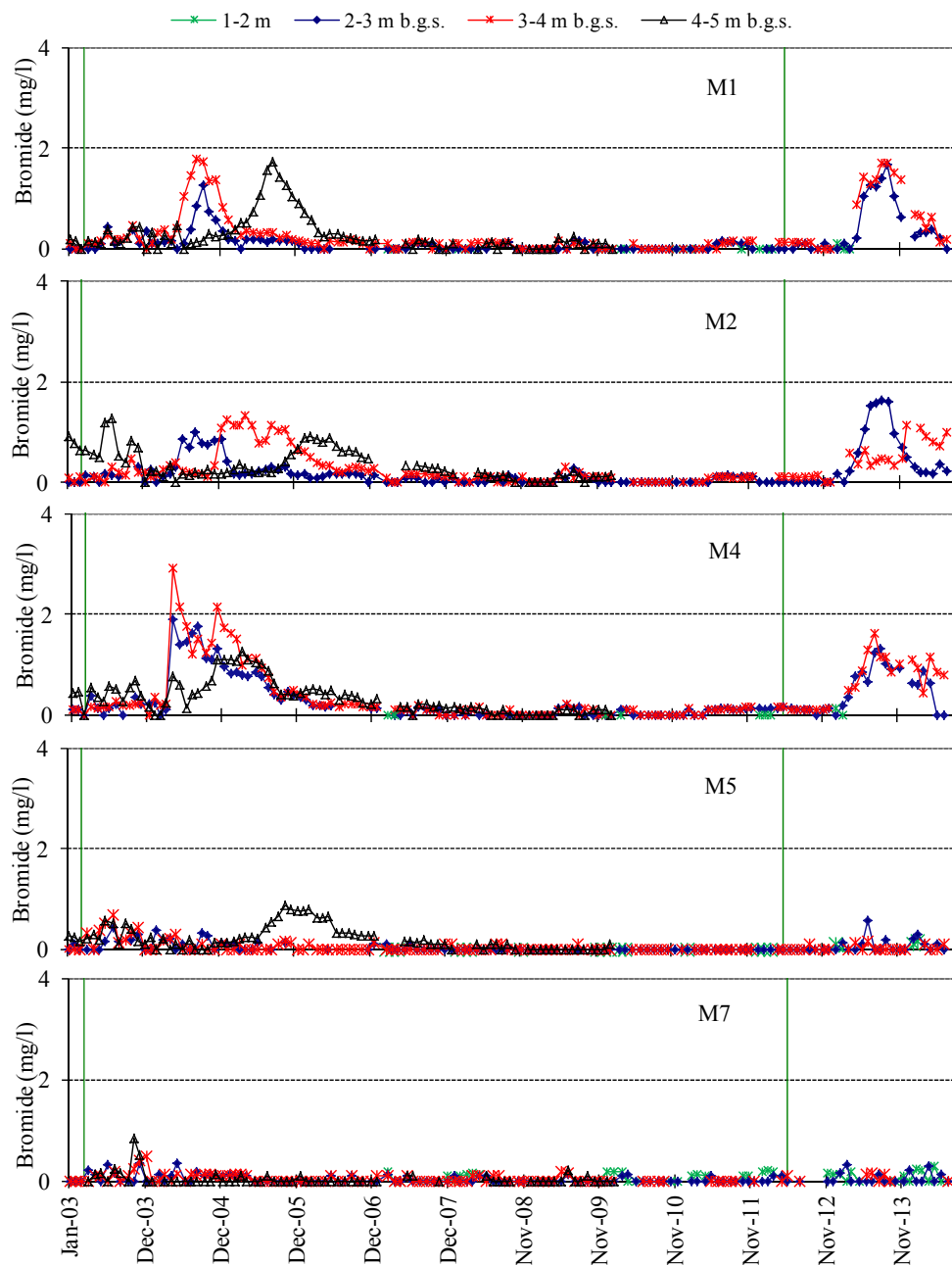


Figure 3.4. Bromide concentration in the groundwater at **Jyndeved**. The data derive from monitoring wells M1, M2, M4, M5 and M7. Screen depth is indicated in m b.g.s. The green vertical lines indicate the dates of bromide applications.

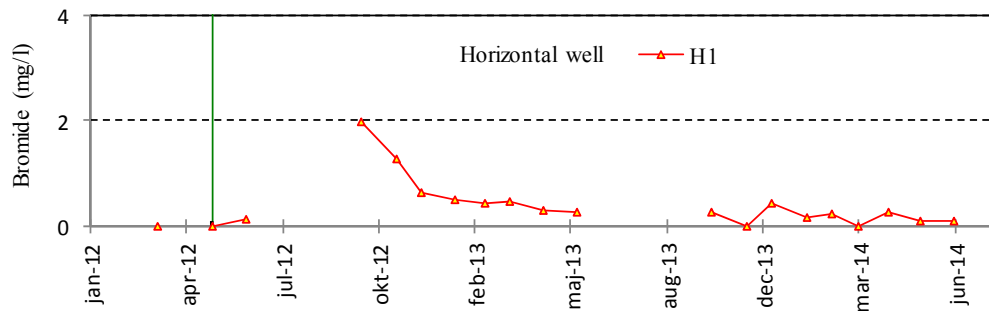


Figure 3.5. Bromide concentration in the groundwater at **Jyndeved**. The data derive from the horizontal monitoring well H1. The green vertical line indicates the date of bromide application.

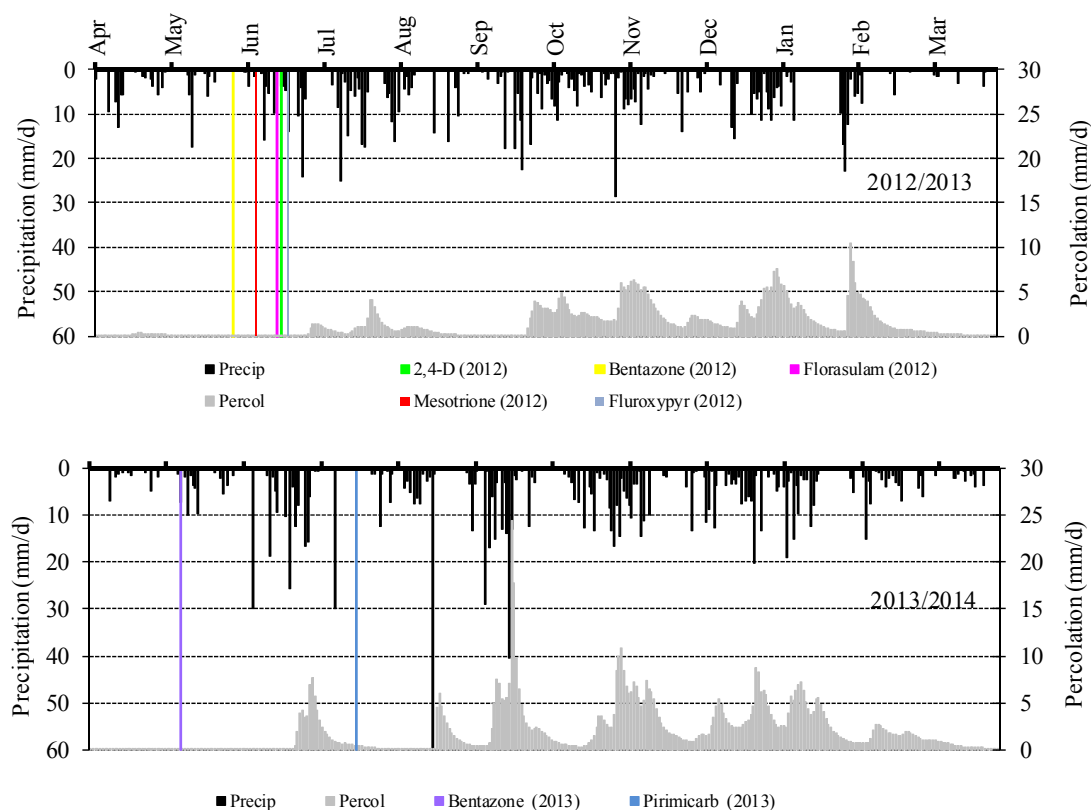


Figure 3.6. Application of pesticides included in the monitoring programme, precipitation and irrigation (primary axis) together with simulated percolation 1 m b.g.s. (secondary axis) at **Jynde vad** in 2012/2013 (upper) and 2013/2014 (lower).

3.2.3 Pesticide leaching

Monitoring at Jynde vad 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 2014 are not evaluated in this report.

The current report focuses on the pesticides applied from 2012 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).

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 not possible to extract sufficient water from S2 to perform all pesticide analyses. For some of the compounds (metalaxyl-M, PPU and PPU-desamino) there was not sufficient data to calculate weighted leachate concentration, why the reported 2010 values in Table 3.2 refers to suction cups S1 only. For the same reason concentration of CGA 62826 and CGA 108906 in S2 was not measured in S2 during the first months after applications.

Table 3.2. Pesticides analysed at **Jynde vad**. 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	Analysed pesticide	Applica. date	End monito.	Y 1 st precip.	Y 1 st percol.	M 1 st precip.	M 1 st 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 13	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	Jun 12	1160	592	137	13	0.02 ¹⁾
		PPU-desamino(M)	Jun 10	Jun 12	1160	592	137	13	<0.01 ¹⁾
	Ridomil Gold	Metalaxyl-M(P)	Jul 10	Jun 14*	1073	613	161	41	0.02 ¹⁾
	MZ Pepite	CGA108906(M)	Jul 10	Jun 14*	1073	613	161	41	0.37-0.6**
		CGA62826(M)	Jul 10	Jun 14*	1073	613	161	41	0.16-0.19**
Spring barley 2011	DFF	Diflufenican(P)	Apr 11	Jun 13	1315	742	126	3	<0.01
		AE-05422291(M)	Apr 11	Jun 13	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 14*	993	512	109	11	<0.01
	Callisto	AMBA(M)	Jun 12	Jun 14*	993	512	109	11	<0.01
	Callisto	MNBA(M)	Jun 12	Jun 14*	993	512	109	11	<0.01
	Fighter 480	Bentazone(P)	May 12	Jun 14*	994	513	114	2	0.04-0.22**
Peas 2013	Fighter 480	Bentazone(P) ²⁾	May 13	Jun 14*	1174	702	84	1	0.02-0.16**
Potatoes 2014	Comand CS	Clomazone(P)	Apr 14	Jun 14*	224	40	85	17	<0.01
		FMC 65317(M)	Apr 14	Jun 14*	224	40	85	17	<0.02
	Maxim 100 FS	CGA 339833(M)	Apr 14	Jun 14*	-	-	-	-	<0.01
	(Fludioxonil P)	CGA 192155(M)	Apr 14	Jun 14*	-	-	-	-	<0.03

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

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

²⁾Bentazone applied on 7 May and 16 May 2013.

* monitoring continues the following year.

** if difference between S1 and S2.

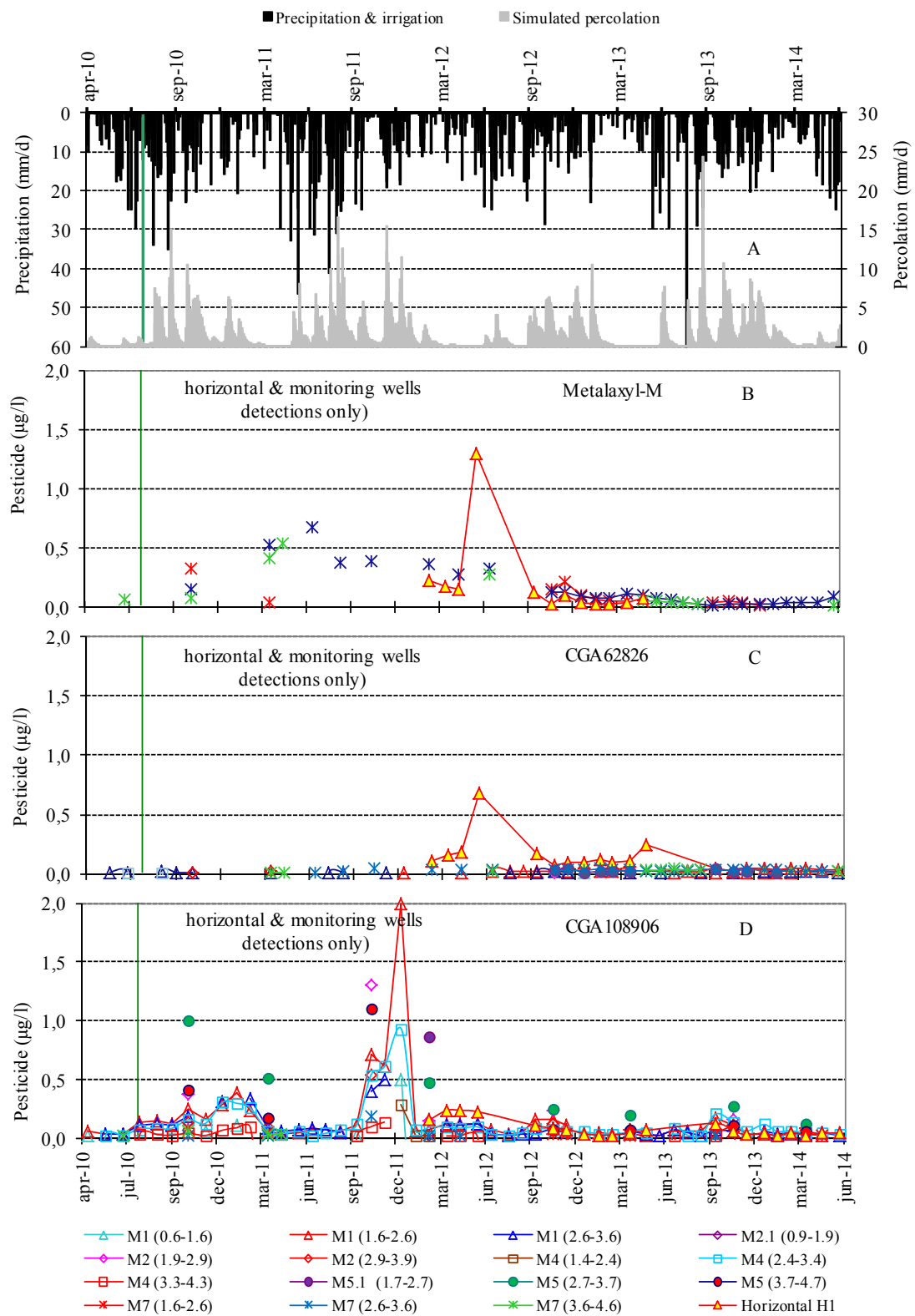


Figure 3.7. Precipitation, irrigation and simulated percolation 1 m b.g.s. in Jydevad. (A) together with measured concentrations (µg/L) in downstream (M1, M2, M4 and H1) and upstream horizontal and monitoring wells (M7) of metalaxyl-M (B), CGA 62826 (C) and CGA 108906 (D) at Jydevad. The numbers in parentheses indicate the depths of the analysed 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 CGA 62829 and CGA 108909 leached from the root zone (1 m b.g.s.) - the two latter in average concentrations exceeding 0.1 µg/L (Table 3.2, Figure 3.7 and Figure 3.8). Both degradation products were detected in decreasing concentrations in water from suction cups 1 m b.g.s. at the end of the last monitoring period, indicating that leaching was ceasing.

Results from the saturated zone suggested that previous application occurring at upstream neighbouring fields also have induced leaching to the groundwater of metalaxyl-M, CGA 62826 and CGA 108906. 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). CGA 108906 was also detected 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 field, but originated from the upstream neighbouring fields, where metalaxyl-M have also been applied (Brüsch et al., 2013).

The two degradation products CGA 62826 and CGA 108906 were detected in the monitoring period 2010–June 2014 in approximately 75% of all samples from the variably-saturated zone, and in up to 74% of all groundwater samples.

The background concentration of CGA 108906, detected 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 field 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 detected in 21 analysed samples between March 2012 and June 2014 in concentrations from 0.03-0.24 µg/L (Figure 3.7D). The findings in mixed water 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 concentrations reaching 0.68 µg/L, but it was not detected in water from the downstream groundwater monitoring wells. Metalaxyl-M was detected in 12 water samples, collected from the horizontal well H1, in concentrations reaching 1.3 µg/L in June 2012. CGA 62826 was only detected in low concentrations in water from the vertical groundwater wells, whereas it was detected in concentrations between 0.11 µg/L and 0.68 µg/L in water from H1 in the period March 2012 to June 2012. In the following period (July 2012 to June 2014) CGA 62826 was detected in all 21 analysed 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 market 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 three 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.

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 be 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. This is an assumption not corresponding to the regulatory assessment, reporting the final endpoints for DT_{50} to be less than 18 days (Danish EPA, 2007).

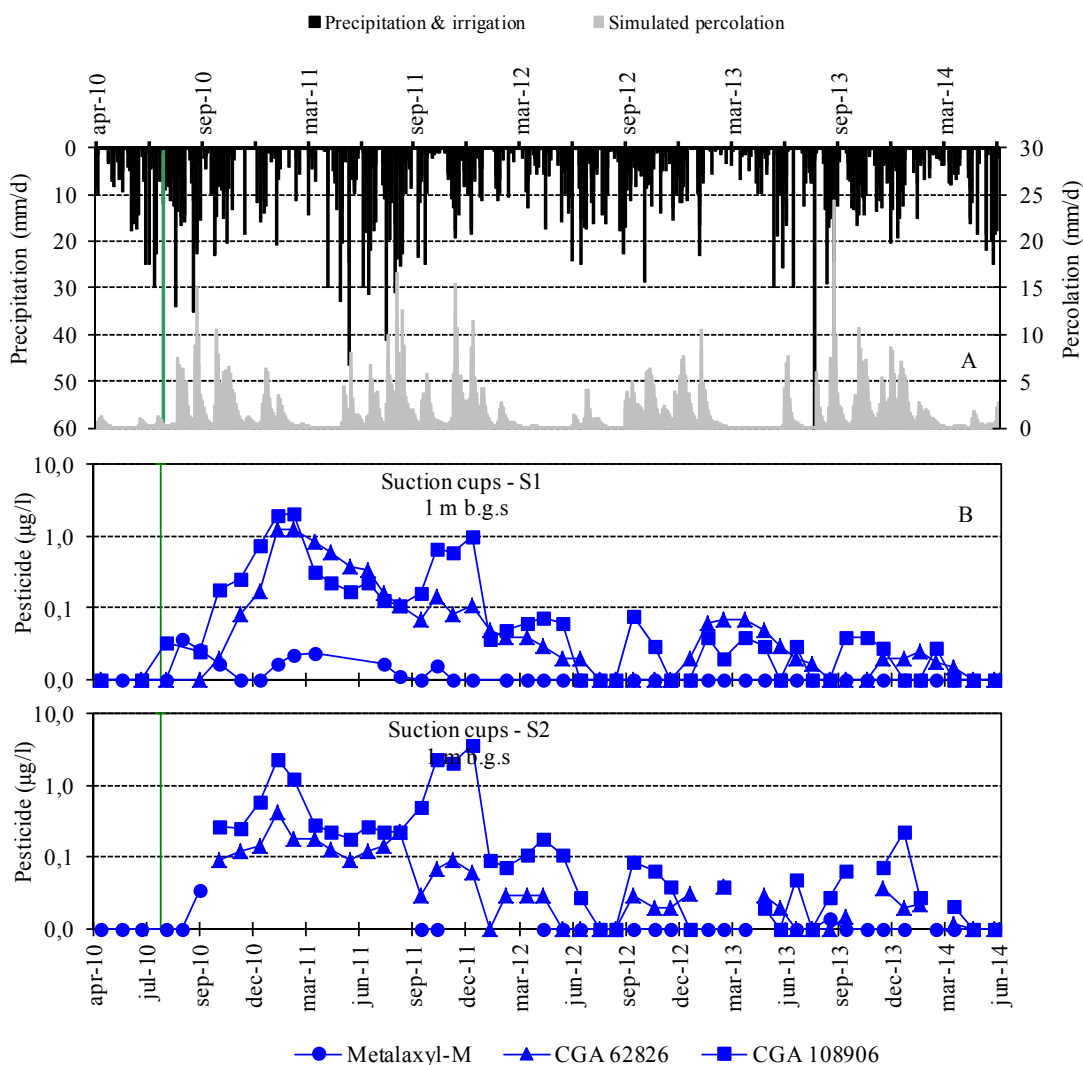


Figure 3.8. Precipitation, irrigation and simulated percolation 1 m b.g.s. (A) together with measured concentrations of Metalaxyl-M, CGA 62826 and CGA 108906 at Jyndeved. The green vertical line indicates the date of pesticide application.

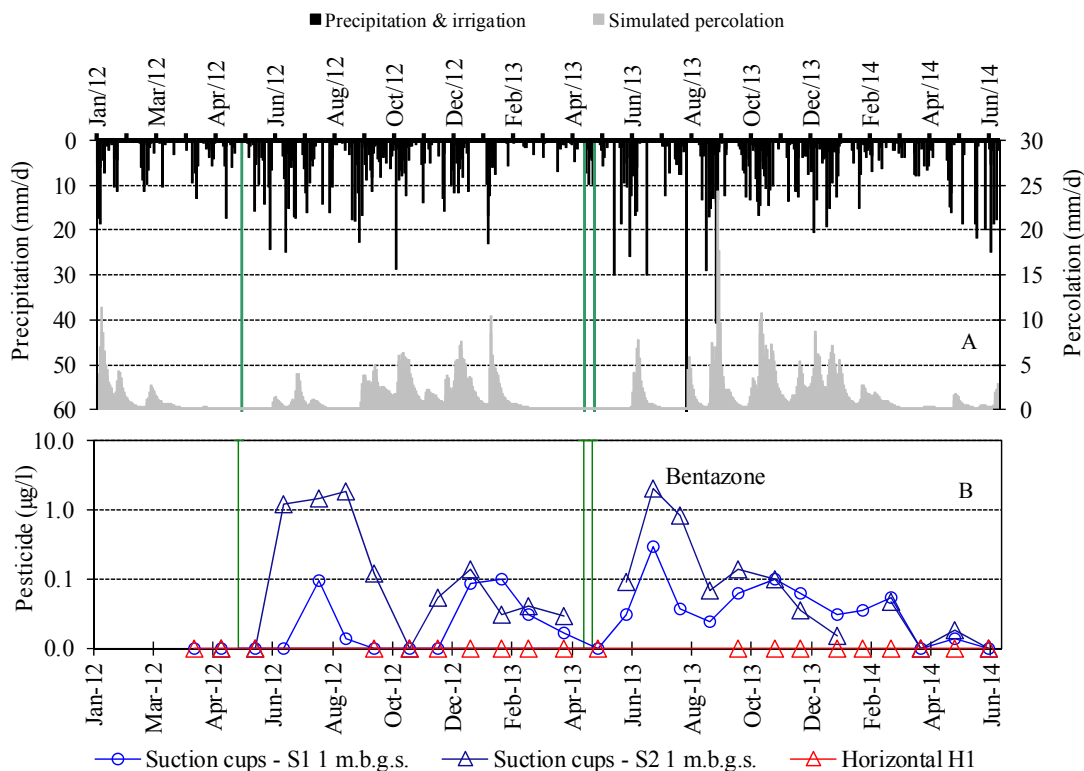


Figure 3.9. Precipitation, irrigation and simulated percolation 1 m b.g.s. (A) together with measured concentrations of bentazone in suction cups S1 and S2 and horizontal well H1 at **Jynde vad**. The green vertical lines indicate the dates of bentazone application.

After the application of bentazone on maize in May 2012, bentazone was not detected in any of the samples from the vertical monitoring wells, whereas 0.01 µg/L was detected in H1 on 14 February 2013. However, bentazone was detected frequently in samples from suction cups in the variably-saturated zone, 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 0.24 µg/L.

Bentazone was again applied on peas in May 2013, and again bentazone was detected frequently in the variably-saturated zone, in average concentrations between 0.02 and 0.16 µg/L (Figure 3.9). Figure 3.9 show that bentazone was found in low concentration in the variably-saturated zone before the applications in May 2013, but also that the concentration increased to 1.4 µg/L in October 2013, after which the concentrations decreased. As after the application in May 2013, bentazone was not found in any of the 91 analysed groundwater samples from vertical and horizontal wells.

Diffenican, 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 mesotrione nor two of its degradation products, AMBA and MNBA, were detected in water samples from the variably-saturated or saturated zone in the monitoring period.

Clomazone, mancozeb and fludioxonil were applied on potatoes in April and June 2014.

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 detected 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 field 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 2012-2014 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.

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 on 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.

Very few wheat plants survived the winter, likely due to a combination of the late sowing and harsh winter conditions. Therefore, the winter wheat was replaced by spring barley (cv. Quenc) sown on 3 May 2013, emerging on 16 May. The herbicides ioxynil and bromoxynil was sprayed on the spring barley on 30 May 2013, and both were included in the monitoring programme. On 25 June the fungicide azoxystrobin was applied. Azoxystrobin and its degradation product CyPM were included in the monitoring.

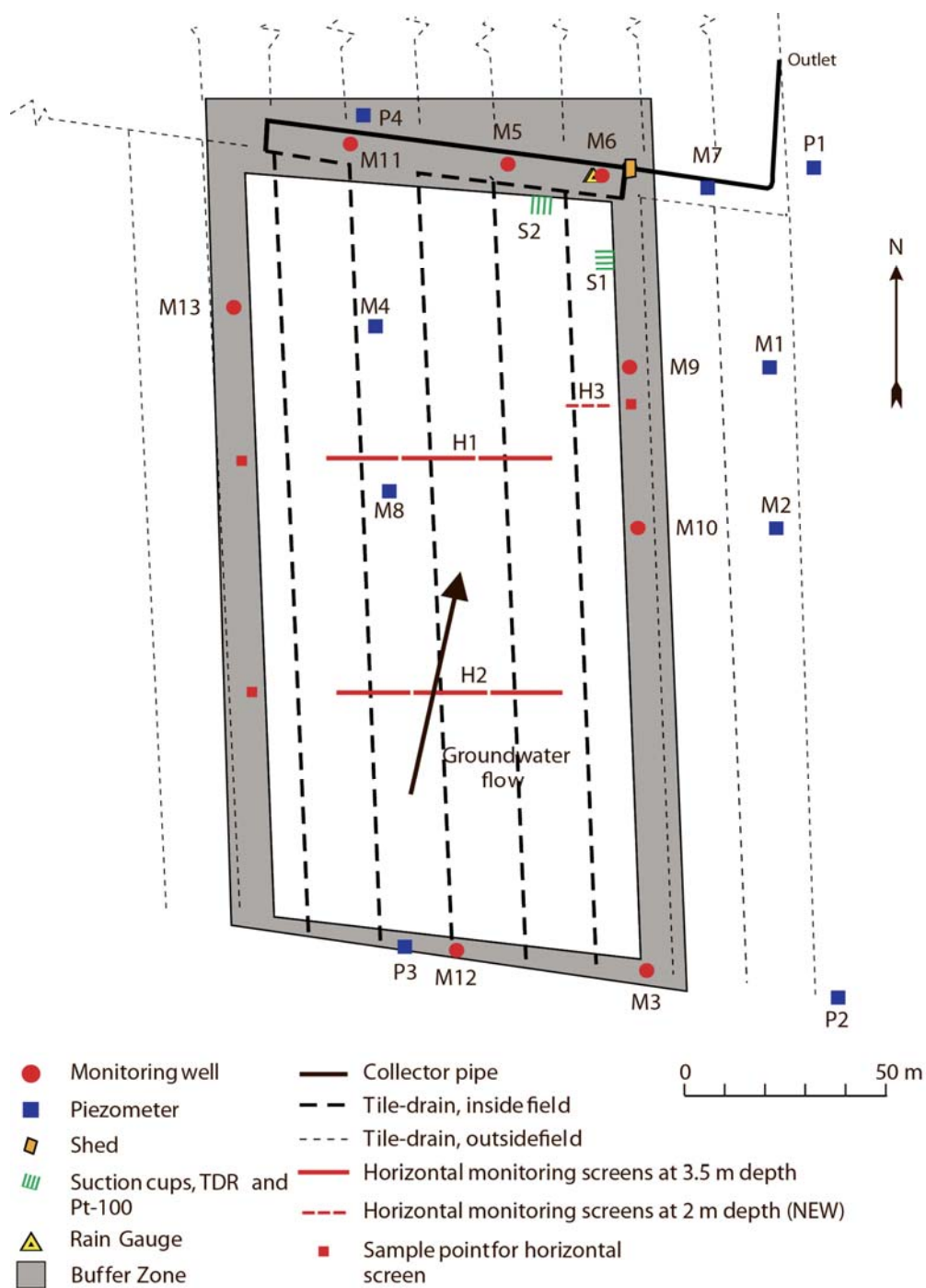


Figure 4.1. Overview of the **Silstrup** field. The innermost white area indicates the cultivated land, while the grey area indicates the surrounding buffer zone. The positions of the various installations are indicated, as is the direction of groundwater flow (by an arrow). Pesticide monitoring is conducted 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 Brüschi *et al.* (2013b), a year of validation was added to the MACRO setup for the Silstrup field. The setup was hereby calibrated for the monitoring period May 1999-June 2004 and validated for the monitoring period July 2004-June 2014. 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. 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 Brüschi *et al.* (2015), 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 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 soil in 60 and 110 cm depth as being more dry during the summer period than actually measured by the upper TDR probes (Figure 4.2E and 4.2F). This could be the cause of the approximately one week delay in the simulated initiation of the drainage period in October 2013 compared to the measured.

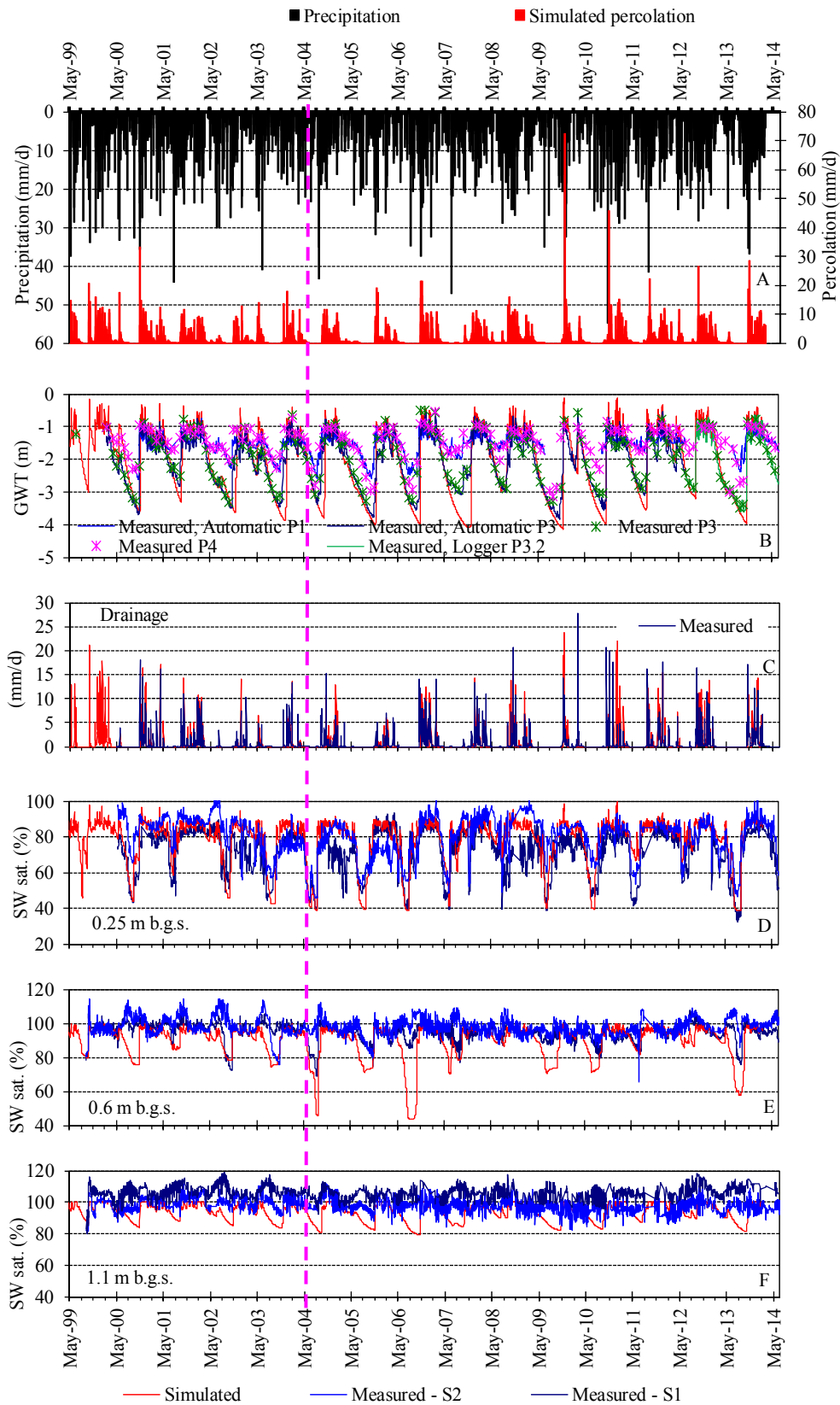


Figure 4.2. Soil water dynamics at **Silstrup**: Measured precipitation and simulated percolation 1 m b.g.s. (A), simulated and measured groundwater table, GWT (B), simulated and measured drainage (C), and simulated and measured soil water saturation (SW sat.) at three different soil depths (D, E and 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 2014).

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⁾
01.07.99–30.06.00 ¹⁾	976	1.175	457	–	443	275 ⁴⁾
01.07.00–30.06.01	976	909	413	217	232	279
01.07.01–30.06.02	976	1.034	470	227	279	338
01.07.02–30.06.03	976	879	537	81	74	261
01.07.03–30.06.04	976	760	517	148	97	94
01.07.04–30.06.05	976	913	491	155	158	267
01.07.05–30.06.06	976	808	506	101	95	201
01.07.06–30.06.07	976	1.150	539	361	307	249
01.07.07–30.06.08	976	877	434	200	184	242
01.07.08–30.06.09	976	985	527	161	260	296
01.07.09–30.06.10	976	835	402	203	225	230
01.07.10–30.06.11	976	1.063	399	172	569	492
01.07.11–30.06.12	976	1.103	432	230	321	444
01.07.12–30.06.13	976	1.020	469	249	333	302
01.07.13–30.06.14	976	1.067	558	275	335	234

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 measurements were lacking, simulated drainage 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 14 years, the recent hydraulic year July 2013–June 2014 was characterised by having high precipitation, the highest simulated actual evapotranspiration, and the second highest measured drainage. Precipitation of this year was characterised by July being the driest and October the wettest since the monitoring started and a very wet September–February (Appendix 4). Due to this precipitation pattern continuous percolation was simulated for the whole hydrological year (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 as compared to the other hydrological years (Figure 4.2B and 4.2C). Compared to the hydrological year July 2012–June 2013, 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.

As described earlier, the simulated drainage (Figure 4.2C) captured the measured drainage quite well except for the initiation of the continuous drainage period in October 2013. This also included drainage measured in connection with snowmelt.

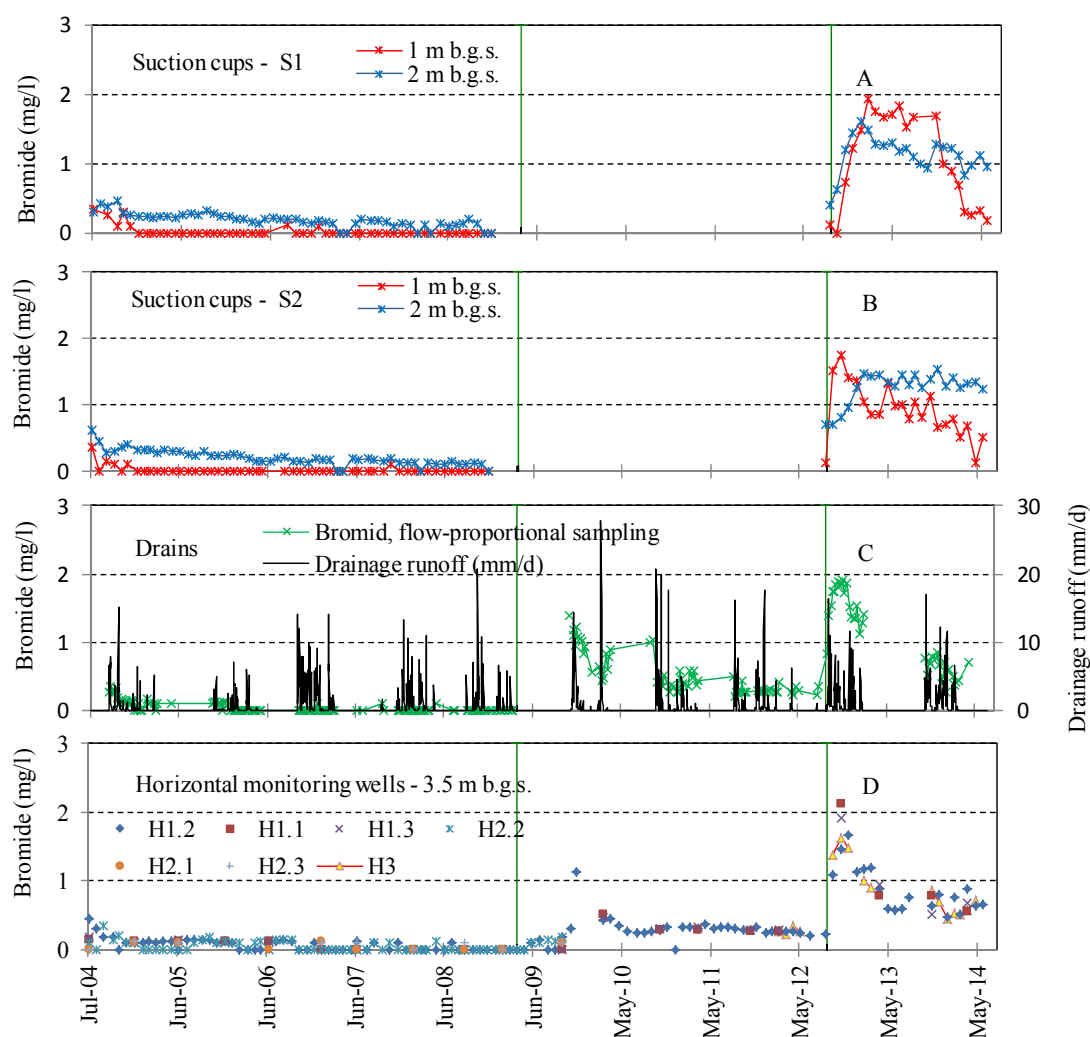


Figure 4.3. Bromide concentration at **Silstrup**. A and B refer to suction cups located at S1 and S2 (see Figure 4.1). The bromide concentration is also shown for drainage runoff (C) and the horizontal monitoring wells H1, H2 and H3 (D). From January 2009 to September 2012, bromide measurements in the 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 potassium bromide was done, 30.5 kg/ha.

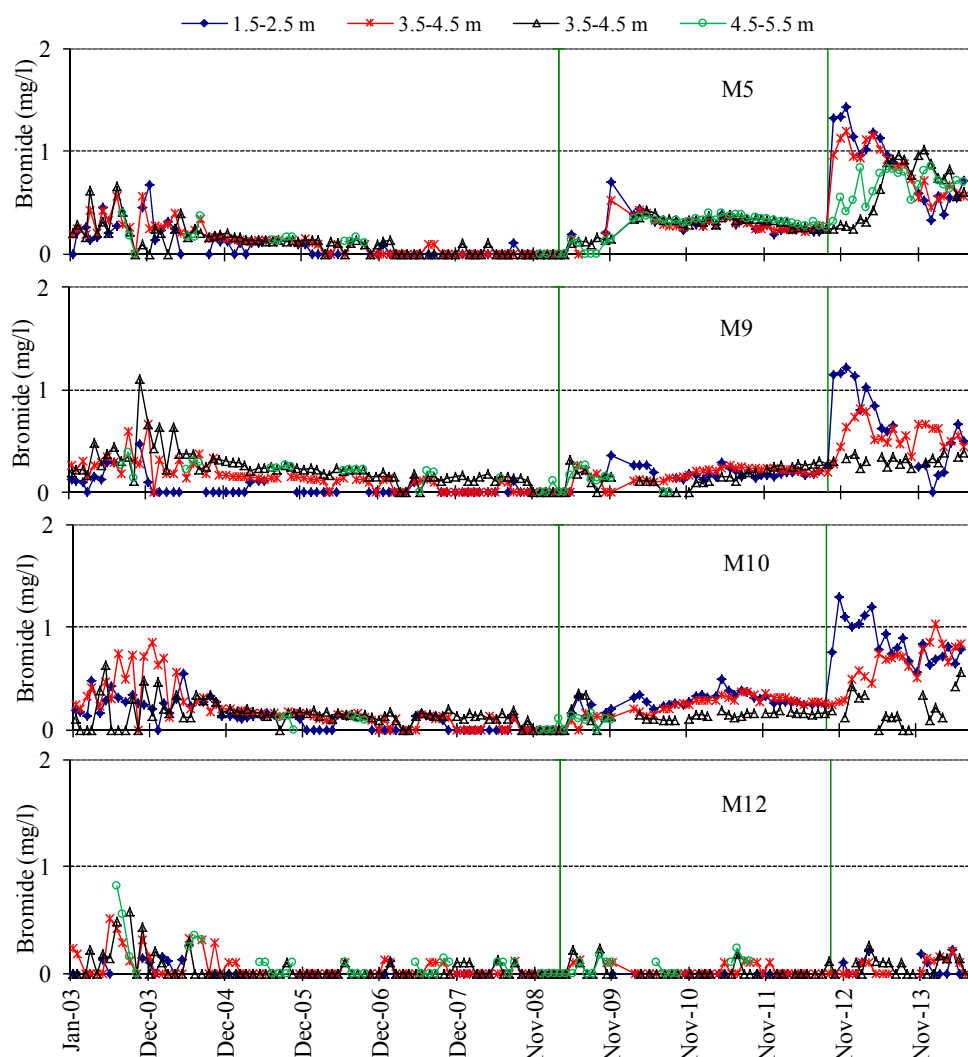


Figure 4.4. Bromide concentration at **Silstrup**. The data derive from the vertical monitoring wells (M5, M9, M10 and M12). In September 2008, monitoring wells M6 and M11 were suspended (Appendix 2). Screen depth is indicated in m b.g.s. The green vertical lines indicate the dates of bromide applications.

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, 2012-2013 and 2013-2014 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 2014 are not evaluated in this report and hence not included in Table 4.2.

Table 4.2. Pesticides analysed at **Silstrup**. Precipitation (precip.) and percolation (percol.) are accumulated within the first year (Precip 1st year, Percol 1st year) and first month (Precip 1st month, Percol 1st 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	Analysed pesticide	Applica. date	End monito.	Y 1 st precip.	Y 1 st percol.	M 1 st precip.	M 1 st percol.	C _{mean}	
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 14*	1067	584	112	56	0.009	
		AE-05422291(M)	Apr 12	Jun 14*	1067	584	112	56	<0,01	
		AE-B107137(M)	Apr 12	Jun 14*	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 14*	1073	581	127	64	0.074	
	Glyfonova 450 Plus	Glyphosate(P)	Sep 12	Jun 14*	836	514	207	121	0.15	
		AMPA(M)	Sep 12	Jun 14*	836	514	207	121	0.067	
Winter wheat 2012	DFF	Diflufenican	Nov 12	Jun 14*	463	270	68	69	0.006	
		AE-05422291(M)	Nov 12	Jun 14*	463	270	68	69	<0.01	
		AE-B107137(M)	Nov 12	Jun 14*	463	270	68	69	0.01	
Spring barley 2013**	Duotril 400 EC	Ioxynil (P)	May 13	Jun 14*	804	543	222	188	<0.01	
	Duotril 400 EC	Bromoxynil (P)	May 13	Jun 14*	804	543	222	188	<0.01	
	Amistar	CyPM (P)	Jun 13	Jun 14*	1059	534	15	0	0,132	
	Glyfonova 450 Plus	Glyphosate (P)	Aug 13	Jun 14*	1008	538	125	0	0,01	
		AMPA (M)	Aug 13	Jun 14*	1008	538	125	0	0,01	
Winter wheat 2014	Oxitril CM	Ioxynil (P)	Oct 13	Jun 14*	804	542	222	189	<0.01	
	Oxitril CM	Bromoxynil (P)	Oct 13	Jun 14*	804	542	222	189	<0.01	
	DFF	Diflufenican (P)	Oct 13	Mar 14	804	542	222	189	0.01	
		AE-05422291(M)	Oct 13	Mar 14	804	542	222	189	<0.01	
		AE-B107137(M)	Oct 13	Mar 14	804	542	222	189	<0.01	

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

* monitoring continues the following year.

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

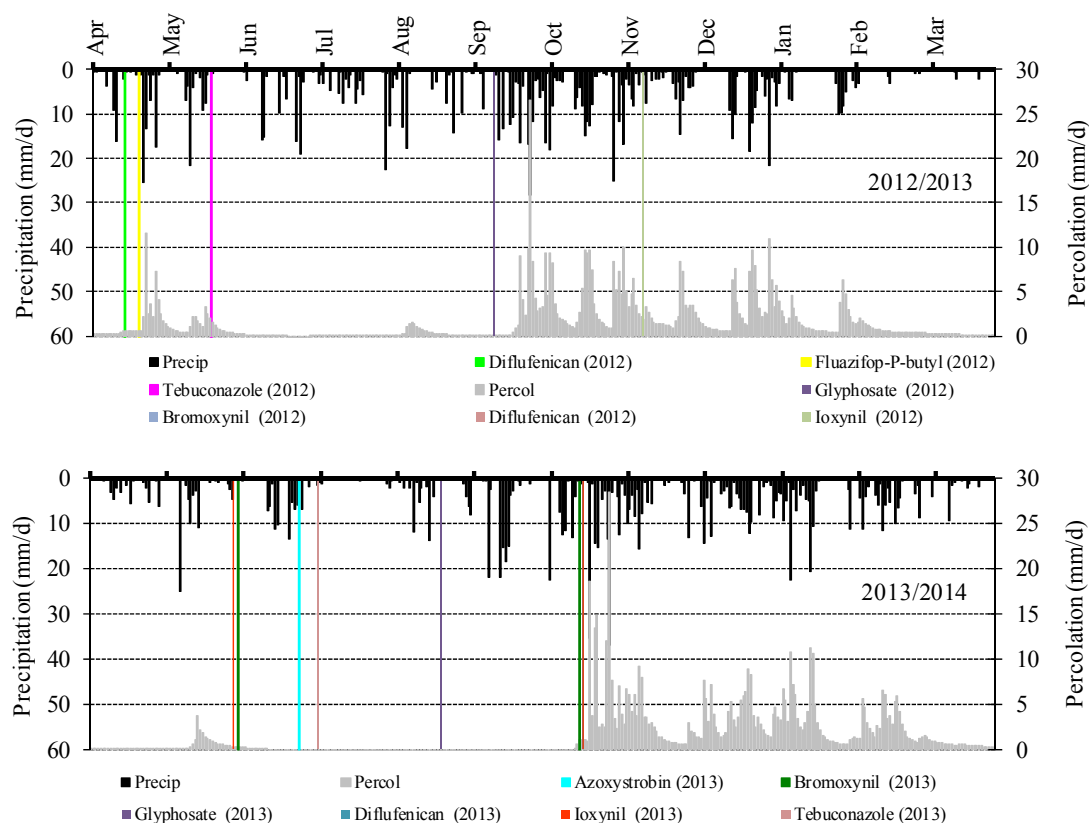


Figure 4.5. Pesticides included in the monitoring programme, precipitation and irrigation (primary axis) and simulated percolation 1 m b.g.s. (secondary axis) at **Silstrup** in 2012/2013 (upper) and 2013/2014 (lower).

The current report focuses on the pesticides applied from 2012 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, the 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, focus has been on TFMP. In Figure 4.6A, B and C it can be seen that after application of 375 g a.i./ha of fluazifop-P-butyl (3.0 L/ha Fusilade Max) in 2008 TFMP concentrations rose above 0.1 µg/L in both drainage and groundwater. Exceedance of the 0.1 µg/L was first seen in the groundwater and then later on in the drainage water, indicating a preferential transport. Subsequently, the Danish EPA 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, in April 2010 and April 2011 (Figure 4.6B) this seemed to have reduced the environmental impact. However, a fifth application in April 2012, illustrated that there still was a problem, even when 187.5 g a.i./ha of fluazifop-P-butyl was applied on a dense crop of seed grass. The hydrological setting at the time of spraying was similar when comparing the third and fourth application with the fifth.

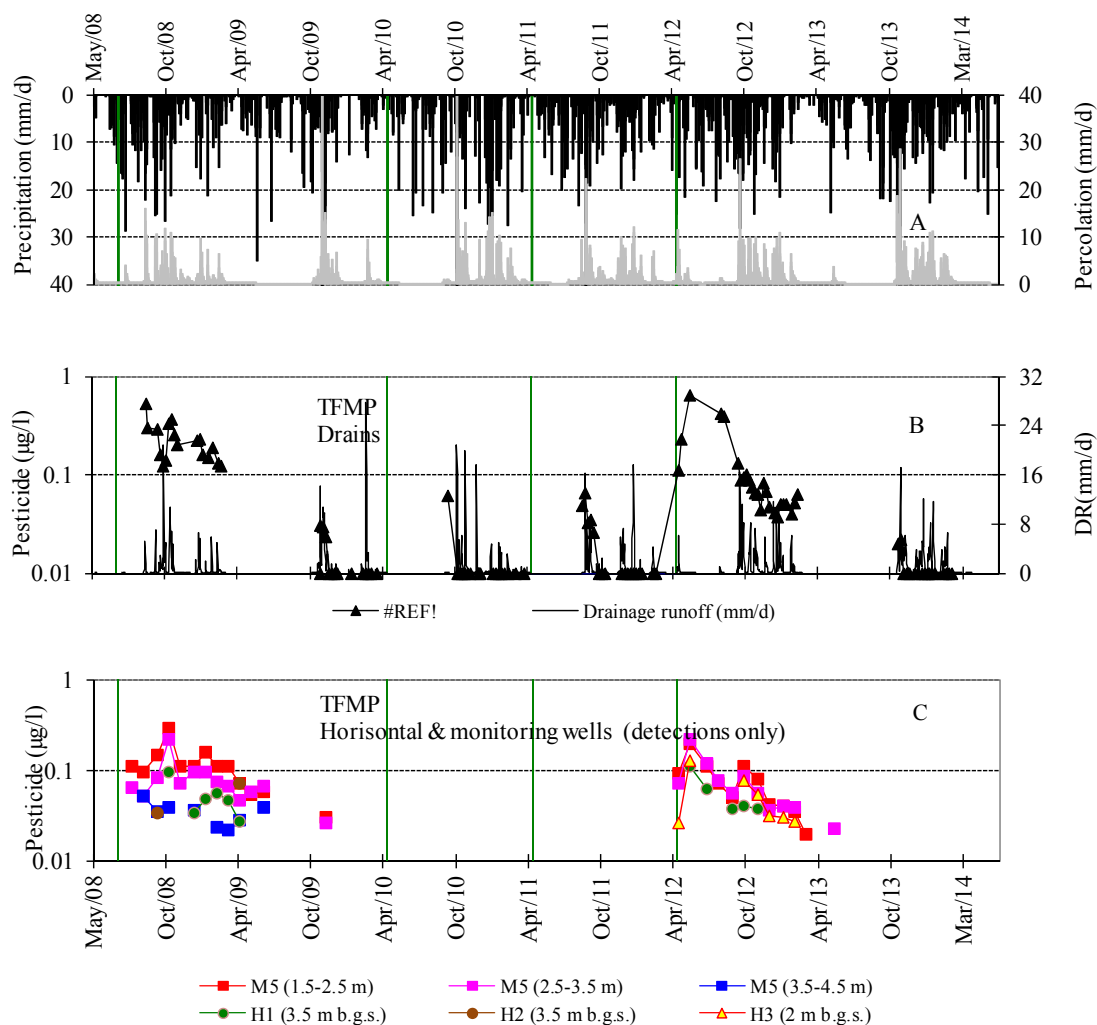


Figure 4.6. Precipitation and simulated percolation 1 m b.g.s. (A) together with the concentration of TFMP (B) in the drainage runoff, and the concentration of TFMP (C) in the groundwater monitoring screens (including horizontal screens) at **Silstrup**. The green vertical lines indicate the dates of fluzifop-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.

Since 5 May 2013 and 30 October there have been no detections of TFMP neither in the groundwater (Figure 4.6C) nor in the drainage water (Figure 4.6B).

The use of fluzifop-P-butyl is no longer allowed in Danish agriculture. Fluzifop-P-butyl was not approved by the EU commission in 2014, and fluzifop-P-butyl has not been reapplied in Denmark.

Tebuconazole was applied on red fescue in May 2012 and was detected in two drainage water samples on 8 August and 26 September 2012 (0.013 and 0.084 µg/L).

Measurements of 1,2,4-triazole, a degradation product of tebuconazole, has not been possible within the present monitoring period, due to analytical problems.

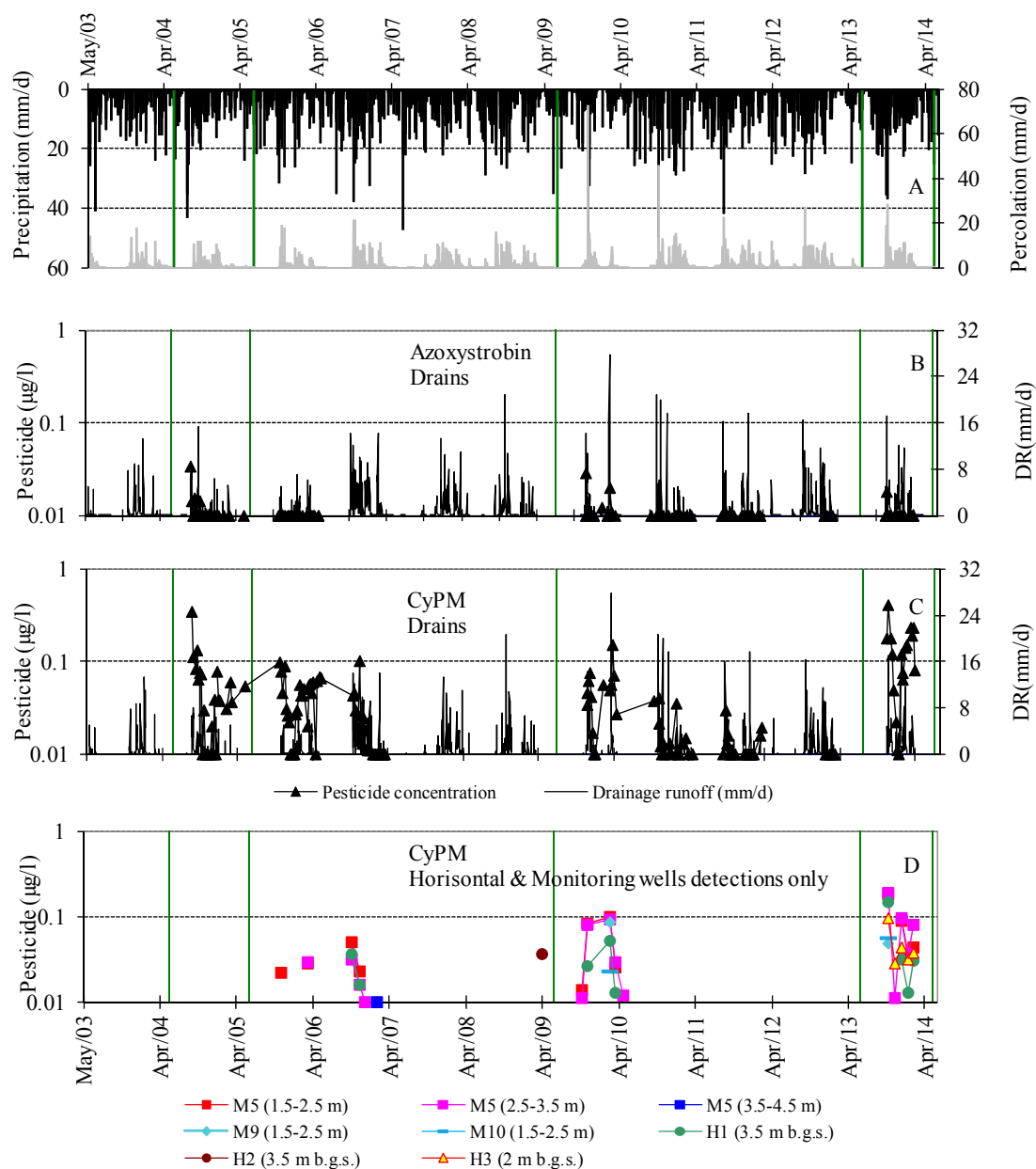


Figure 4.7. Precipitation and simulated percolation 1 m b.g.s. (A) together with the concentration of azoxystrobin (B) and CyPM (C) in the drainage runoff, and the concentration of CyPM (D) in the groundwater monitoring screens (including horizontal screens) at **Silstrup**. The green vertical lines 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).

In total, azoxystrobin has been applied at Silstrup five times between June 2004 and June 2014 (Figure 4.7). Concentrations of azoxystrobin have never exceeded 0.1 µg/L in neither drainage water (Figure 4.7B) nor in groundwater (not shown). The metabolite CyPM, on the other hand, has been detected above 0.1 µg/L in drainage water in several instances, in particular following the 2013 application (Figure 4.7C). In groundwater the concentrations of CyPM have been 0.1 µg/L or above on four occasions (Figure 4.7D).

Diflufenican applied in April 2012 and in November 2012 (in red fescue and winter wheat) has been detected 11 times in drainage water samples. One sample taken on 25 April 2012 contained 0.12 µg/L (not shown). The only detection of diflufenican in

groundwater was 0.47 µg/L on 7 November 2012). Two metabolites of diflufenican, AE-B107137 and AE-05422291 was monitored, but only the aforementioned was detected and only in five drainage water samples with a maximum concentration being 0.13 µg/L on 2 May 2012.

Ioxynil and bromoxynil were applied on 30 May as well as on 16 October 2013. The two substances were detected neither in the drainage nor in the groundwater.

Glyphosate (2.160 kg a.i./ha) was applied on 10 September 2012, on a stand of red fescue. Both glyphosate and AMPA were detected in drainage water nine days later, maximum concentration of glyphosate being 0.66 µg/L on 26 September (Figure 4.8B) and 0.14 µg/L of AMPA on 10 October.

Still having problems with grass weeds, an additional spraying of glyphosate (1.080 kg a.i./ha) was done in the crop of spring barley on 20 August 2013, i.e. before the harvest of the spring barley.

Whereas the spraying in 2012 lead to detections of glyphosate and the metabolite AMPA in drainage water only nine days after application, it took two months before glyphosate and AMPA were detected in the drainage water following the 2013 application (Figure 4.8B and C). Differences in the hydrological setting rather than differences in dosage, seems a likely reason. In 2012 drainage commenced shortly after the spraying, whereas two months passed before the onset of drainage in 2013. The first detections of glyphosate and AMPA in the vertical monitoring wells were done shortly after the 2013 spraying (Figure 4.8D and E). It could be the aftermaths of the 2012 spraying rather than of the 2013. However, bearing in mind that preferential flow could cause leaching of TFMP, a metabolite of fluazifop-P-butyl (Figure 4.6C), this transport process might also be responsible in this case.

August 2012 was quite rainy. This ample rain concided with a low crop water demand during the ripening the soil matrix had become more or less saturated (Figure 4.2C-F). At the same time the groundwater table was located around 3.5 m.b.g.s (Figure 4.2B). The preferentially leached glyphosate and AMPA therefore had landed at the top of the groundwater table, from where it could be sampled by the monitoring well M5 (Figure 4.8D and E). Note also the lower concentrations of AMPA and in particular of glyphosate prior to the 2013 application and subsequent leaching (Figure 4.8D and E).

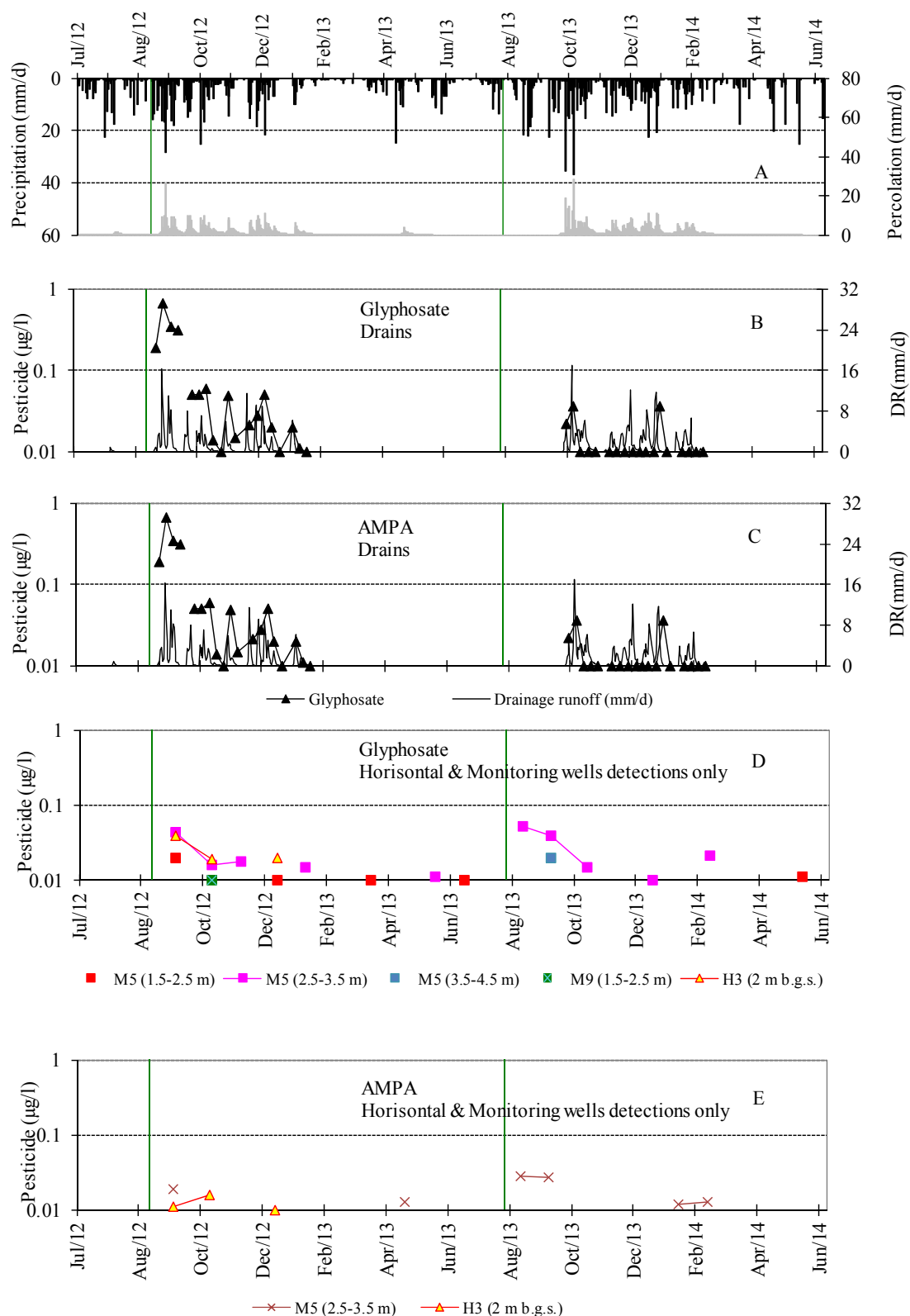


Figure 4.8. Precipitation and simulated percolation 1 m b.g.s. (A) together with the concentration of glyphosate (B) and AMPA (C) in the drainage runoff, and the concentration of glyphosate (D) and AMPA (E) in the groundwater monitoring screens at **Silstrup**. The green vertical lines indicate the dates 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 fields. The test field covers a cultivated area of 1.3 ha (105 x 120 m) and is virtually flat (Figure 5.1). The field is highly heterogeneous with considerable variation in both topsoil and aquifer characteristics (Lindhardt *et al.*, 2001). Such heterogeneity is quite common for this geological formation, however. Based on three profiles excavated in the buffer zone bordering the field the soil was classified as Abrupt Argiudoll, Aqua Argiudoll and Fragiaquic Glossudalf (Soil Survey Staff, 1999). The topsoil is characterised as sandy loam with a clay content of 10–20%, and an organic carbon content of 1.7–7.3%. A C-horizon of low permeability also characterises the field. 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 fields (Table 1.1). The geological structure is complex comprising 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 field 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 part 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 2013-2014 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.

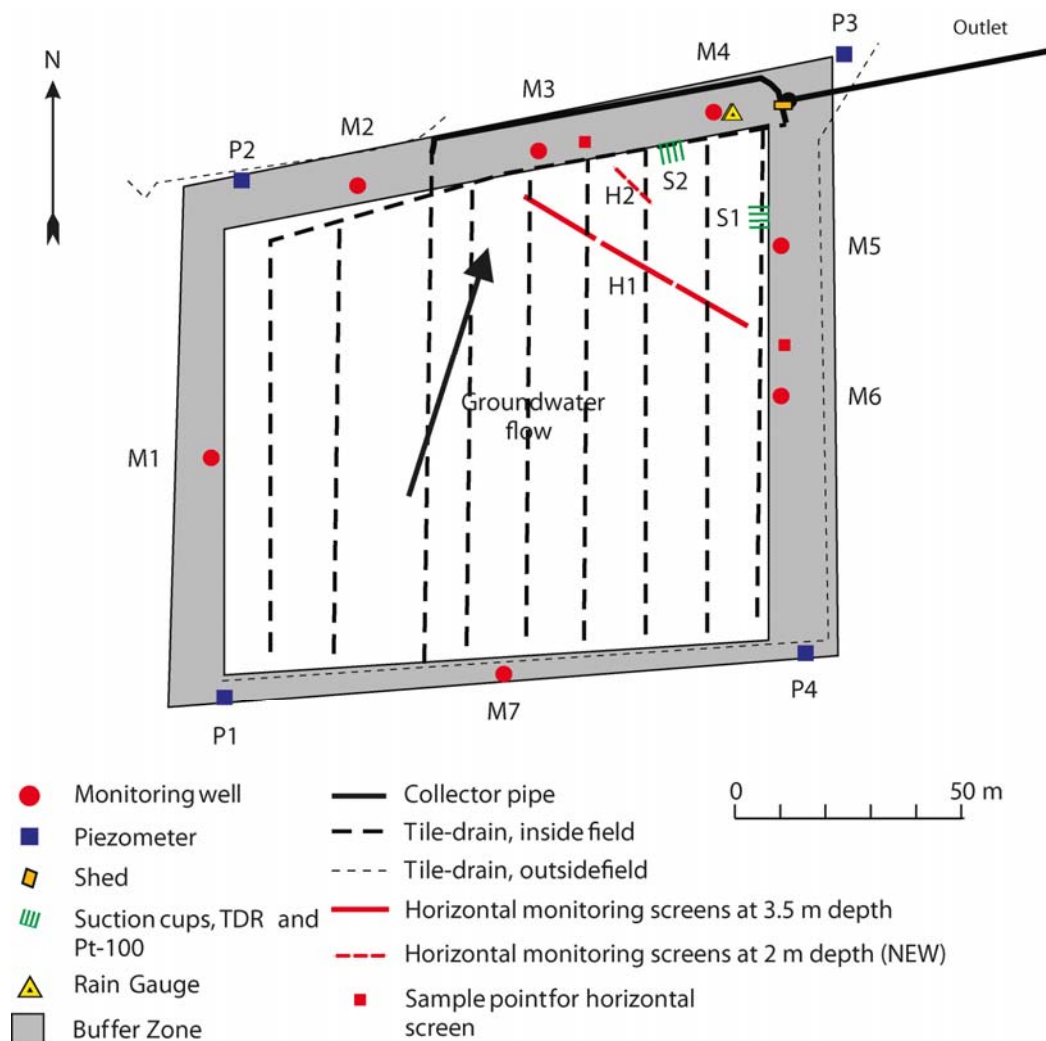


Figure 5.1. Overview of the **Estrup** field. The innermost white area indicates the cultivated land, while the grey area indicates the surrounding buffer zone. The positions of the various installations are indicated, as the direction of groundwater flow (by an arrow). Pesticide monitoring is conducted 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 FMC 65317 were included in the monitoring. A spraying of aphids was done on 16 May using cypermethrin, however the substance was not included in the monitoring programme. Similarly with the pirimicarb applied on 13 July. Due to infestation with couch grass (*Agropyron repens* L.) glyphosate was applied on to the crop 21 August. Both glyphosate and the degradation product AMPA was included in the monitoring programme. The peas were harvested on 6 September yielding 49.8 hkg/ha (86% dry matter) and 24.4 hkg/ha of straw, being shredded at harvest.

A crop of winter wheat was sown directly in the stubble on 13 September 2013, using a combined power harrow sowing machine. The winter wheat emerged on 21 September. The herbicides bromoxynil, ioxynil and diflufenican were applied on 11 November.

Only diflufenican and its two degradation products, AE-B107137 and AE-0542291, were included in the monitoring programme. Additional sprayings of weeds was done on 22 April using fluroxypyr and on 15 May using florasulam. Neither of these was included in the monitoring programme. Spraying against fungi was done twice using tebuconazol on 20 May and azoxystrobin on 2 June. Azoxystrobin as well as its degradation product CyPM was included, whereas tebuconazol was not. Cypermethrin, was used against pests on 24 June, but not included in the monitoring programme.

5.1.3 Model setup and calibration

The numerical model MACRO (version 5.2, Larsbo *et al.*, 2005) was applied to the Estrup field 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 2014 and to establish an annual water balance.

Compared to the setup in Brusch *et al.* (2015), a year of validation was added to the MACRO setup for the Estrup field. The setup was subsequently calibrated for the monitoring period May 1999-June 2004 and validated for the monitoring period July 2004-June 2014. 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, 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 field. 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 fields, 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 no or low precipitation (Figure 5.2A and 5.2B). Contrarily to the other years the simulated groundwater table seemed to capture these drops. 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 July 2014. As in previous years (Brüsch *et al.*, 2015), the simulated groundwater table often fluctuates slightly above the drain depth resulting in long periods with drainage.

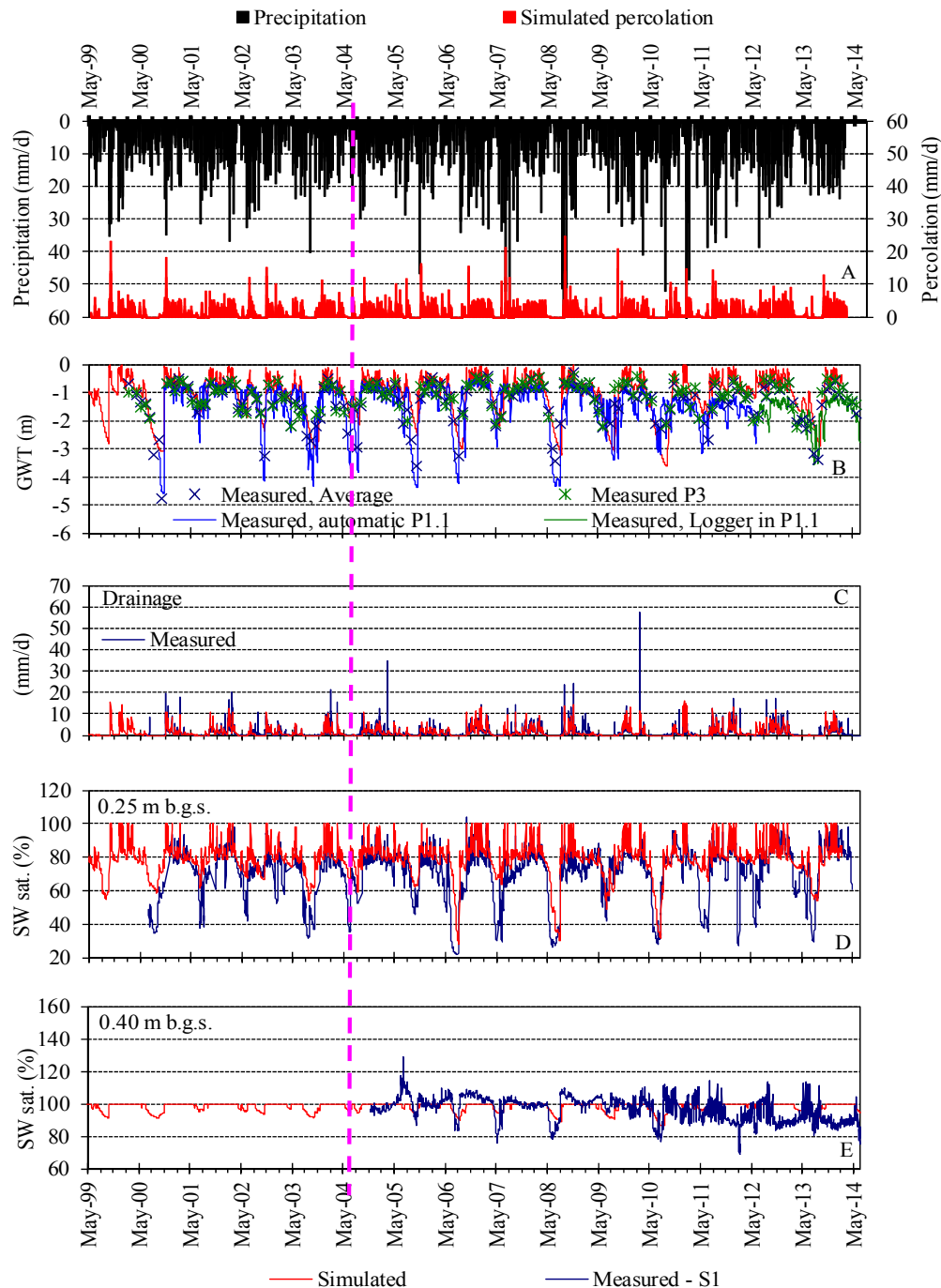


Figure 5.2. Soil water dynamics at **Estrup**: Measured precipitation and simulated percolation 0.6 m b.g.s. (A), simulated and measured groundwater table, GWT (B), simulated and measured drainage (C), and simulated and measured soil saturation (SW sat.) at two different soil depths (D and E). The measured 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 2014).

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⁾
01.07.99–30.06.00 ¹⁾	968	1.173	466	–	553	154 ⁴⁾
01.07.00–30.06.01	968	887	420	356	340	111
01.07.01–30.06.02	968	1.290	516	505	555	270
01.07.02–30.06.03	968	939	466	329	346	144
01.07.03–30.06.04	968	928	499	298	312	131
01.07.04–30.06.05	968	1.087	476	525	468	86
01.07.05–30.06.06	968	897	441	258	341	199
01.07.06–30.06.07	968	1.365	515	547	618	303
01.07.07–30.06.08	968	1.045	478	521	556	46
01.07.08–30.06.09	968	1.065	480	523	362	62
01.07.09–30.06.10	968	1.190	533	499	523	158
01.07.10–30.06.11	968	1.158	486	210	341	462
01.07.11–30.06.12	968	1.222	404	479	577	3.397
01.07.12–30.06.13	968	1.093	386	503	564	204
01.07.13–30.06.14	968	1.015	513	404	449	97

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 measurements are lacking, simulated drainage was used to calculate groundwater recharge.

The simulated drainage (Figure 5.2C) captured the measured drainage quite well except for the presence of two minor drainage events in September and the initiation of the continuous drainage period in October 2013. Drainage measured in connection with snowmelt seemed more or less captured this hydrological year. Only the amount of drainage initiated in February after a two weeks period with air temperature below 0° C was not fully captured by the MACRO-model of Estrup. Drainage was high during the whole monitoring period compared to that of the other two clayey till fields 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 14 years, the recent hydrological year July 2013–June 2014, was characterized by having intermediate precipitation, a high simulated actual evapotranspiration, and low measured drainage. Precipitation in the months of this year was characterized by July being the driest and September being the wettest since PLAP-monitoring started (Appendix 4). The period September–February was registered to be very wet like at Silstrup. Due to this precipitation pattern, the simulated percolation pattern of the year July 2013–June 2014 resulted in more or less continuously percolation at 1 m depth (Figure 5.2A) with a minor input to the groundwater recharge (Table 5.1) as compared to the other PLAP-years.

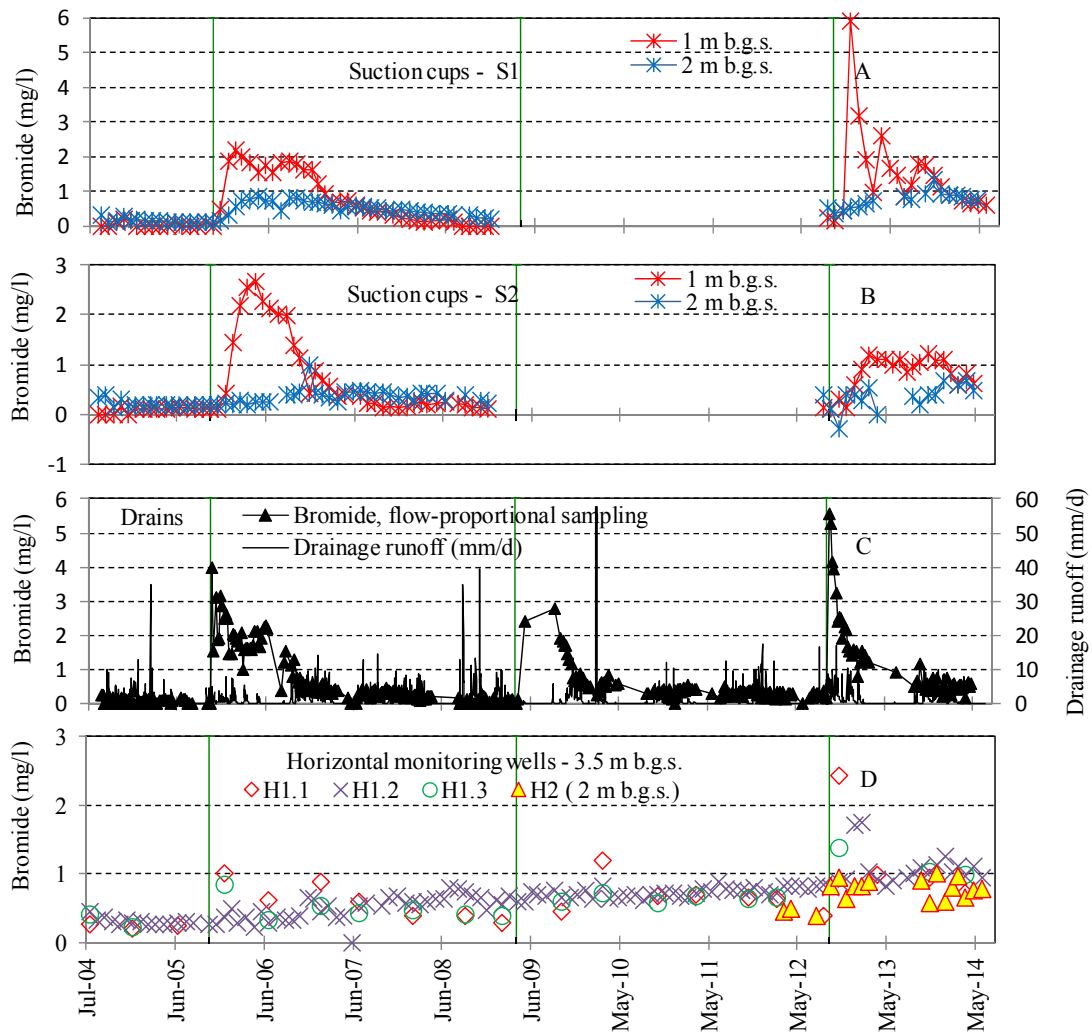


Figure 5.3. Bromide concentration at **Estrup**. A and B refer to suction cups located at S1 and S2, respectively. The bromide concentration is also shown for drainage runoff (C) and the horizontal monitoring well H1 and H3 (D). From September 2008 to August 2012, bromide measurements in the suction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

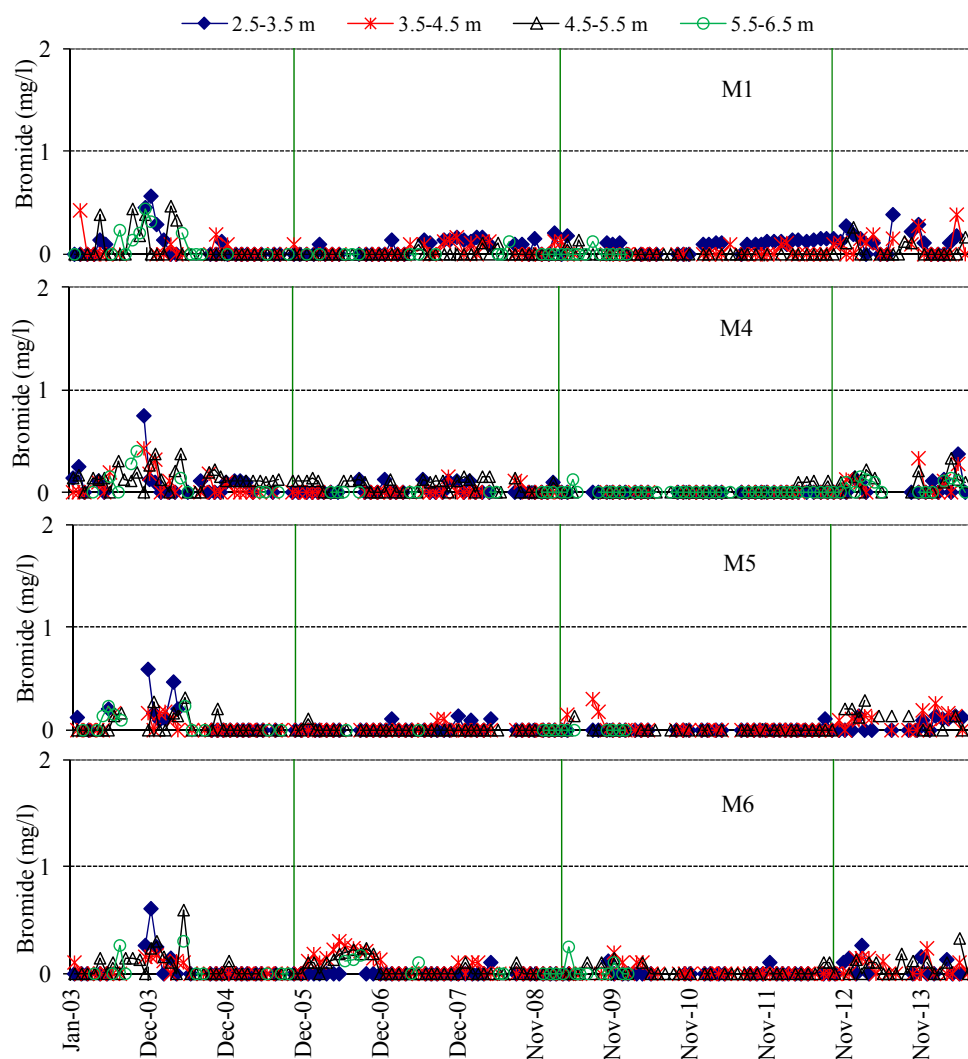


Figure 5.4. Bromide concentration at **Estrup**. The data derive from the vertical monitoring wells (M1, M4, M5 and M6). Screen depth is indicated in m b.g.s. In September 2008, monitoring wells M3 and M7 were suspended. The green vertical lines indicate the dates of the three most recent bromide applications.

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 (2007-2014) and Table A7.4 in Appendix 7 (2000-2007). Pesticide application during the most recent growing season (2012-2014) 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 2014 are not evaluated in this report and hence not included in Table 5.2.

Table 5.2. Pesticides analysed 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	Analysed pesticide	Applica. date	End monito.	Y 1 st precip	Y 1 st percol	M 1 st precip	M 1 st percol	C _{mean}
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	Aug 12	823	176	97	31	0.01
	Fox 480 SC	Bifenox(P)	Apr 11	Dec 12	1217	276	45	2	<0.01
		Bifenox acid(M)	Apr 11	Dec 12	1217	276	45	2	0.003
		Nitrofen	Apr 11	Dec 12	1217	276	45	2	<0.01
	Flexity	Metrafenone(P)	May 11	Jun 14*	1219	283	114	6	0.02
	Spring barley 2012	Amistar	Azoxystrobin	Jun 12	Jun 14*	1083	281	151	29
CyPM			Jun 12	Jun 14*	1083	281	151	29	0.24
Fox 480 SC		Bifenox	May 12	Dec 12	1090	281	39	13	< 0.02
		Bifenox acid	May 12	Dec 12	1090	281	39	13	0.011
		Nitrofen	May 12	Dec 12	1090	281	39	13	< 0.02
Mustang forte		Aminopyralid	May 12	Jun 14*	1098	285	50	14	< 0.01
Roundup Max		Glyphosate(P)	Oct 11	Jun 14*	1150	295	94	26	0.88
		AMPA(M)	Oct 11	Jun 14*	1150	295	94	26	0.26
Pea 2013	Fighter 480	Bentazone(P)**	May 13	Jun 14*	1071	248	35	10	0.059
		Clomazone	Apr 13	Jun 14*	1094	243	61	17	<0.01
	Command CS	FMC-65317(M)	Apr 13	Jun 14*	1094	243	61	17	<0.02
	Glyfonova 450 plus	Glyphosate (P)	Aug 13	Jun 14*	928	237	131	13	0.10
		AMPA(M)	Aug 13	Jun 14*	928	237	131	13	0.07
Winter weat 2014	DFF	Diflufenican	Nov 13	Jun 14*	582	165	86	30	0.19
		AE-05422291	Nov 13	Jun 14*	582	165	86	30	< 0.01
		AE-B107137	Nov 13	Jun 14*	582	165	86	30	0.03

Systematic chemical nomenclature for the analysed 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.

The current report focuses on pesticides applied from 2012 and onwards, while leaching risk of pesticides applied in 2011 and before has been evaluated in previous monitoring reports (see http://pesticidvarsling.dk/publ_result/index.html).

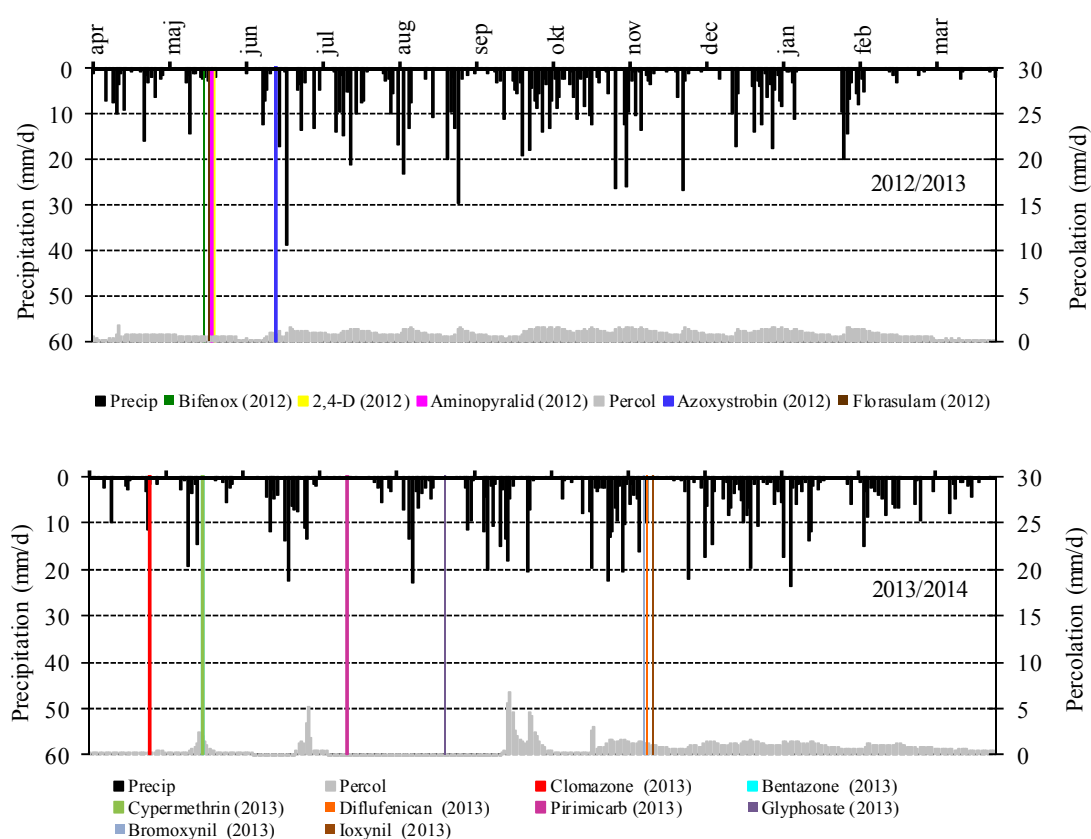


Figure 5.5. Application of pesticides included in the monitoring programme and precipitation (primary axis) together with simulated percolation 0.6 m b.g.s. (secondary axis) at **Estrup** in 2012/2013 (upper) and 2013/2014 (lower).

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 degradation product are shown in Figure 5.6B and 5.6C. The maximum measured concentration of azoxystrobin was 1.4 $\mu\text{g/L}$ on 24. August 2006 and 2.1 $\mu\text{g/L}$ of CyPM on 11 September 2008. The 0.13 $\mu\text{g/L}$ of CyPM detection in the new horizontal H3 well on 3 October 2012 was the first ever exceedance of the 0.1 limit in the groundwater at Estrup, (Figure 5.6D). Within the year of application as well as the following year, the average concentrations of CyPM in drainage water were always above 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 detected in the drainage water in concentrations above 0.1 $\mu\text{g/L}$, ranging between 0.022 and 0.29 $\mu\text{g/L}$. Differences in persistence for the two substances are further underlined by the fact that only two out of 618 groundwater samples contained azoxystrobin (0.04 $\mu\text{g/L}$, data not shown) whereas 19 samples contained CyPM, maximum concentration being 0.13 $\mu\text{g/L}$ (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.

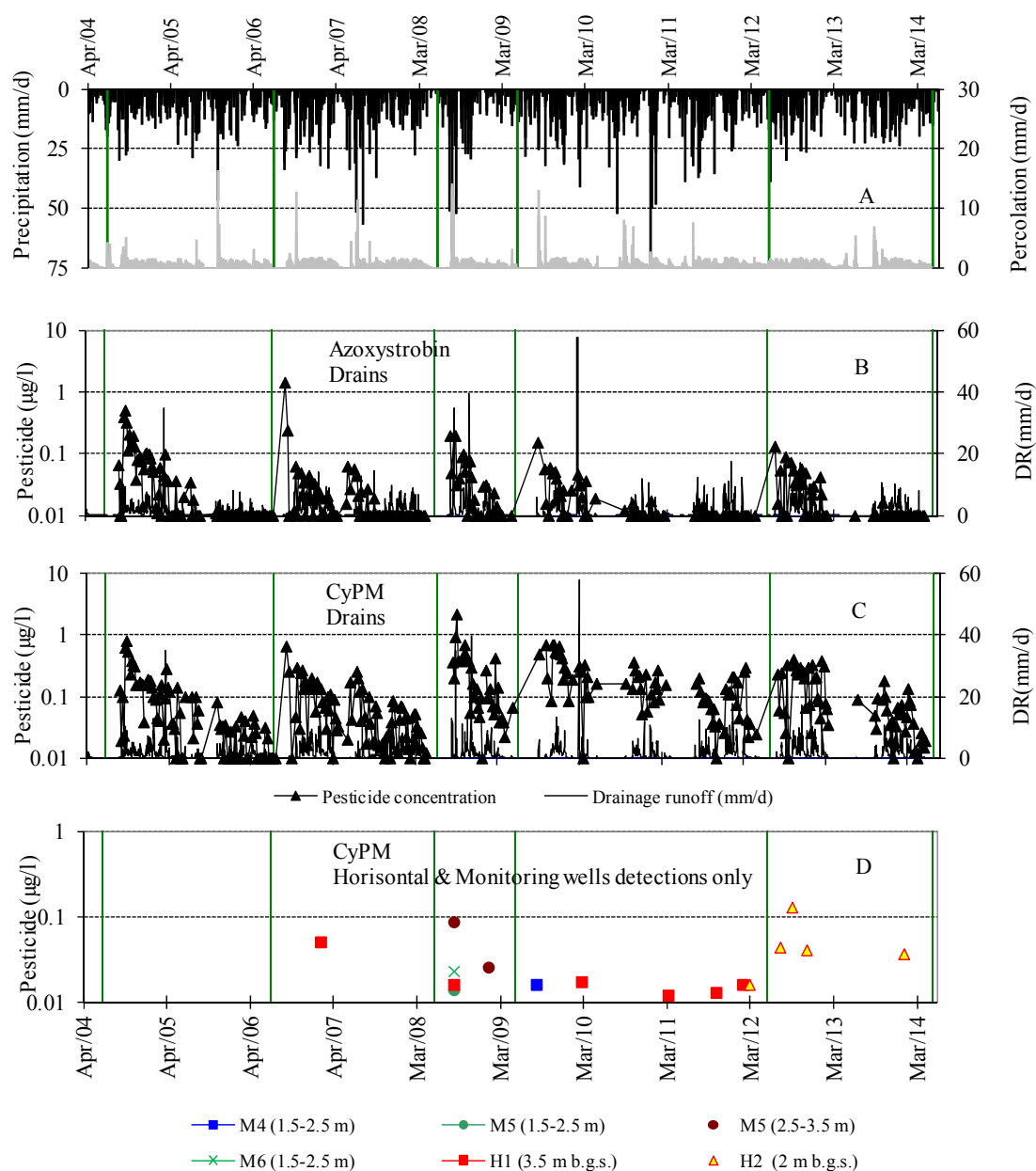


Figure 5.6. Precipitation and simulated percolation 0.6 m b.g.s. (A) together with concentration of azoxystrobin (B) and CyPM (C) in the drainage runoff (DR on the secondary axis) at **Estrup**. Detections of CyPM in groundwater monitoring screen are indicated in D. Azoxystrobin was only detected twice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

The leaching pattern in drainage water, following the fifth application of azoxystrobin on 13 June 2012, was similar to those following the first four applications i.e. both parent compound and degradation product were leached, the degradation product in the highest concentrations (Figure 5.6A and 5.6B).

The herbicide glyphosate has now been applied six times at Estrup (Figure 5.7 and 5.8). Following all applications, both glyphosate and AMPA could be detected in the drainage. Out of 510 drainage water samples analysed for glyphosate and AMPA within the period from 31 October 2000 to 11 June 2014, the concentrations of glyphosate and AMPA exceeded 0.1 µg/L in 111 and 116 samples, respectively (Figure 5.7B, 5.8B,

5.7C and 5.8C). During that period AMPA has never exceeded 0.1 µg/L in groundwater (Figure 5.7E, 5.8E and Table A5.4 in Appendix 5), whereas glyphosate has done 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).

The concentrations of both glyphosate and AMPA in drainage, following the glyphosate application on 21 August 2013 onto the crop of peas were, on average, lower than those following all previous sprayings in the autumn after harvest of the crops.

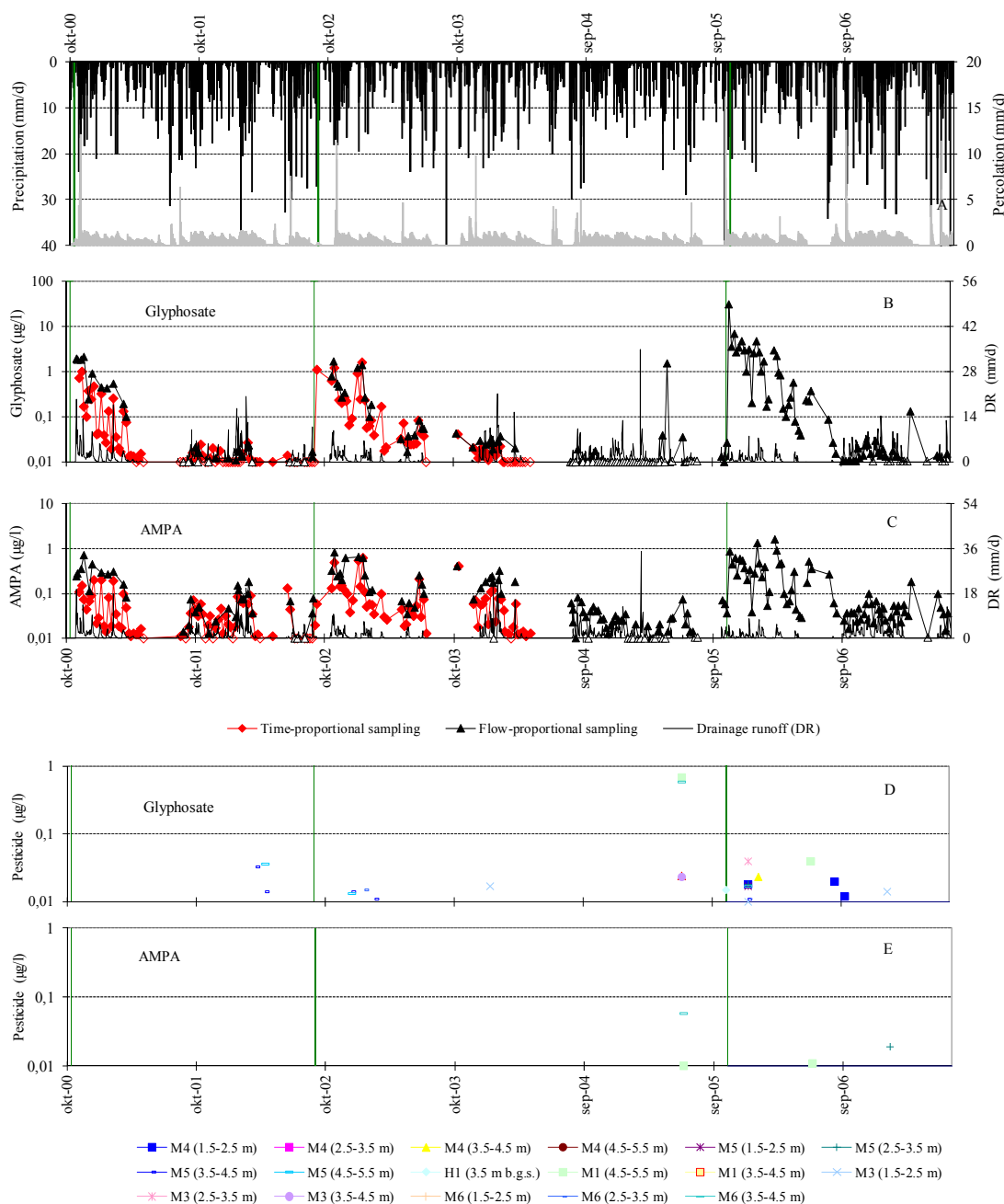


Figure 5.7. Precipitation and simulated percolation 0.6 m b.g.s. (A) together with the concentration of glyphosate (B) and AMPA (C) in the drainage runoff (DR on the secondary axis) at **Estrup** from October 2000 until July 2007. Data represent a seven-year period including four applications of glyphosate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

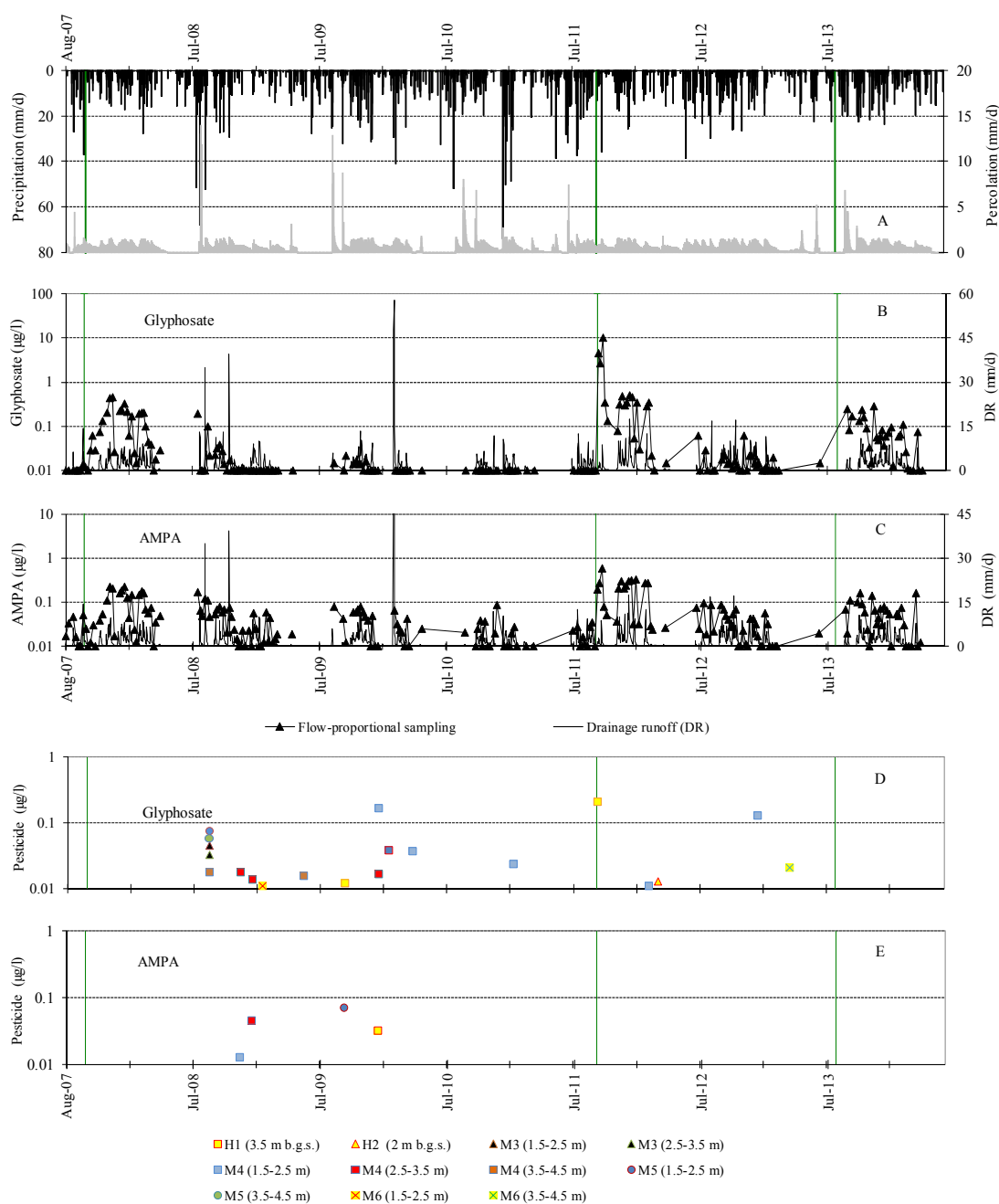


Figure 5.8. Precipitation and simulated percolation 0.6 m b.g.s. (A) together with the concentration of glyphosate (B) and AMPA (C) in the drainage runoff (DR on the secondary axis) at **Estrup** from July 2007 until June 2013. Data represent a six-year period including four applications of glyphosate 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 (Norgaard et al 2014).

The fungicide metrafenone was applied twice, on 9 May and 7 June 2011. Between 28 July 2011 and 11 June 2014, a total of 92 water samples were taken. Thereof 20 samples contained metrafenone, but all in concentrations below 0.1 µg/L. In a total of 159 groundwater samples taken between 7 April 2011 and 11 June 2014 a single contained metrafenone; 0.04 µg/L on 7 November 2012 (data not shown).

The most recent application of the herbicide bifenox took place on 15 May 2012. A single detection of bifenox, 0.023 µg/L in drainage, was done two months later (data not shown, see Brusch *et al.*, 2013). The degradation product bifenox acid was detected twice in drainage water, 0.088 µg/L on 18 July and 0.14 µg/L on 27 December 2012. Neither bifenox nor bifenox acid was detected in the groundwater following the application in May 2012. Since 2012 the use of bifenox has been banned in Denmark.

The herbicide diflufenican (Figure 5.9) was used on 11 November 2013 together with ioxynil and bromoxynil, the later two not included in the monitoring, however. The parent compound, as well as its two metabolites, AE-05422291 and AE-B107137 were monitored. Until June 2014 there have been no detections of diflufenican in groundwater. However, in 29 of the drainage water samples 13 contained more than 0.1 µg/L, maximum being 0.49 µg/L two days after the spraying. The metabolite AE-B107137 has been detected in 14 of 30 samples, none of them where above 0.1 µg/L, though. In groundwater there was a single detection of 0.016 µg/L on 8 January 2014. The metabolite AE-05422291 was never detected in drainage or groundwater.

Bentazone was used in the peas on 16 May 2013. The parent compound was detected in both drainage and groundwater (Figure 5.10). A total of 32 drainage water samples contained bentazone, three were above 0.1 µg/L, a maximum of 2.8 µg/L was detected 1.5 months after the application. Out of 49 groundwater samples analysed, 14 contained bentazone, none of them above 0.1 µg/L, however.

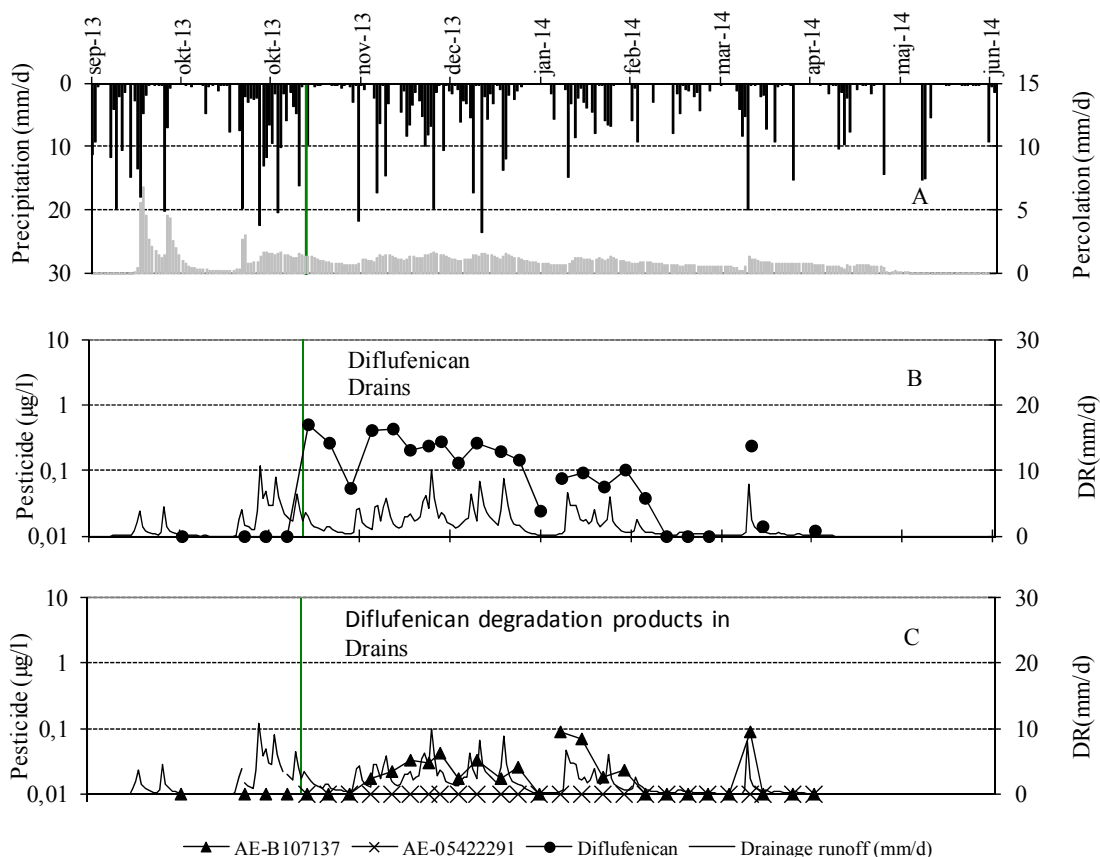


Figure 5.9. Precipitation and simulated percolation 1 m b.g.s. (A) together with the concentration of diflufenecane, and the two degradation products **AE-05422291** and **AE-B107137** (B) in the drainage runoff at Estrup. The green vertical lines indicate the dates of diflufenecane applications.

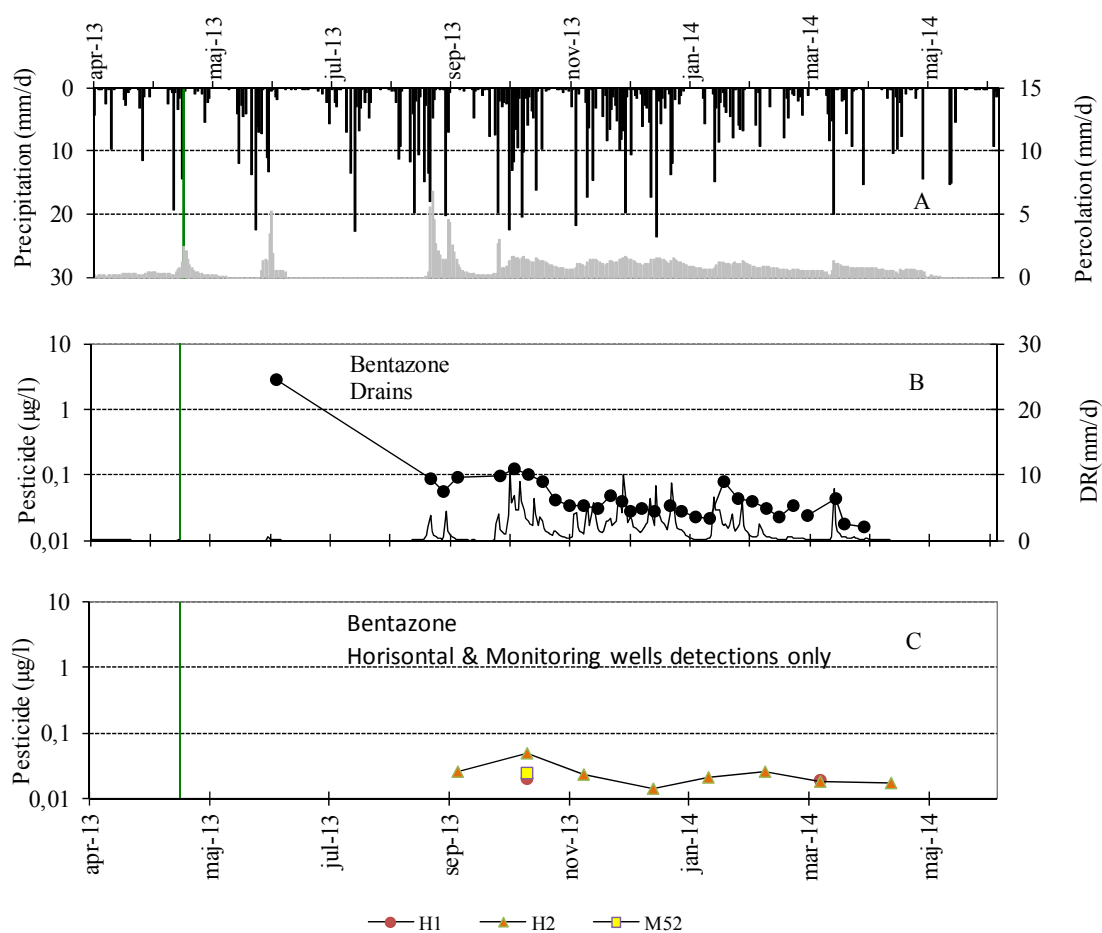


Figure 5.10. Precipitation and simulated percolation 1 m b.g.s. (A) together with the concentration of bentazone (B) in the drainage runoff at **Estrup** and in groundwater. The green vertical lines indicate the dates of bentazone applications.

The herbicide aminopyralid was applied on 18 May 2012 together with florasulam and 2,4-D. Florasulam and 2,4-D were not monitored, and the aminopyralid did not leach to drainage or groundwater (data not shown).

The herbicide clomazone was applied on 25 April 2013. Neither the parent compound nor the metabolite FMC 65317 was detected in any of the samples taken from drainage and groundwater.

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 a 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 in 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 field 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.

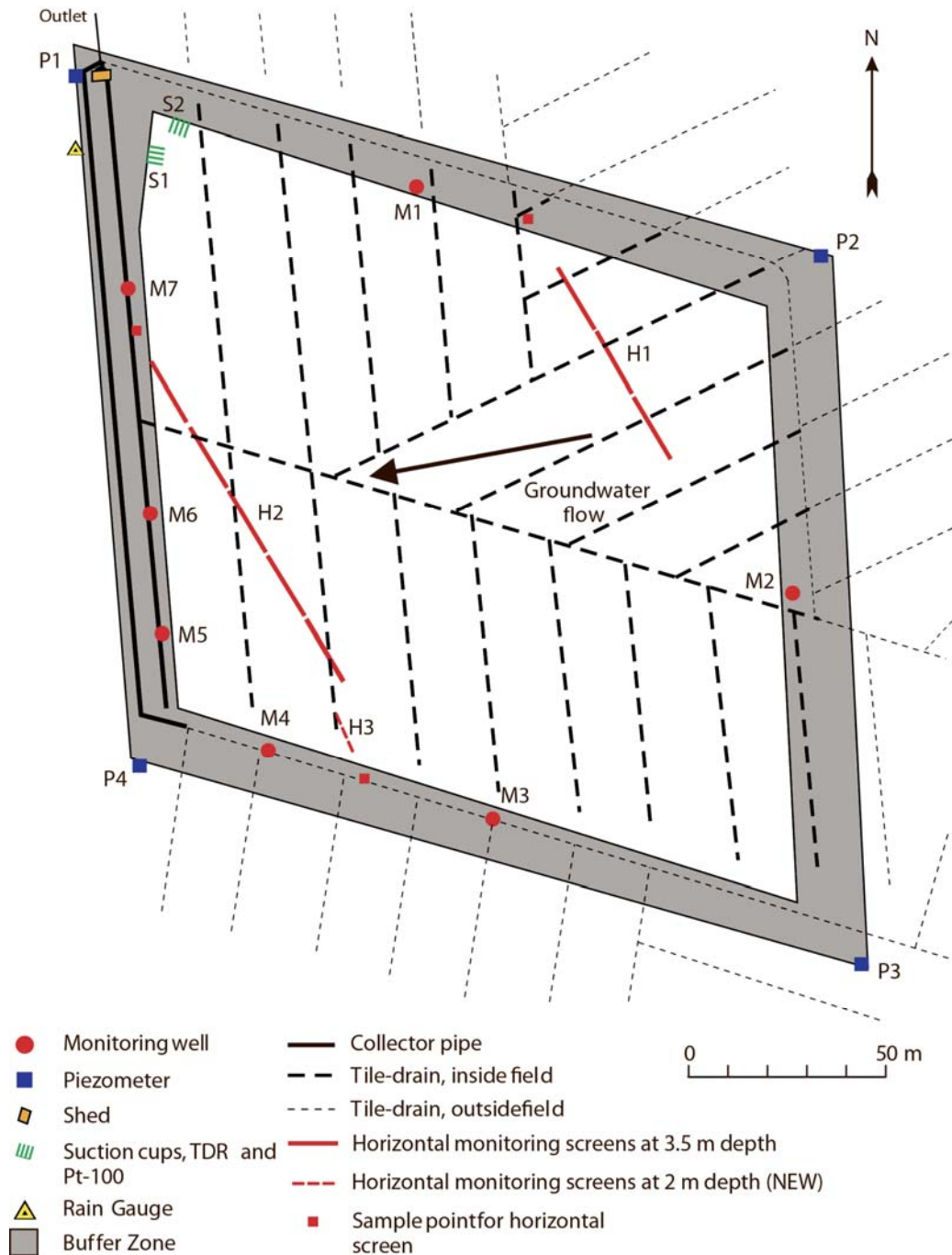


Figure 6.1. Overview of the **Faardrup** field. The innermost white area indicates the cultivated land, while the grey area indicates the surrounding buffer zone. The positions of the various installations are indicated, as the direction of groundwater flow (by an arrow). Pesticide monitoring is conducted 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 2013-2014 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 26 January 2013 white clover, established in spring barley in April 2012, was sprayed with the fungicide propyzamid and on 14 May 2013 with the herbicide bentazone. Bentazone and propyzamid as well as three of its degradation products RH-24580, RH-24644 and RH-24655 were included in the monitoring programme. Pests were sprayed with lambda-cyhalothrin twice, on 31 May 2013 and 12 June 2013. This compound, however, was not included in the monitoring programme. Yield of clover seed, harvest on 28 July 2013, was 1.56 hkg/ha.

On 7 October 2013 the field was ploughed and sown with winter wheat (cv. Mariboss), which emerged on 18 October. Spraying of weeds was done on 28 April 2014 using ioxynil, bromoxynil and fluroxypur - none of them were included in the monitoring programme. The fungicide azoxystrobin was used on 15 May, but also not included. The winter wheat was harvested on 30 July, yielding being 56.6 hkg/ha of grain (85% dry matter). After spraying with the herbicide glyphosate on 26 August (glyphosate and AMPA not monitored since August 2012), 70 hkg/ha of straw (fresh weight), shredded at harvest, was incorporated by ploughing on 23 September 2014.

6.1.3 Model setup and calibration

The numerical model MACRO (version 5.2) was applied to the Faardrup field 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 2014 and to establish an annual water balance.

Compared to the setup in Brusch *et al.* (2015), a year of validation was added to the MACRO setup for the Faardrup field. The setup was accordingly calibrated for the monitoring period May 1999-June 2004 and validated for the monitoring period July 2004-June 2014. 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. Data acquisition and model setup are described in Barlebo *et al.* (2007).

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.

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⁾
01.07.99–30.06.00	626	715	572	192	152	-50
01.07.00–30.06.01	626	639	383	50	35	206
01.07.01–30.06.02	626	810	514	197	201	99
01.07.02–30.06.03	626	636	480	49	72	107
01.07.03–30.06.04	626	685	505	36	19	144
01.07.04–30.06.05	626	671	469	131	55	72
01.07.05–30.06.06	626	557	372	28	16	158
01.07.06–30.06.07	626	796	518	202	212	77
01.07.07–30.06.08	626	645	522	111	65	12
01.07.08–30.06.09	626	713	463	46	20	204
01.07.09–30.06.10	626	624	415	54	43	155
01.07.10–30.06.11	626	694	471	133	184	90
01.07.11–30.06.12	626	746	400	98	106	247
01.07.12–30.06.13	626	569	456	62	92	50
01.07.13–30.06.14	626	593	425	44	88	124

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 field (see detailed text above).

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

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 2013–June 2014 were generally well described by the model (Figure 6.2D, 6.2E and 6.2F). Yet, the model did not capture the level of the measured water saturation at 25 cm b.g.s. (Figure 6.2D) both during summer and winter. The cause for this discrepancy could be, not only the uncertainty in the simulations but also the fact that the TDR-probes in 25 cm depth were removed when ploughing. If a good soil-contact is not re-established, a lower level of measured water saturation could be obtained. To address this issue there will be a future focus on the re-establishment of TDR in 25 cm depth.

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 2013–June 2014 was characterised by having the third lowest precipitation, a medium actual evapotranspiration, the third lowest measured drainage, and medium simulated drainage. This resulted in the medium groundwater recharge estimated for this field within the PLAP-period. Precipitation in this year was characterised by medium monthly precipitation compared to the other PLAP-years, although July 2013 was the driest ever registered in PLAP (Appendix 4) and the period December 2013–February 2014 was very wet. Due to this precipitation pattern, the duration of the simulated percolation period of the year July 2013–June 2014 was represented by continuous percolation throughout the period November–April (Figure 6.2A), which were of a shorter duration than in previous PLAP-years. 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 minor contributions to the drains in January and February (Figure 6.2B and 6.2C). The discrepancy between the measured and simulated drainage amount in Table 6.1 seems to be caused by a drainage event, being simulated when there is a drop in the air temperature below 0° C.

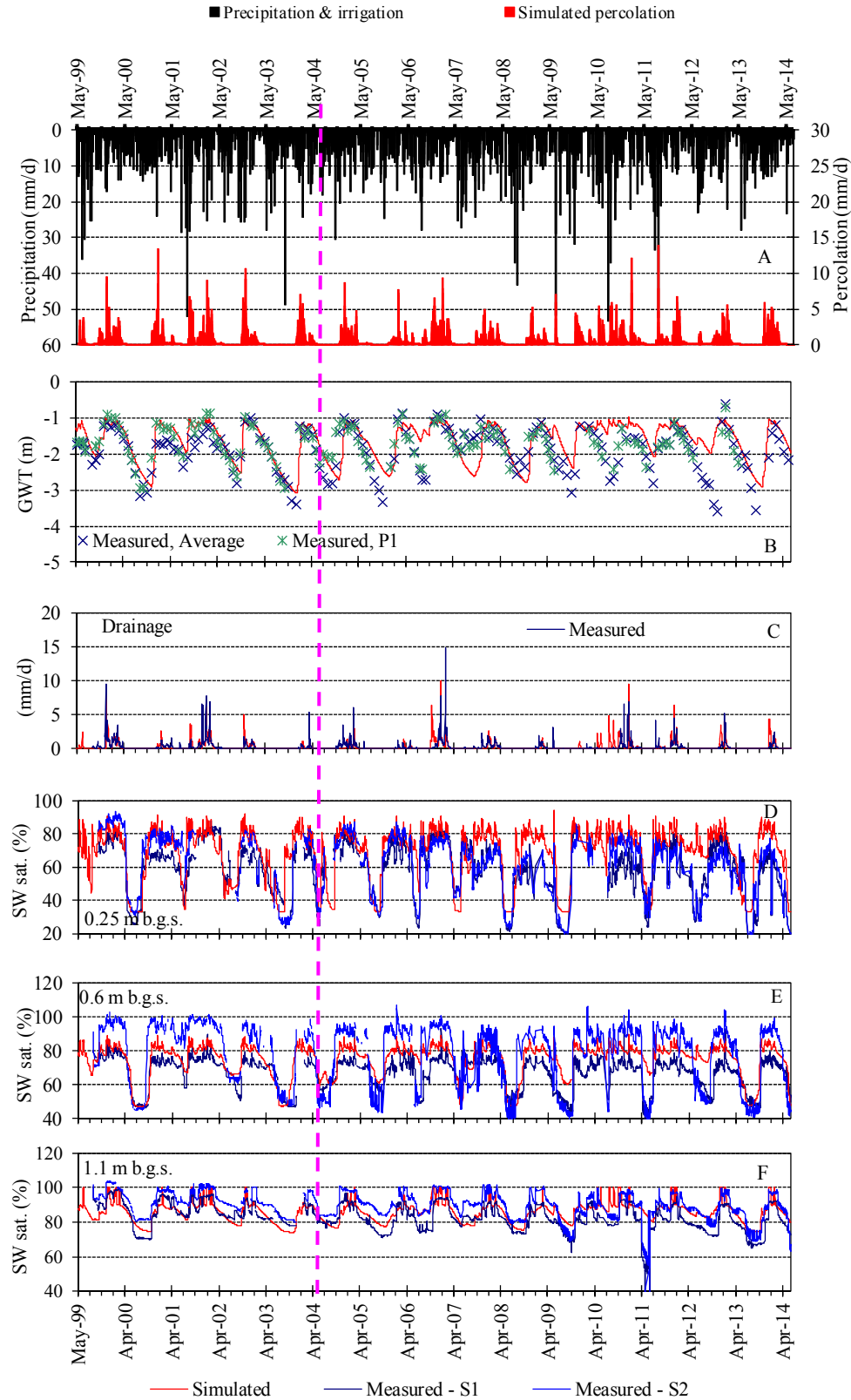


Figure 6.2. Soil water dynamics at **Faardrup**. Measured precipitation and simulated percolation 1 m b.g.s. (A), simulated and measured groundwater table, GWT (B), simulated and measured drainage (C), and simulated and measured soil water saturation (SW sat.) at three different soil depths (D, E and 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 2014).

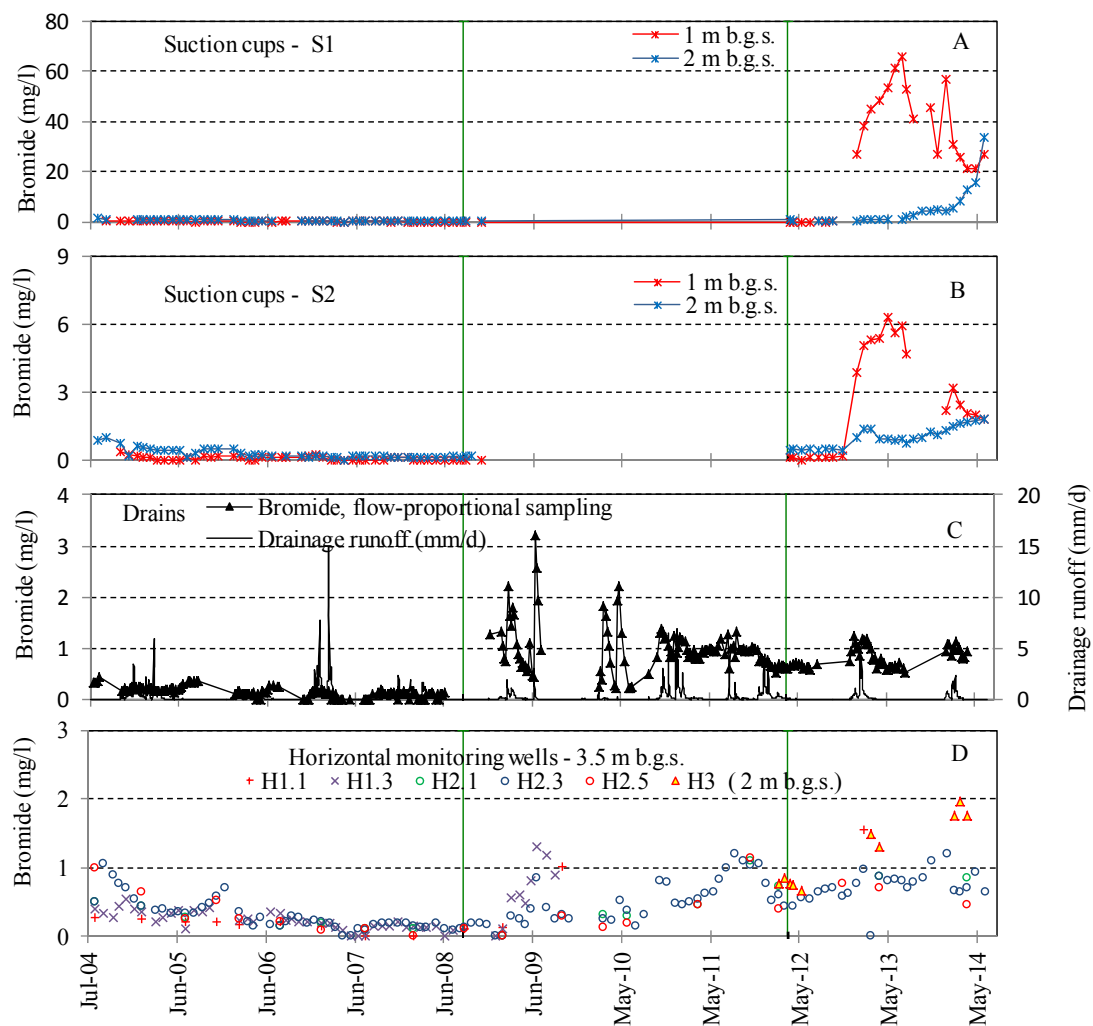


Figure 6.3. Bromide concentrations at **Faardrup** in the period July 2004–June 2014. A and B refer to suction cups located at S1 and S2. The bromide concentration is also shown for drainage runoff (C) and the horizontal monitoring wells. The horizontal wells H1 and H2 are situated 3.5 m b.g.s., and 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 within the period.

Much more simulated water is leached into the drains than observed. As seen before, the amount and speed by which the precipitation is transferred via the soil media to the drainage do not seem to be fully captured by the MACRO-model of Faardrup during snow accumulation and melt.

6.2.2 Bromide leaching

The bromide concentration shown in Figure 6.3 and 6.4 relates to the bromide applied in May 2000, August 2008 and April 2012, where 30 kg ha^{-1} potassium bromide was applied each 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). To follow the leaching of bromide through the variably-saturated zone into the drainage and groundwater in more detail, water from the suction cups were analysed for its

concentration of bromide in connection with the application of bromide on 4 April 2012. The outcome revealed a factor ten in concentrations measured in water from suction cups of S1 and S2 indicating a much higher bromide source term at S1 than S2. Common for S1 and S2 was a drastic increase in bromide concentration at 1 m depth in January 2013, which seems to be the result of snowmelt transporting bromide down to the level of the groundwater table situated at approximately depth of the tile drains and the suction cups at 1 m depth. Bromide leaching also seems to reach 2 m depth at both S1 and S2 at approximately the same initial concentrations in January 2013. The high level in bromide concentration at 2 m depth in S1 was, however, also reached at the end of the hydrological year 2013/2014. This high concentration level of bromide at S1 is not comparable to the detections in water from the other installations at Faardrup (Figure 6.3 and 6.4) or the other PLAP-fields. Such difference can only delineate that water sampling with suction cups in low permeable fractured soil media like clayey till will give a very local and uncertain picture of the overall bromide leaching.

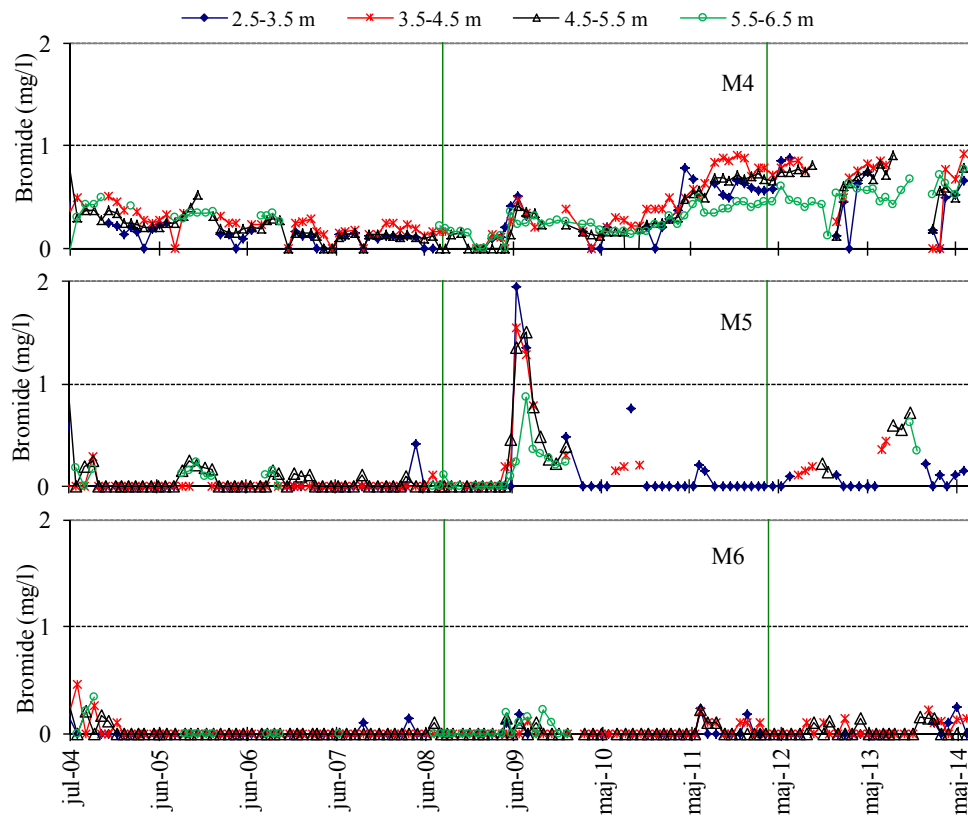


Figure 6.4. Bromide concentrations at **Faardrup** in the period July 2004–June 2014. The data derive from the vertical monitoring wells (M4, M5 and M7). Screen depth is indicated in m b.g.s. The green vertical lines indicate the dates of the two most recent bromide applications.

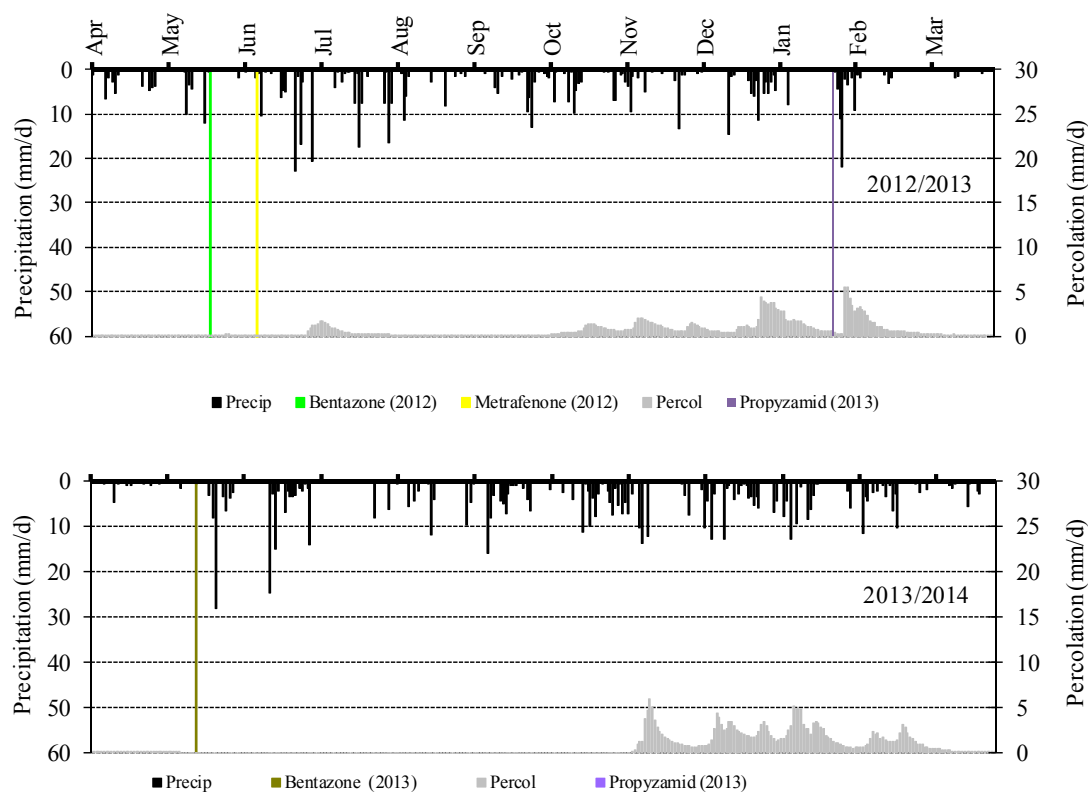


Figure 6.5. Application of pesticides included in the monitoring programme and precipitation (primary axis) together with simulated percolation (secondary axis) at **Faardrup** in 2012/2013 (upper), in 2013/2014 (lower).

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 analysed 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	Analysed pesticide	Applica. date	End monito.	Y 1 st precip.	Y 1 st percol.	M 1 st precip.	M 1 st 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
		Metamitron(P)		Jun 11	609	146	42	2	0.02
	Safari	Desamino-metamitron(M)	Apr 09	Jun 11	609	146	42	2	0.06
		Triflusalufuron-methyl(P)		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 Red fescue 2010	Fighter 480	Bentazone(P)	Jun 10	Jun 12*	693	327	49	29	<0.01
	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
Red fescue 2011	Fusilade Max	Nitrofen(M)		Jun 12	351	190	75	72	0.01
		Fluazifop-P(M)	May 11	Mar 12	730	0	59	0	<0.01
		TFMP(M)		Jun 14*	730	0	59	0	<0.01
Spring barley and White clover 2012	Glyphogan	Glyphosate(P)	Oct 11	Aug 12	425	17	56	17	<0.01
		AMPA(M)		Aug 12	425	17	56	17	<0.01
	Fighter 480	Bentazone(P)	May 12	Jun 14*	527	220	29	4	<0.01
	Flexity	Metrafenone(P)	Jun 12	Jun 14*	580	215	96	14	<0.01
White clover 2013	Fighter 480	Bentazone(P)	May13	Jun 14*	711	213	82	0	0.02
	Kerb 400 SC	Propyzamid (P)	Jan 13	Jun 14*	740	213	64	0	<0.01
		RH24560 (M)		Jun 14*	740	213	64	0	<0.01
		RH24644 (M)		Jun 14*	740	213	64	0	<0.01
		RH24655 (M)		Jun 14*	740	213	64	0	<0.01
Winter wheat 2014	Folicur EC250	1,2,4-triazol (M)**							
		Tebuconazole (P)							

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

*Monitoring continues the following year.

**Monitoring started in May 2014 – will be reported in the next report.

The current report focuses on the pesticides applied from 2012 and onwards, while the leaching risk of pesticides applied before 2012 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 2012, bentazone and metrafenone; and in 2013 bentazone and propyzamide.

These three pesticides and the degradation products of propyzamide RH24580, RH24644 and RH24655 have all been included in the PLAP-monitoring programme from 2012 for Faardrup – only bentazone has been tested at this field before 2011 (Table A7.5 in Appendix 7). TFMP, which has been included in this programme since April 2011, has not been detected in water from any of the installations yet.

In the hydrological years 2012/2013 and 2013/2014, bentazone was applied to test its leaching potential in cereal (spring barley) with under sowings (bentazone is not allowed to be used in cereal without under sowing) of white clover 2012 and on white clover alone in 2013. The application onto spring barley and white clover on 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 seems to be caused by snowmelt resulting in high percolation and a sudden rise in the groundwater table during this month (Figure 6.7) as described by the bromide leaching (section 6.2.2). From the time of this detection until May 2013, where bentazone was applied a second time on white clover, bentazone was not detected. The leaching scenario of bentazon following this second application was similar to the scenario following the first application except for bentazon being detected seven times in the drainage at 1.2 m depth and twice in the horizontal well H3 situated at 2 m depth (at approx. 0.02 µg/L) – all caused by snowmelting.

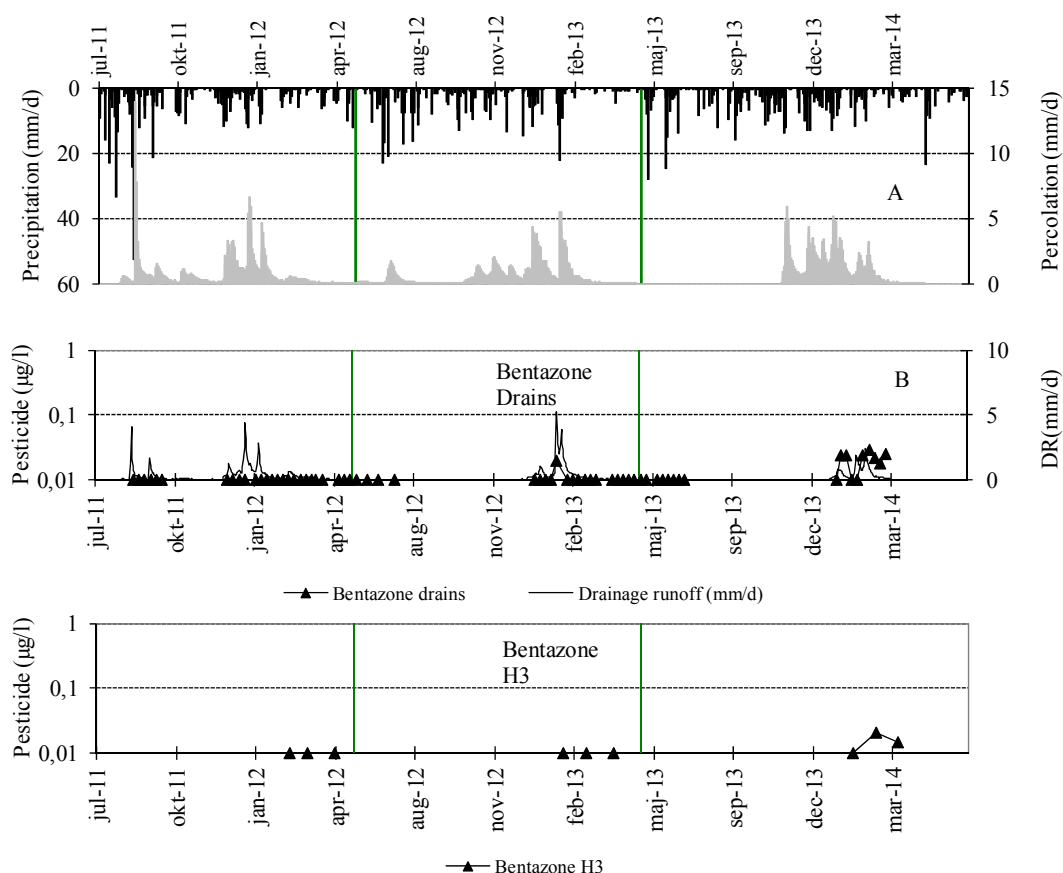


Figure 6.7. Precipitation and simulated percolation 1 m b.g.s. (A) together with the concentration of bentazone (B) in the drainage at **Faardrup**. The green vertical lines indicate the dates of bentazone application.

Metrafenone, which was applied on spring barley under sowing with white clover in June 2012, has not been detected during the hydrological years 2012/2013 and 2013/2014.

Neither propyzamide nor its three degradation products have been detected in 2013/2014, following the application of propyzamide on white clover at the end of January 2013.

7 Pesticide analysis quality assurance

Reliable results and scientifically valid methods of analysis are essential for the integrity of the present monitoring programme. Consequently, the field monitoring work has been supported by intensive quality assurance entailing continuous evaluation of the analyses employed. Two types of sample are used in the quality control 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 2013 to June 2014 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 analyses were carried out at a commercial laboratory selected on the basis of a competitive tender. In order to assure the quality of the analyses, the call for tenders included requirements as to the laboratory's quality assurance (QA) system comprising both an internal and an external control procedure. In addition to specific quality control under the PLAP, the laboratory takes part in the proficiency test scheme employed by the Danish 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 analysed 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

Three times during the period July 2013 to June 2014, two external control samples per test field were analysed at the laboratories along with the various water samples from the five fields. 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 external QC 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 pesticides included and their concentration in the solution is indicated in Table 7.1.

Blank samples consisting only of ultra-pure 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 QA controls, blanks or true samples.

Table 7.1. Pesticides included in the **external** QA control samples in the period 1.7.2013-30.6.2014. Concentrations in both the original ampoules and in the resulting high-level and low-level external control samples used.

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	0.117	0.050
Aminopyralid	1000	3	0.117	0.050
Bentazone	1000	1	0.117	0.050
Boscalid	1000	1	0.117	0.050
CGA108906	1000	1	0.117	0.050
CyPM	1000	1	0.117	0.050
Diflufenican	1000	1	0.117	0.050
Glyphosate	1000	2	0.117	0.050
Metrafenone	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
1,2,4-triazole	1000	3	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 analyses, single analyses being excluded. The analysis can be divided into three stages:

1. **Normality:** An initial test for normality is made as this is an underlying assumption for the one-way ANOVA.
2. **Between-day contribution:** 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 analysed, the QA applied is pesticide-specific. In the current reporting period internal quality data was available for 30 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 0.007 and S_t was 0.009, 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 ten compounds. For these compounds, the results indicate that day-to-day variation makes a significant contribution. Among the compounds meeting the normality requirement, four out of 16 compounds had ratios above two, where the highest S_b/S_w ratio in this group was 3.0 and observed for MNBA (a degradation product from mesotrione). The three other compounds were metalaxyl-M with a ratio of 2.7, azoxystrobin with a ratio of 2.6, and prosulfocarb with a ratio of 2.4. These are rather low ratios compared to ratios in the previous report.

MNBA meets the normality criterium, but it is apparent that the high S_b/S_w ratio is caused by the relatively high between-day deviation (S_b), indicating that it may be possible to improve the analytical procedure for this compound to bring down this deviation.

For metalaxyl-M the ratio of 2.7 is still a little too high to meet the criteria but both S_b and S_w are low values. Compared to last year's reporting period, where the ratio was 2.5 but the compound did not meet the normality criteria, the analytical procedure now seems to have improved and in good control with lower S_b and S_w and it is apparent that the high S_b/S_w ratio is caused by the higher between-day deviation (S_b) relative to the very low S_w .

As for metalaxyl-M, the analysis of azoxystrobin has improved from last year's reporting period. The compound now meets the requirement for normality and the ratio has decreased although still a little too high. The analytical procedure now seems to have improved and in good control with lower S_b and S_w and it is apparent that the high S_b/S_w ratio is caused by the high between-day deviation (S_b) relative to the very low S_w . Both S_w and S_b are still low values.

The ratio S_b/S_w has slightly increased from last year's reporting period for prosulfocarb, but both the between-day deviation (S_b) and with-in day (S_w) variation has decreased and it is apparent that the increased S_b/S_w ratio is caused by the high between-day deviation (S_b) relative to the very low S_w . However, both S_w and S_b are still low values, actually indicating an analytical procedure in good control.

When all compounds are considered, no compounds have S_b/S_w ratios higher than 3.4 (observed for RH-24655) which is a clear improvement compared to last year's report, where several compounds had much higher ratios, the highest last year being clomazone (6.8), propyzamide (4.9), RH-24580 (4.6), and RH-24655 (4.5) (note normality criteria were not met for any of these compounds). This year's high S_b/S_w ratios are due to relatively high between-day deviation (S_b) indicating that it may be possible to improve the analytical procedure for these compounds to bring down this deviation. It should, however, be noted that all ratios have been lowered compared to last reporting year and the ratios > 2 this year, are due to very low with-in day deviation and relatively, but acceptable, higher between-day deviations.

Table 7.2. Internal QA of pesticide analyses carried out in the period 1.7.2013-30.6.2014. 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 ($\mu\text{g/L}$)	S_b ($\mu\text{g/L}$)	S_t ($\mu\text{g/L}$)	Ratio S_b/S_w	N	Conc. ($\mu\text{g/L}$)
AE-05422291*	-	-	0.004	0.006	0.007	1.7	40	0.05
AE-B107137*	-	-	0.011	0.012	0.017	1.1	36	0.10
AMBA*	yes	yes	0.011	0.002	0.011	0.2	10	0.10
AMPA*	yes	-	0.002	0.004	0.004	1.7	38	0.03
Aminopyralid	-	-	0.008	0.020	0.022	2.6	41	0.10
Azoxystrobin	yes	-	0.003	0.009	0.009	2.6	37	0.05
Bentazone	-	-	0.004	0.007	0.008	1.8	51	0.05
Bromoxynil	-	-	0.007	0.008	0.011	1.2	25	0.05
CGA 108906*	yes	-	0.012	0.014	0.018	1.2	12	0.10
CGA 192155*	yes	yes	0.001	0.001	0.002	0.6	3	0.05
CGA 339833*	-	yes	0.010	0.004	0.011	0.4	3	0.05
CGA 62826*	yes	-	0.007	0.007	0.010	1.0	12	0.10
Clomazone	yes	-	0.003	0.006	0.007	1.9	34	0.05
CyPM*	yes	-	0.005	0.010	0.011	2.0	32	0.05
Diiflufenican	-	-	0.002	0.005	0.005	2.5	40	0.05
EBIS*	yes	yes	0.001	0.002	0.002	1.6	3	0.03
FMC 65317*	-	-	0.004	0.003	0.005	0.9	33	0.05
Glyphosate	-	-	0.002	0.002	0.003	1.5	39	0.03
Ioxynil	yes	-	0.006	0.005	0.008	0.9	25	0.05
MNBA*	yes	-	0.006	0.019	0.020	3.0	10	0.10
Mesotrione	yes	-	0.007	0.009	0.011	1.2	11	0.10
Metalaxyl-M	yes	-	0.001	0.004	0.004	2.7	12	0.05
Metrafenone	-	-	0.002	0.006	0.006	2.6	41	0.05
Propyzamide	-	-	0.002	0.005	0.005	2.2	21	0.05
Prosulfocarb	yes	-	0.004	0.009	0.010	2.4	11	0.05
RH-24580*	-	-	0.002	0.006	0.006	2.3	21	0.05
RH-24644*	-	-	0.003	0.006	0.006	1.9	21	0.05
RH-24655*	-	-	0.002	0.008	0.008	3.4	21	0.05
TFMP*	yes	-	0.005	0.008	0.010	1.5	29	0.05
1,2,4-triazol*	yes	yes	0.002	0.001	0.002	0.8	3	0.03

*Degradation product.

The total standard deviation (S_t) of the various analyses of pesticides and degradation products lie within the range 0.002-0.022 $\mu\text{g/L}$, the highest value being observed for aminopyralid (but the total standard deviation for the compound has improved significantly from last year's report, where it was 0.041 $\mu\text{g/L}$). In general, the data suggest that the analytical procedure used for the quantification of the compounds has in general improved from last year's report, but there is still room for improvement and optimisation of, especially, the within-day variation (S_b).

7.2.2 External QA

As described above the external QA program was based on samples spiked at the field. As part of the quality control a set of blanks made from HPLC water were also analysed to evaluate the possibility of false positive findings in the programme. From these results it can be concluded that contamination of samples during collection, storage and analysis is not likely to occur. A total of 34 blank samples made from HPLC water were analysed and no compounds were detected in any of these analysed blank samples. On the basis of this, samples analysed in the monitoring program and detected 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 1.7.2013-30.6.2014. Average recovery (%) of the nominal concentration at low/high concentration level is indicated for each field. 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. $n_{total\ analysed}$ 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 %		Jyndeved %		Silstrup %		Estrup %		Faardrup %		Average %	$n_{low}/$ n_{high}	n_{total} analysed
	Low	High	Low	High	Low	High	Low	High	Low	High			
AMBA			86	91							88	3/3	6
AMPA						20		34			28	0/5	9
Aminopyralid	68	48					82	51			60	5/6	11
Bentazone			100	100			100	96	100	94	98	9/9	18
CGA 108906	119	86	92	84							95	6/6	12
CyPM					94	86	100	108			97	6/6	12
Diiflufenican					93	93	92	88			92	6/6	12
Glyphosate					57	56	54	57			56	6/6	12
Metrafenone							81	81	84	66	78	6/6	12
RH-24644									74	59	66	3/3	6
TFMP					72	43			86	61	65	6/6	12
1,2,4-triazole							160	128	100	102	122	2/2	4

**The concentration of glyphosate and AMPA in ampoule 2 Dr. Ehrenstorfer A/S was not correct.*

Table 7.3 provides an overview of the recovery of all externally spiked samples. Since the results for each field 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 QA external data, especially for AMPA, glyphosate and 1,2,4-triazole, points to the need of keeping track of these particular compounds.

In reports before 2011 the recoveries of AMPA at Estrup and Faardrup were good and within the acceptable range. However, in last year's report and this present reporting period, very low recoveries are observed 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. Last year, the discrepancy in the glyphosate and AMPA recoveries was due to a flawed ampoule used in the program. Subsequent analysis of the initial ampoule 2 containing AMPA and glyphosate showed that the low recoveries and false negative samples was in fact due to a failure in production of ampoule 2 (initial concentration of AMPA and glyphosate in the ampoule was too low - especially the AMPA concentration was too low). This flawed batch of ampoules was unfortunately used in the external control program throughout the reporting period. Unfortunately, subsequent analysis of the ampoules ordered for this year's reporting period, also showed that the initial concentration in the ampoules used for spiking was incorrect. Due to this, a new procedure has been implemented. Every year upon arrival of the new ampoule, the concentration of glyphosate/AMPA is now tested at the commercial laboratory before the ampoule is used in the QA control sample program.

In regard to reliability of the glyphosate and 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).

In general, all recoveries of the low external QA are within the acceptable range, except for 1,2,4-triazole. The degradation product has an elevated recovery of 160%, which might be due to a background concentration of the compound. 1,2,4-triazole has recently been included in the program and the recoveries rely only on two samples. However, in combination with the internal QA (although this similarly relies on a few data points, but all statistical criteria are met) these findings do not cause a general concern, but the compound will be followed closely in the future.

Except for AMPA, all the compounds included in the spiking procedure (Table 7.1) were detected in the commercial laboratory.

During the 2013/2014 monitoring period a total of eight pesticides (azoxystrobin, bentazone, diflufenican, fluazifop-P-buthyl, glyphosate, metalaxyl-M, prosulfocarb, tebuconazole) and seven degradation products (CyPM, AE-B107137, TFMP, AMPA, CGA 108906, CGA 62826, 1,2,4-triazol) 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 analyses was good, and has improved since last year, with total standard deviation (S_t) in the range 0.002-0.022 µg/L.
- As demonstrated by the external QA, recovery was generally good in externally spiked samples. The low recoveries of AMPA and glyphosate are solely related to the flawed ampoules used for spiking in the external QA program in the reporting period. Therefore, the reliability of the AMPA and glyphosate analyses 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 2014 17 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 fields Silstrup and Estrup. CyPM leached into the drainage water in average concentrations exceeding 0.1 µg/L at both the Silstrup and Estrup fields, while azoxystrobin only leached in concentrations exceeding 0.1 µg/L at Estrup (Table 8.1 and 8.2). At both fields, 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 lower concentrations in 2012. In the 2012/13 monitoring period azoxystrobin was not detected, while CyPM was detected in one drain water sample. After application in 2013 CyPM was detected in 38 samples: 16 detections in drain water (10 > 0.1 µg/L, 17 analysed) and in 22 groundwater samples (3 > 0.1 µg/L, 59 analysed). Azoxystrobin was detected in 2 drain sample and in one from groundwater (< 0.1 µg/L).


Azoxystrobin was applied at Estrup in June 2012, and both azoxystrobin and CyPM leached in high concentrations to drain water in concentrations ≥ 0.1 µg/L. The degradation product CyPM was detected in four groundwater samples from one

horizontal well, and in one sample the concentration was $\geq 0.1 \mu\text{g/L}$. There were no findings in groundwater monitoring wells. At the loamy Faardrup field azoxystrobin and CyPM were detected in four samples from the drainage water up till 2007, and in no samples from the sandy Jyndeved field 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 fields. The colours indicate the degree of leaching. Pesticides applied in spring 2014 are not included in the table.

Risk	Pesticide	Tylstrup	Jynde vad	Silstrup	Estrup	Faardrup
High	Azoxystrobin					
	Bentazone					
	Bifenox					
	Di flufenican					
	Ethofumesate					
	Fluazifop-P-butyl					
	Fluroxypyr					
	Glyphosate					
	Met alaxyl-M					
	Metamitron					
	Metribuzin					
	Picolinafen					
	Pirimicarb					
	Propyzamide					
	Rimsulfuron					
	Tebuconazole					
	Terbutylazine					
Low	Amidosulfuron					
	Bromoxynil					
	Clomazone					
	Dimethoate					
	Epoxiconazole					
	Flamprop-M-isopropyl					
	Ioxynil					
	MCPA					
	Mancozeb					
	Mesosulfuron-methyl					
	Metrafenone					
	Pendimethalin					
	Phenmedipham					
	Propiconazole					
	Prosulfocarb					
	Pyridate					
	Triflusalufuron-methyl					
None	Aclonifen					
	Aminopyralid					
	Boscalid					
	Chlormequat					
	Clopyralid					
	Cyazofamid					
	Desmedipham					
	Fenpropimorph					
	Florasulam					
	Fludioxonil					
	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 field with maximum concentration ($\mu\text{g/L}$). 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 $\mu\text{g/l}$. The pesticide and degradation products are mentioned if analysed under compound. N: number of samples with detections. M: maximum concentration.

Risk	Pesticide	Analyte	Tylstrup		Jyndeved		Silstrup		Estrup		Faardrup	
			N	M	N	M	N	M	N	M	N	M
High	Azoxystrobin	Azoxystrobin	0		0		13	0.11	127	1.40	0	
		CyPM	0	-	0	-	96	0.56	291	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	75	2.00	45	6.40	193	20.00	28	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	Nitrofen	0	-	0	-	5	0.34	0	-	6	0.16
		AE-B107137			0	-	5	0.13	14	0.09		
	Diflufenican	Diflufenican			0	-	11	0.12	21	0.49		
		Ethofumesate					20	0.23	35	3.36	14	12.00
	Fluazifop-P-butyl	Fluazifop-P	0	-	0	-	0	-			9	3.80
		TFMP					53	0.64			0	-
	Fluroxypyr	Fluroxypyr	0	-	0	-	0	-	3	1.40	1	0.19
	Glyphosate	AMPA			1	0.01	150	0.35	439	1.60	15	0.11
		Glyphosate			0	-	87	4.70	317	31.00	5	0.09
	Metalaxyl-M	CGA 108906	86	4.80	67	3.70						
		CGA 62826	33	0.12	68	1.20						
	Metalaxyl-M	Metalaxyl-M	4	0.03	11	0.04						
		Desamino-metamitron					58	0.67	49	5.55	16	2.50
	Metamitron	Metamitron					45	0.55	42	26.37	12	1.70
		Desamino-diketo-metribuzin	63	2.10	0	-						
	Metribuzin	Diketo-metribuzin	184	0.62	3	0.09						
		CL153815			0	-			31	0.50		
	Picolinafen	Picolinafen			1	0.02			17	0.07		
		Pirimicarb	0	-	0	-	14	0.05	40	0.08	7	0.06
	Pirimicarb	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	RH-24644	0	-			15	0.05			4	0.02
		RH-24655	0	-			0	-			1	0.02
	Rimsulfuron	PPU	153	0.09	194	0.29	0	-				
		PPU-desamino	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	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	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	-	1	0.28
		FMC 65317	0	-	0	-			0	-	1	0.30
	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	1	0.03			5	0.18			0	-
	Pyridate	PHCP			0	-	4	2.69				
	Triflurosulfuron-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 fields (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	Pesticide	Tylstrup	Jynde vad	Silstrup	Estrup	Faardrup
High	Azoxystrobin					
	Bentazone					
	Bifenox					
	Diflufenican					
	Ethofumesate					
	Fluazifop-P-butyl					
	Fluroxypyr					
	Glyphosate					
	Metalaxyl-M					
	Metamitron					
	Metribuzin					
	Picolinafen					
	Pirimicarb					
	Propyzamide					
	Rimsulfuron					
	Tebuconazole					
	Terbutylazine					
Low	Amidosulfuron					
	Bromoxynil					
	Clomazone					
	Dimethoate					
	Epoxiconazole					
	Flamprop-M-isopropyl					
	Ioxynil					
	MCPA					
	Mancozeb					
	Mesosulfuron-methyl					
	Metrafenone					
	Pendimethalin					
	Phenmedipham					
	Propiconazole					
	Prosulfocarb					
	Pyridate					
	Triflusaluron-methyl					
None	Aclonifen					
	Aminopyralid					
	Boscalid					
	Chlormequat					
	Clopyralid					
	Cyazofamid					
	Desmedipham					
	Fenpropimorph					
	Florasulam					
	Fludioxonil					
	Iodosulfuron-methyl					
	Linuron					
	Mesotrione					
	Thiacloprid					
	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 field with the maximum concentration (µg/L). Only high and low risk included. The parent pesticide and degradation products are mentioned if analysed under Parent. Pesticides applied in spring 2014 are not included. N: number of samples with detections. M: maximum concentration.

Risk	Pesticide	Analyte	Tylstrup		Jyndevad		Silstrup		Estrup		Faardrup	
			N	M	N	M	N	M	N	M	N	M
High	Azoxystrobin	Azoxystrobin	0		0		1	0.02	2	0.04	0	
		CyPM	0	-	0	-	50	0.19	19	0.13	0	-
	Bentazone	2-amino-N-isopropyl-benzamide	0	-	0	-	0	-	1	0.03	0	-
		Bentazone	0	-	1	0.01	29	0.44	30	0.05	15	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
	Diflufenican	AE-B107137			0	-	0	-	1	0.02		
		Diflufenican			0	-	1	0.47	0	-		
	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	24	0.08	8	0.07	2	0.03
		Glyphosate			0	-	27	0.05	47	0.67	5	0.03
	Metalaxyl-M	CGA 108906	244	1.50	239	2.70						
		CGA 62826	17	0.04	137	0.68						
		Metalaxyl-M	17	0.08	68	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	58	0.05	374	0.23						
		PPU-desamino	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	Dimethoate	Dimethoate	0	-	0	-	1	0.09	-	-	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	-	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	4	0.03			1	0.03			0	-
	Pyridate	PHCP			0	-	14	0.31				
	Triflurosulfuron-methyl	IN-M7222					1	0.05			0	-
	Desmedipham	Desmedipham					1	0.03			0	-
	Fenpropimorph	Fenpropimorph	0	-	1	0.03	0	-	0	-	1	0.02
	Triasulfuron	Triazinamin	0	-			0	-	1	0.04		

- **Bentazone** leached through the root zone (1 m b.g.s.) in average concentrations exceeding 0.1 µg/L to the drainage system at the loamy fields 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 Jyndeved, but was only detected once 1 m b.g.s. at Tylstrup. At Jyndeved many 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 in 2012 and 2013. 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 fields, 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 detected 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 Jyndeved, 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 May 2013 been applied 17 times to the five tests fields. Bentazone has in the period from 2001 to 2014 been detected in four groundwater samples from Silstrup in 2003 and in 2005 in four groundwater samples from Faardrup in concentration ≥ 0.1 µg/L. Bentazone has been detected in lower concentration in 74 groundwater samples out of 3.898 analysed samples. In total bentazone has been analysed in 5.518 water samples from drain and groundwater. Monitoring of bentazone is ongoing.
- 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 fields of Silstrup, Estrup and Faardrup. While the 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 detected in very high concentrations in drainage water from Faardrup, in a yearly average concentration of 2.54 µg/L (Table 6.2). In 2011/2012 bifenox acid leached, but in low concentrations, and bifenox was only detected in few water samples. Another degradation product from bifenox, nitrofen, was detected in drainage water from Faardrup, often in low concentrations, but 0.16 µg/L was detected in one drainage water sample in November 2010. In Silstrup, 0.34 and 0.22 µg/L was detected in two drainage water 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.
- **Diflufenecan** and AE-B107137 have been analysed after application at Silstrup and Estrup in 2012 and 2013, where both diflufenecan and the degradation product AE-B107137, were detected frequently in drainage water. Diflufenecan was detected in one groundwater sample (0.47 µg/L) from Silstrup and AE-B107137 was detected in one groundwater sample (0.016 µg/L) from Estrup. Monitoring stopped in June 2014.

- 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 fields, 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 one to six months 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 0.1 µg/L, neither ethofumesate nor metamitron was detected in the analysed water samples. The monitoring of ethofumesate and metamitron stopped in June 2011.
- **Fluroxypyr** have been analysed on all test fields. Fluroxypyr have been detected in few drain water from Estrup and only in two groundwater samples from Estrup and Faardrup (< 0.1 µg/L). Monitoring stopped in June 2008.
- **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, another 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-months period, following application (Figure 4.6, Table 8.3 and 8.4). At the onset of drainage 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 drainage water was 0.24 µg/L in 2008/09. The leaching pattern of TFMP indicates pronounced preferential flow also in periods with a relatively dry vadose zone. After use in low doses at Silstrup no leaching was observed, but in 2012 after application in April 2012, TFMP was detected in increasing concentrations in drainage water, where 0.64 µg/L was measured in June 2012. In Silstrup TFMP was detected in groundwater at the end of April, and it is possible that preferential flow caused the quick leaching. TFMP was detected in low concentrations in both groundwater and drains until October 2013. At Faardrup fluazifop-P-butyl was applied May 2011 in the new dose, and TFMP was not detected in drain or groundwater. Up till now the

pesticide has been applied ten times at four test fields. Monitoring of TFMP is ongoing.

- **Glyphosate** and AMPA were found to leach through the root zone at high average concentrations on loamy soils. At the loamy fields Silstrup and Estrup, glyphosate has been applied ten or nine times (in 2000, 2001, 2002, 2003, 2005, 2007, 2011, 2012 and 2013) within the monitoring period. All ten 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 from 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 a few samples). Glyphosate and AMPA were also detected in drainage water at the loamy field of Faardrup (as well as at the now discontinued Slaeggerup field), 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 detected in concentrations up to 0.66 µg/L in drainage from Silstrup, but not in concentrations in groundwater exceeding 0.1 µg/L. After application in August 2013 glyphosate was detected in drainage water in low concentrations up to 0.036 µg/L, and AMPA in concentrations up to 0.054 µg/L. Glyphosate and AMPA was detected in low concentrations in nine groundwater samples in concentrations up to 0.052 µg/L. Glyphosate and its degradation product AMPA have been detected frequently in high concentrations \geq 0.1 µg/L in drainage water from Estrup after application in October 2011 and in August 2013, and glyphosate was detected in one groundwater samples in concentrations \geq 0.1 µg/L (0.13 µg/L) after the 2012 application. Neither AMPA nor glyphosate were detected in groundwater from Estrup after the August 2013 application. Monitoring at Faardrup of glyphosate stopped August 2012.
- Two degradation products of **metribuzine**, diketo-metribuzine and desamino-diketo-metribuzine, 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 metribuzine and its degradation products have long-term sorption and dissipation characteristics (Rosenbom *et al.*, 2009). At both sandy fields (Tylstrup and Jyndevad), previous applications of metribuzine 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 detected in low concentrations in few samples from the variably-saturated zone at Tylstrup. Two degradation products (CGA 62829 and CGA 108906) however, were leached from the root zone (1 m b.g.s.) and CGA 108906 in average concentrations exceeding 0.1 µg/L (Table 2.2, Figure 2.6, Table 8.1-8.4). CGA 108906 was detected in 95% of the analysed groundwater samples, and in 32% of the analysed samples the concentration exceeded 0.1 µg/L. Similar to the other compounds CGA 108906 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 CGA 108906 was detected more frequently and in higher concentrations at Tylstrup and Jyndevad in both the variably-saturated and the saturated zone. Both degradation products were detected at Jyndevad in concentrations exceeding 0.1 µg/L and in increasing concentrations. In the third and fourth monitoring year metalaxyl-M and degradation products were detected in decreasing and low concentrations mostly < 0.1 µg/L in both suction cups and groundwater at Tylstrup and Jyndevad. Even in the last monitoring year, June 2013-June 2014, metalaxyl-M and one or both degradation products were detected in 80% of the water samples in concentrations up to 0.28 µg/L (10% > 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 detected in the sandy soil Jyndevad after application in October 2007 (Table 8.1, 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 fields. 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 fields (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 fields, 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 and RH-24580) were detected in drainage or groundwater. The monitoring is still ongoing at Faardrup.
- 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 field at Jyndevad. Minor leaching of PPU was also seen at the sandy field 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 2011/2012, whereas it was detected in low concentration <0.1 µg/L at Tylstrup (Table 8.3 and 8.3). At both fields, 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 fields 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 did 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-months 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 fields 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 concentrations (< 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 fields (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 field, the average drainage concentration

exceeded 0.1 µg/L. Leaching of these two degradation products was at both fields confined to the drainage system. None of the two degradation products were detected from groundwater monitoring screen at Estrup, whereas at Faardrup both were detected, but at low frequencies of detection and concentrations. The monitoring of terbuthylazine stopped June 2009.

- **Tebuconazole** has been applied in autumn 2007 at Tylstrup, Jyndeved, 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 snowmelt 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 fields 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 of tebuconazole stopped in December 2012. After applying tebuconazole on winter wheat at Estrup in May 2014, the degradation product 1,2,4-triazole have been monitored. The monitoring results of 1,2,4-triazole from both Estrup, Faardrup, Tylstrup and Jyndeved will be reported in the next report.

The monitoring data also indicate leaching 1 m b.g.s. of 17 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 field as well as the maximum concentration. Apart from slight leaching of ETU (Kjær *et al.*, 2002) and amidosulfuron, within this group of 17 pesticides (or their degradation products) leaching from 1 meter was only observed at the loamy soil fields, 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 available.

17 of the 51 pesticides applied or their degradation products – about 33% – did not leach at all from 1 m b.g.s. during the monitoring period (Table 8.1). The group of 17 includes the four different sulfonylureas - metsulfuron-methyl, triasulfuron, iodosulfuron-methyl-sodium and tribenuron-methyl - applied at several fields. For example, tribenuron-methyl was applied at four different fields 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. In total 103 pesticides and degradation products have been analysed up to June 2014: 51 pesticides and 52 degradation products.

The leaching patterns of the sandy and loamy fields are further illustrated in Figure 8.1 and 8.2A-C 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.

At the loamy fields 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 fields (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 detected in selected screens at Faardrup and Silstrup. Hitherto at the Estrup, leaching of pesticides has mainly been confined to the depth of the drainage system. Apart from 99, 92, 81 and 87 water samples containing glyphosate and/or 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, e.g. nitrate in the drainage (Ernsten *et al.*, 2015). Compared to the Silstrup and Faardrup fields, the C horizon (situated beneath the drainage depth) at Estrup is low permeable with less preferential flow through macropores (see Kjær *et al.* 2005c for details). The movement of water and solute to the groundwater, are therefore slower at Estrup. An indication of this is the long period with groundwater table over depth of the tile drain system generating a higher degree of water transported via drainage than on the other two clayey till fields. Comparing the loamy fields, 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 hydro-geochemical 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.

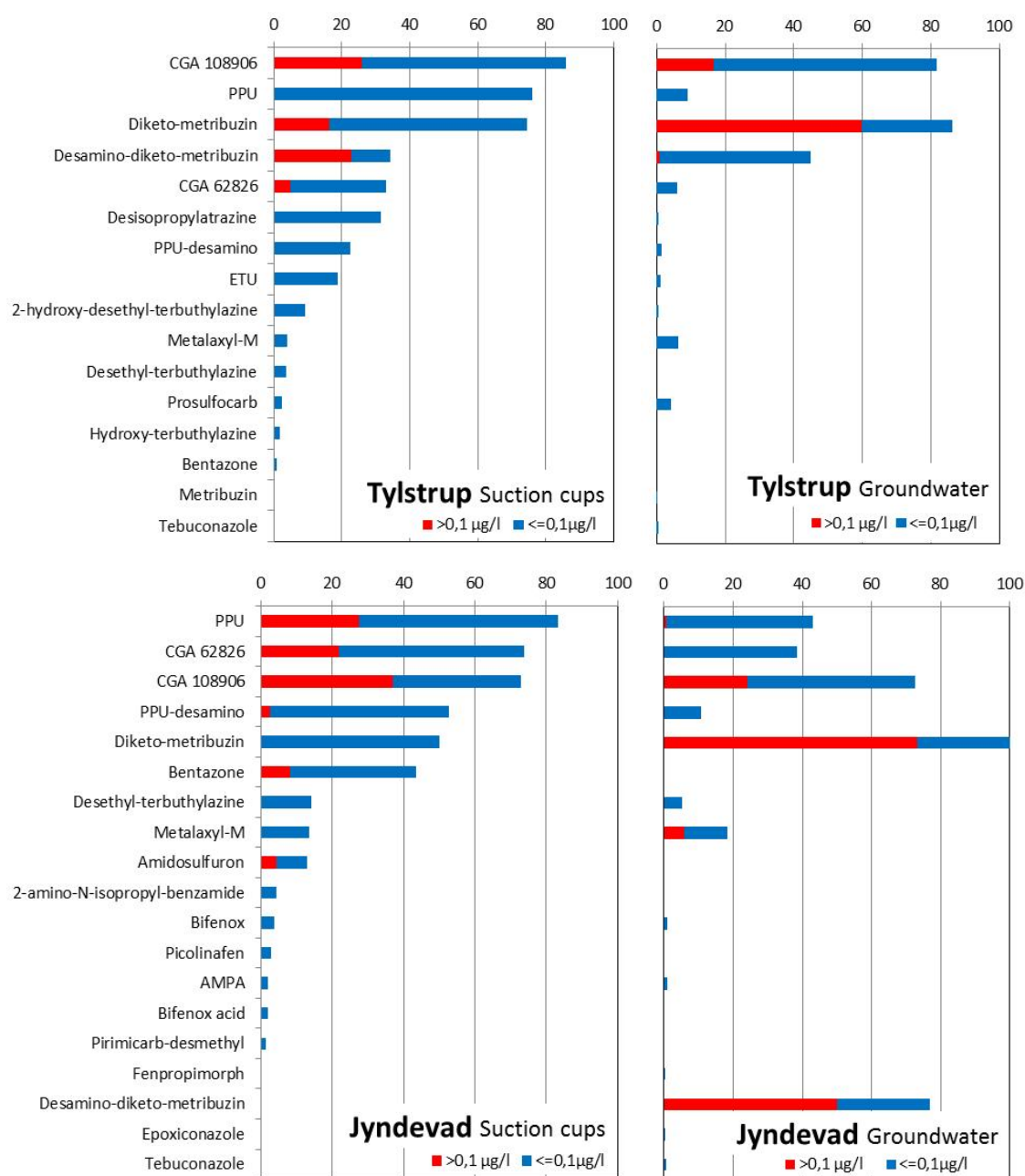


Figure 8.1. Frequency of detection in samples from the suction cups (left) and groundwater monitoring screens located deeper than the suction cups (right) at the sandy fields: **Tylstrup** and **Jyndeved**. Frequency is estimated for the entire monitoring period up to July 2014. The time the different pesticides have been included in the programme and the number of analysed samples varies. The figure includes pesticides detected in suction cups and in groundwater.

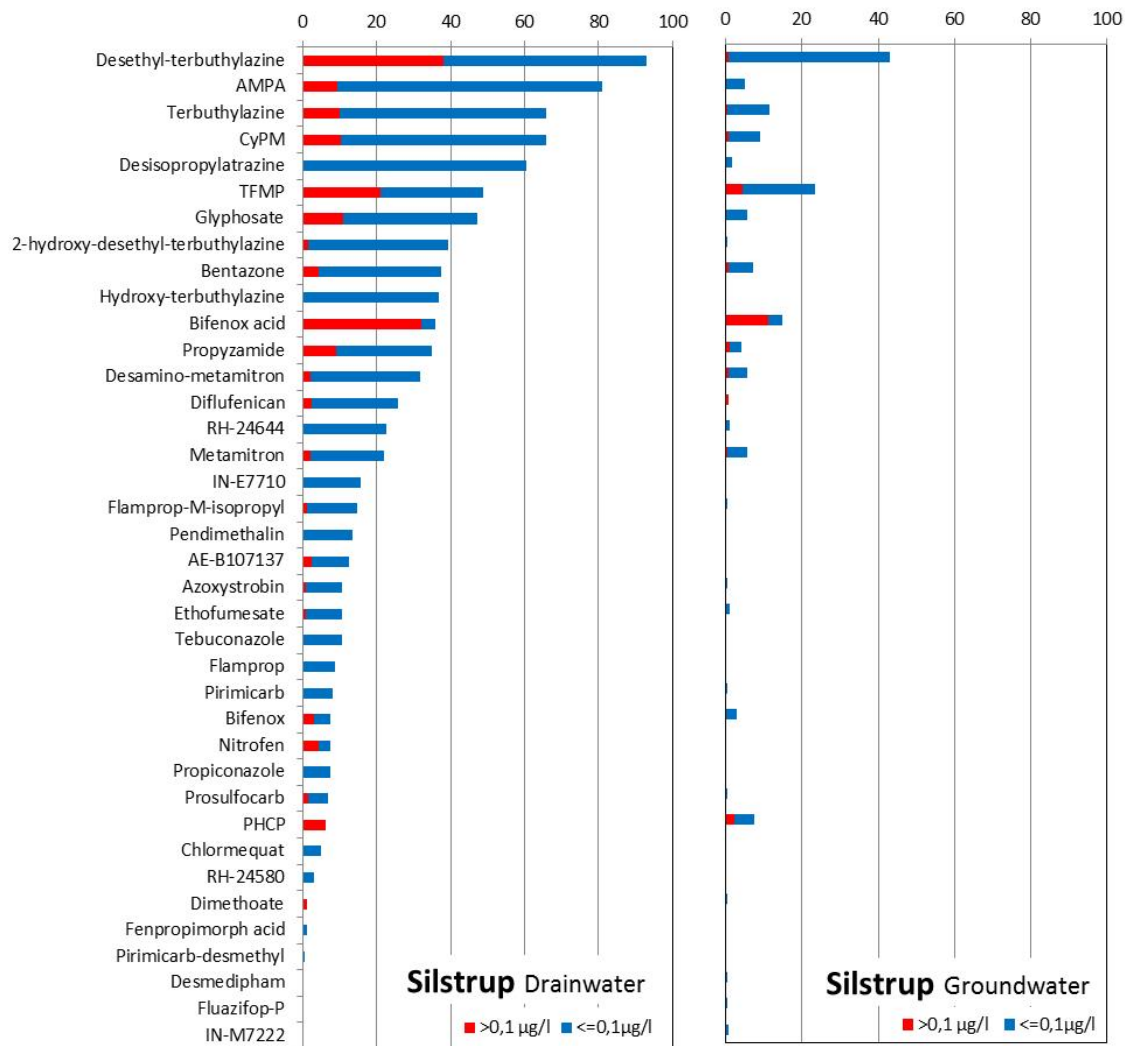


Figure 8.2A. Frequency of detection in samples from the drainage system (left) and groundwater monitoring screens located deeper than the drainage system (right) **at the loamy field Silstrup**. Frequency is estimated for the entire monitoring period up to July 2014. The time the different pesticides have been included in the programme and the number of analysed samples varies. The figure includes pesticides detected in drain- and groundwater.

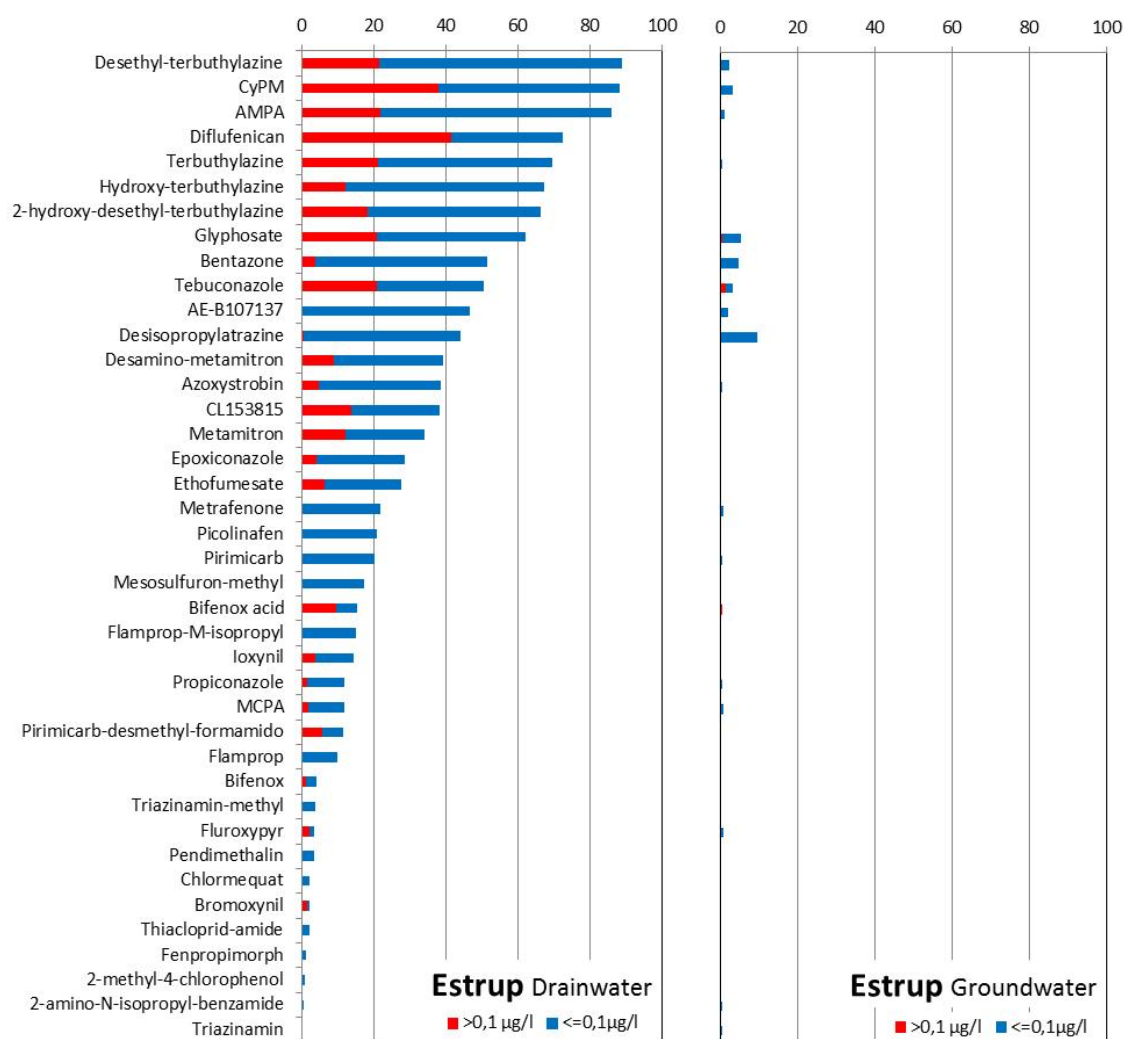


Figure 8.2B. Frequency of detection in samples from the drainage system (left) and groundwater monitoring screens located deeper than the drainage system (right) **at the loamy field Estrup**. Frequency is estimated for the entire monitoring period up to July 2014. The time the different pesticides have been included in the programme and the number of analysed samples varies. The figure includes pesticides detected in drain- and groundwater.

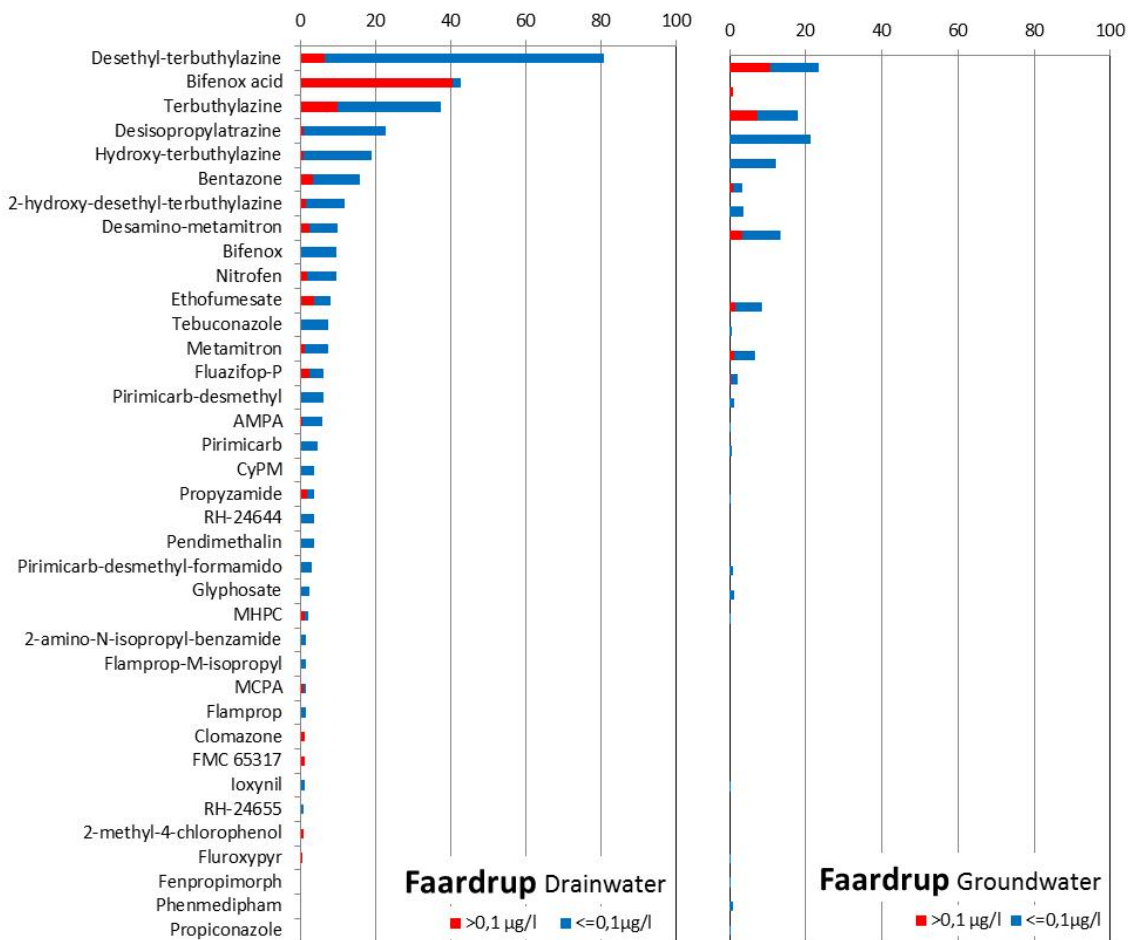


Figure 8.2C. Frequency of detection in samples from the drainage system (left) and groundwater monitoring screens located deeper than the drainage system (right) **at the loamy field Faardrup**. Frequency is estimated for the entire monitoring period up to July 2014. The time the different pesticides have been included in the programme and the number of analysed samples varies. The figure includes pesticides detected in drain- and groundwater.

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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). N: total number of samples analysed in PLAP inclusive QA samples. Monitoring is ongoing if latest analysis date is in June 2014.

Parent pesticide	P/M	Analyte	Systematic name	Latest analysis	N
Aclonifen	P	Aclonifen	2-chloro-6-nitro-3-phenoxyaniline	18.06.13	471
Amidosulfuron	P	Amidosulfuron	N-[[[(4,6-dimethoxy-2-pyrimidinyl)amino]carbonyl]-amino]sulfonyl]-N-methylmethanesulfonamide	01.03.06	562
Amidosulfuron	M	desmethyl-amidosulfuron	3-(4-hydroxy-6-methoxy-2-pyrimidin-2-yl)-1-(N-methyl-N-methylsulfonyl-aminosulfonyl)-urea	01.03.06	129
Aminopyralid	P	Aminopyralid	4-amino-3,6-dichloropyridine-2-carboxylic acid	17.06.14	446
azoxystrobin	P	Azoxystrobin	Methyl (E)-2-{2-[(6-(2-cyanophenoxy)-4-pyrimidin-4-yloxy]phenyl}-3-methoxyacrylate	11.06.14	2880
azoxystrobin	M	CyPM	E-2-(2-[6-cyanophenoxy]-pyrimidin-4-yloxy)-phenyl)-3-methoxyacrylic acid	11.06.14	3033
bentazone	P	Bentazone	3-(1-methylethyl)-1H-2,1,3-benzothiadiazin-4(3H)-one 2,2 dioxide	17.06.14	4197
bentazone	M	2-amino-N-isopropyl-benzamide	2-amino-N-isopropylbenzamide	28.06.07	2139
Bifenox	P	Bifenox	methyl 5-(2,4-dichlorophenoxy)-2-nitrobenzoate	27.12.12	1190
Bifenox	M	Bifenox acid	5-(2,4-dichlorophenoxy)-2-nitrobenzoic acid	27.12.12	1109
Bifenox	M	Nitrofen	2,4-dichlorophenyl 4'-nitrophenyl ether	27.12.12	1190
Boscalid	P	Boscalid	2-chloro-N-(4'-chlorobiphenyl-2-yl)nicotinamide	11.12.12	190
bromoxynil	P	Bromoxynil	3,5-dibromo-4-hydroxybenzonitrile	03.06.14	1888
Chlormequat	P	Chlormequat	2-chloroethyltrimethylammonium chloride	10.07.08	335
clomazon	P	Clomazone	2-[(2-chlorophenyl)methyl]-4,4-dimethyl-3-isoxazolidione	17.06.14	945
clomazon	M	FMC 65317	(N-[2-chlorophenyl)methyl]-3-hydroxy-2,2-dimethyl propanamide (Propanamide-clomazone)	17.06.14	911
clopyralid	P	Clopyralid	3,6-Dichloropyridine-2-carboxylic acid	12.03.09	843
Cyazofamid	P	Cyazofamid	4-chloro-2-cyano-N,N-dimethyl-5-p-tolylimidazole-1-sulfonamide	12.06.12	417
desmedipham	P	Desmedipham	Ethyl 3-(phenylcarbamoyloxy)phenylcarbamate	24.06.03	973
desmedipham	M	EHPC	Carbamic acid, (3-hydroxyphenyl)-ethyl ester	24.06.03	652
Diflufenican	P	Diflufenican	2',4'-difluoro-2-(α,α,α -trifluoro-m-tolyloxy)nicotinamide	11.06.14	496
Diflufenican	M	AE-B107137	2-[3-(trifluoromethyl)phenoxy]pyridine-3-carboxylic acid	11.06.14	517
Diflufenican	M	AE-05422291	2-[3-(trifluoromethyl)phenoxy]pyridine-3-carboxamide	11.06.14	496
dimethoat	P	Dimethoate	O,O-dimethyl S-methylcarbamoylmethyl-phosphorodithioate	13.06.05	2038
epoxiconazole	P	Epoxiconazole	(2RS, 3SR)-1-(2-(2-chlorophenyl)-2,3-epoxy-2-(4-fluorophenyl)propyl)-1H-1,2,4-triazol	02.12.09	1527
ethofumesat	P	Ethofumesate	(\pm)-2-ethoxy-2,3-dihydro-3,3-dimethylbenzofuran-5-yl-methanesulfonate	30.06.11	1826
fenpropimorph	P	Fenpropimorph	Cis-4-[3-[4-(1,1-dimethylethyl)-phenyl]-2-methylpropyl]-2,6-imethylmorpholine	17.06.03	2494
fenpropimorph	M	Fenpropimorph acid	Cis-4-[3-[4-(2-carboxypropyl)-phenyl]-2-methylpropyl]-2,6-dimethylmorpholine	17.06.03	2341
flamprop-M-isopropyl	P	Flamprop-M-isopropyl	Isopropyl N-benzoyl-N-(3-chloro-4-fluorophenyl)-D-alaninate	13.06.05	1987
flamprop-M-isopropyl	M	Flamprop	N-benzoyl-N-(3-chloro-4-fluorophenyl)-D-alanine	13.06.05	1996
florasulam	P	Florasulam	2',6',8'-Trifluoro-5-methoxy-s-triazolo [1,5-c]pyrimidine-2-sulfonanilide	19.06.08	578
florasulam	M	Florasulam-desmethyl	N-(2,6-difluorophenyl)-8-fluoro-5-hydroxy[1,2,4]triazolo[1,5-c]pyrimidine-2-sulfonamide	19.06.08	275
fluazifop-P-buthyl	P	Fluazifop-P-butyl	butyl (R)-2-[4-[5-(trifluoromethyl)-2-pyridyloxy]phenoxy]propionate	24.06.03	402
fluazifop-P-buthyl	M	Fluazifop-P	(R)-2-(4-((5-(trifluoromethyl)-2-pyridinyl)oxy)phenoxy)-propanoic acid	28.03.12	1769
fluazifop-P-buthyl	M	TFMP	5-trifluoromethyl-pyridin-2-ol	12.06.14	834
Fludioxonil	M	CGA 192155	2,2-difluoro-benzo[1,3]dioxol-4-carboxylic acid	17.06.14	70
Fludioxonil	M	CGA 339833	3-carbamoyl-2-cyano-3-(2,2-difluoro-benzo[1,3]dioxol-4-yl)-oxirane-2-carboxylic acid	17.06.14	70
fluroxypyr	P	Fluroxypyr	(4-amino-3,5-dichloro-6-fluoro-2-pyridinyl)oxy]acetic acid	12.06.08	2047
glyphosat	P	Glyphosate	N-(phosphonomethyl)glycine	11.06.14	3747
glyphosat	M	AMPA	Amino-methylphosphonic acid	11.06.14	3746
Iodosulfuron-methyl-natrium	P	Iodosulfuron-methyl	sodium salt of methyl 4-iodo-2-[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl]amino]sulfonyl]benzoate	22.12.10	355
Iodosulfuron-methyl-natrium	P	Metsulfuron-methyl	methyl 2-(4-methoxy-6-methyl-1,3,5-triazin-2-ylcarbamoylsulfamoyl)benzoate	22.12.10	1346
ioxynil	P	Ioxynil	4-hydroxy-3,5-diiodobenzonitrile	03.06.14	1893
linuron	P	Linuron	3-(3,4-dichlorophenyl)-1-methoxy-1-methylurea	13.09.01	389
Mancozeb	M	EBIS	ethylene bisisothiocyanate sulfide	17.06.14	38
mancozeb	M	ETU	Ethylenethiourea	03.04.01	278
MCPA	P	MCPA	(4-chloro-2-methylphenoxy)acetic acid	29.06.06	1465
MCPA	M	2-methyl-4-chlorophenol	2-methyl-4-chlorophenol	29.06.06	1458

Parent pesticide	P/M	Analyte	Systematic name	Latest analysis	N
mesosulfuron-methyl	P	Mesosulfuron-methyl	Methyl 2-[3-(4,6-dimethoxypyrimidin-2-yl)ureidosulfonyl]-4-methanesulfonamidomethylbenzoate	02.12.09	647
mesosulfuron-methyl	M	Mesosulfuron	2-[[[(4,6-dimethoxy-2-pyrimidinyl)amino]carbonyl]amino]sulfonyl]-4-[(methylsulfonyl)amino]methyl]benzoic acid	02.12.09	270
Mesotrione	P	Mesotrione	2-(4-mesyl-2-nitrobenzoyl)cyclohexane-1,3-dione	17.06.14	234
Mesotrione	M	MNBA	methylsulfonyl-2-nitrobenzoic acid	17.06.14	234
Mesotrione	P	AMBA	2-amino-4-methylsulfonylbenzoic acid	17.06.14	234
Metalaxyl-M	P	metalaxyl-M	methyl N-(methoxyacetyl)-N-(2,6-xylyl)-D-alaninate	17.06.14	903
Metalaxyl-M	M	CGA 62826	2-[(2,6-dimethylphenyl)(methoxyacetyl)amino]propanoic acid	17.06.14	914
Metalaxyl-M	M	CGA 108906	2-[(1-carboxyethyl)(methoxyacetyl)amino]-3-methylbenzoic acid	17.06.14	911
metamitron	P	Metamitron	4-amino-4,5-dihydro-3-methyl-6-phenyl-1,2,4-triazin-5-one	30.06.11	1822
metamitron	M	Desamino-metamitron	4,5-dihydro-3-methyl-6-phenyl-1,2,4-triazine-5-one	30.06.11	1819
Metrafenone	P	Metrafenone	3'-bromo-2,3,4,6'-tetramethoxy-2',6-dimethylbenzophenone	12.06.14	468
metribuzin	P	Metribuzin	4-amino-6-tert-butyl-4,5-dihydro-3-methylthio-1,2,4-triazine-5-one	28.05.02	577
metribuzin	M	Desamino-metribuzin	6-(1,1-dimethylethyl)-3-(methylthio)-1,2,4-triazin-5-(4H)-one	28.05.02	542
metribuzin	M	Diketo-metribuzin	4-amino-6-tert-butyl-4,5-dihydro-1,2,4-triazine-3,5-dione	09.03.11	977
metribuzin	M	Desamino-diketo-metribuzin	6-tert-butyl-4,5-dihydro-3-methylthio-1,2,4-triazine-3,5-dione	09.04.08	891
pendimethalin	P	Pendimethalin	N-(1-ethyl)-2,6-dinitro-3,4-xynile	10.12.09	2881
phenmedipham	P	Phenmedipham	3-[(methoxycarbonyl)amino]phenyl (3-methylphenyl)carbamate	24.06.03	974
phenmedipham	M	3-aminophenol	1-amino-3-hydroxybenzene	26.02.02	391
phenmedipham	M	MHPC	Methyl-N-(3-hydroxyphenyl)-carbamate	24.06.03	968
Picolinafen	P	Picolinafen	4'-fluoro-6-(a,a,a-trifluoro-m-tolxyloxy)pyridine-2-carboxanilide	30.03.10	352
Picolinafen	M	CL153815	6-(3-trifluoromethylphenoxy)-2-pyridine carboxylic acid	30.03.10	352
pirimicarb	P	Pirimicarb	2-(dimethylamino)-5,6-dimethyl-4-pyrimidinylmethylcarbamate	26.06.07	3432
pirimicarb	M	Pirimicarb-desmethyl-formamido	2-methylformamido-5,6-dimethylpyrimidine-4-yl dimethylcarbamate	26.06.07	2678
pirimicarb	M	Pirimicarb-desmethyl	2-(dimethylamino)-5,6-dimethyl-4-pyrimidinylmethylcarbamate	26.06.07	3078
propiconazol	P	Propiconazole	1-[[2-(2,4-dichlorophenyl)-4-propyl-1,3-dioxolan-2-yl]methyl]-1H-1,2,4-triazole	22.03.05	3421
propyzamid	P	Propyzamide	3,5-dichloro-N-(1,1-dimethylprop-2-ynyl)benzamide	12.06.14	1158
propyzamid	M	RH-24644	2-(3,5-dichlorophenyl)-4,4-dimethyl-5-methylene-oxalzone	12.06.14	1158
propyzamid	M	RH-24655	3,5-dichloro-N-(1,1-dimethylpropenyl)benzamide	12.06.14	1059
propyzamid	M	RH-24580	N-(1,1-dimethylacetyl)-3,5-dichlorobenzamide	12.06.14	1158
prosulfocarb	P	Prosulfocarb	N-[[3-(4-methoxy-6-methyl-1,3,5-triazin-2-yl)-3-[2-(3,3,3-trifluoro-propyl)phenylsulfonyl]urea	17.06.14	820
pyridat	P	Pyridate	O-6-chloro-3-phenylpyridazin-4-yl S-octyl thiocarbonate	03.09.02	183
pyridat	M	PHCP	3-phenyl-4-hydroxy-6-chloropyridazine	02.06.04	571
Rimsulfuron	P	Rimsulfuron	N-[[[(4,6-dimethoxy-2-pyrimidinyl)amino]carbonyl]-3-(ethylsulfonyl)-2-pyridinesulfonamide	14.06.06	561
Rimsulfuron	M	PPU-desamino	N-((3-(ethylsulfonyl)-2-pyridyl)-4,6 dimethoxy-2 pyrimidinamine (IN70942)	11.12.12	2311
Rimsulfuron	M	PPU	N-(4,6-dimethoxy-2-pyrimidinyl-N-((3-(ethylsulfonyl)-2-pyridinyl)urea (IN70941)	11.12.12	2311
Tebuconazole	P	Tebuconazole	a-[2-(4-chlorophenyl)ethyl]-a-(1,1-dimethylethyl)-1H-1,2,4-triazole-1-ethanol	27.12.12	1220
Tebuconazole	M	1,2,4-triazol	1,2,4-triazol	12.06.14	22
terbuthylazin	P	Terbuthylazine	6-chloro-N-(1,1-dimethylethyl)-N-ethyl-1,3,5-triazine-2,4-diamine	25.03.09	2116
terbuthylazin	M	2-hydroxy-desethyl-terbuthylazine	6-hydroxy-N-(1,1-dimethylethyl)-1,3,5-triazine-2,4-diamine	19.06.08	1371
terbuthylazin	M	Desisopropyltriazine	6-chloro-N-ethyl-1,3,5-triazine-2,4-diamine	25.03.09	1618
terbuthylazin	M	Desethyl-terbuthylazine	6-chloro-N-(1,1-dimethylethyl)-1,3,5-triazine-2,4-diamine	10.06.09	2619
terbuthylazin	M	Hydroxy-terbuthylazine	6-hydroxy-N-(1,1-dimethylethyl)-N'-ethyl-1,3,5-triazine-2,4-diamine	19.06.08	1520
Thiacloprid	P	Thiacloprid	(Z)-3-(6-chloro-3-pyridylmethyl)-1,3-thiazolidin-2-ylidenecyanamide	28.03.12	168
Thiacloprid	M	Thiacloprid-amide	(3-[(6-chloro-3-pyridinyl)methyl]-2-thiazolidinylidene) urea	28.03.12	168
Thiacloprid	M	Thiacloprid sulfonic acid	sodium 2-[[[(aminocarbonyl)amino]-carbonyl][(6-chloro-3-pyridinyl)-methyl]amino]ethanesulfonate	28.03.12	177
Thiacloprid	M	M34	2-{carbamoyle}[(6-chloropyridin-3-yl)methyl]amino}etanesulfonic acid	28.03.12	176
Thiamethoxam	P	Thiamethoxam	3-(2-chloro-thiazol-5-ylmethyl)-5-methyl[1,3,5]oxadiazinan-4-ylidene-N-nitroamine	18.06.08	559
Thiamethoxam	M	CGA 322704	[C(E)]-N-[(2-chloro-5-thiazolyl)methyl]-N'-methyl-N'-nitroguanidine	18.06.08	559
triasulfuron	P	Triasulfuron	1-[2-(2-chloroethoxy)phenylsulfonyl]-2-(4-methoxy-6-methyl-1,3,5-triazine-2-yl)-urea	04.03.03	445
triasulfuron	M	Triazinamin	2-amino-4-methoxy-6-methyl-1,3,5-triazine	16.12.10	1721
tribenuron-methyl	P	Tribenuron-methyl	methyl 2-[4-methoxy-6-methyl-1,3,5-triazin-2-yl(methyl)carbamoyle]sulfamoyl]benzoate	09.06.01	3
tribenuron-methyl	M	Triazinamin-methyl	4-methoxy-6-methyl-1,3,5-triazin-methylamine	29.08.12	2386
Triflusulfuron-methyl	P	Triflusulfuron-methyl	methyl 2-[4-dimethylamino-6-(2,2,2-trifluoroethoxy)-1,3,5-triazin-2-ylcarbamoyle]sulfamoyl]-m-toluate	30.06.11	430
Triflusulfuron-methyl	M	IN-M7222	6-(2,2,2-trifluoroethoxy)-1,3,5-triazine-2,4-diamine	30.06.11	430
Triflusulfuron-methyl	M	IN-E7710	N-methyl-6-(2,2,2-trifluoroethoxy)-1,3,5-triazine-2,4-diamine	30.06.11	430
Triflusulfuron-methyl	M	IN-D8526	N,N-dimethyl-6-(2,2,2-trifluoroethoxy)-1,3,5-triazine-2,4-diamine	30.06.11	430

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 analyses was reduced. At the loamy sites, pesticide analysis of water sampled from the suction cups was ceased, and the monthly monitoring was restricted to just one monitoring well. At Jyndevad, pesticide analysis of the suction cups located 2 m b.g.s. was ceased and the interval for the intensive monitoring encompassing the larger number of monitoring screens was extended to six months, except for the suction cups 2 m b.g.s. at Tylstrup, where the four-months 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
Faarstrup	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 suction cups installed 2 m b.g.s. are monitored four times a year (see text).

From september 2014 some wells and some deeper wells are monitored more frequent and some of the horizontal wells are monitored every month in water samples from the 3 screens, replacing mixed samples. These samples will be reported in the next report.

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 sampled monthly. Each horizontal well contain three screens and water samples from the screens are mixed to one sample.

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

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

$$M_i = C_i \cdot V_i$$

where:

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

V_i = Weekly accumulated drainage runoff (mm/week)

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

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

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

where:

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

V_i = Weekly accumulated drainage runoff (mm/week)

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

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

C_{t_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 and growth stages - Tylstrup
02-07-2009	BBCH stage 73
08-07-2009	BBCH stage 77
08-07-2009	Biomass 1,072.0 g/m ² - 100% DM
08-07-2009	Irrigation 27mm. Started 08/07. Ended 09/07
08-07-2009	Mavrik 2F (tau-fluvalinate) - pests - 0.1 l/ha (not analysed)
28-07-2009	BBCH stage 87
20-08-2009	Harvest of spring barley. Stubble height 16 cm, grain yield 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
04-04-2010	Potatoes
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 row distance 75 cm, plant distance 25 cm, depth 17 cm, final plant number 4,0/m ²
17-05-2010	Ridging
26-05-2010	BBCH stage 7
26-05-2010	Fenix (aclonifen) – weeds
26-05-2010	Titus WSB (rimsulfuron) - weeds - 10 g/ha
04-06-2010	BBCH stage 9
08-06-2010	BBCH stage 15
08-06-2010	Titus WSB (rimsulfuron) - weeds - 20 g/ha
15-06-2010	Ranman (cyazofamid) - fungi - 0.2 l/ha
15-06-2010	BBCH stage 23
24-06-2010	BBCH stage 40
24-06-2010	Ranman (cyazofamid) - fungi - 0.2 l/ha
01-07-2010	BBCH stage 51
01-07-2010	Ranman (cyazofamid) - fungi - 0.2 l/ha
05-07-2010	BBCH stage 55
05-07-2010	Biomass tubers 119.0 g. Top 222.4 g/10 m row - 100% DM
06-07-2010	Irrigation 29 mm. Started 06/07. Ended 07/07
06-07-2010	BBCH stage 57
09-07-2010	BBCH stage 60
09-07-2010	Ridomil Gold MZ Pepite (mancozeb - metalaxyl-M) - fungi - 2.0 kg/ha
16-07-2010	BBCH stage 64
16-07-2010	Ranman (cyazofamid) - fungi - 0.2 l/ha
23-07-2010	BBCH stage 67
23-07-2010	Ranman (cyazofamid) - fungi - 0.2 l/ha
27-07-2010	BBCH stage 67
27-07-2010	Irrigation 28 mm. Started 27/07. Ended 28/07
02-08-2010	Ranman (cyazofamid) - fungi - 0.2 l/ha
02-08-2010	BBCH stage 69
02-08-2010	Biomass tubers 624.3 g. Top 336.0 g/10 m row - 100% DM
09-08-2010	BBCH stage 72
09-08-2010	Dithane NT (mancozeb) - fungi - 2.0 kg/ha
17-08-2010	BBCH stage 80
17-08-2010	Dithane NT (mancozeb) - fungi - 2.0 kg/ha
23-08-2010	BBCH stage 90
23-08-2010	Biomass tubers 1,009.1 g. Top 301.3 g/10 m row - 100% DM
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	Spring barley
17-04-2011	Ploughed - depth 24 cm. Seed bed preparation, 8 cm depth
18-04-2011	Rolled with concrete roller
19-04-2011	Fertilisation - 138 N, 20 P, 66 K, kg/ha
19-04-2011	Seed bed preparation, 8 cm depth

Date	Management practice and growth stages - Tylstrup
19-04-2011	Spring barley sown, cv. TamTam, seeding rate 180 kg/ha, sowing depth 3.3 cm, row distance 12.5 cm. Final plant number 365/m ²
26-04-2011	BBCH stage 11
10-05-2011	Oxitril CM (ioxynil + bromoxynil) - weeds - 0,4 l/ha (not analysed)
10-05-2011	BBCH stage 22
11-05-2011	BBCH stage 22
11-05-2011	Biomass 85.5 g/m ² - 100% DM
16-05-2011	BBCH stage 25
30-05-2011	BBCH stage 33
06-06-2011	BBCH stage 40
15-06-2011	Biomass 675.7 g/m ² - 100% DM
15-06-2011	BBCH stage 51
20-06-2011	BBCH stage 59
20-06-2011	Bell (boscalid + epoxiconazole) - fungi - 1.5 l/ha (epoxiconazole not analysed)
05-07-2011	BBCH stage 75
08-07-2011	BBCH stage 77
08-07-2011	Biomass 1,175.9 g/m ² - 100% DM
18-07-2011	BBCH stage 80
02-08-2011	BBCH stage 86
10-08-2011	BBCH stage 89
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	Spring barley
22-03-2012	Ploughed - depth 24 cm
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/m ² . Sown with rotor harrow combine sowing machine
03-04-2012	BBCH stage 6-7
10-04-2012	BBCH stage 09
19-04-2012	BBCH stage 11
29-04-2012	BBCH stage 12
29-04-2012	Fertilisation - 123.9 N, 17.7 P, 59 K, kg/ha
30-04-2012	BBCH stage 12
09-05-2012	BBCH stage 14
16-05-2012	BBCH stage 20
21-05-2012	BBCH stage 22
21-05-2012	Biomass 72.2 g/m ² - 100% DM
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
25-05-2012	BBCH stage 29
31-05-2012	BBCH stage 32
31-05-2012	Irrigation 24 mm. Started 31/05. Ended 01/06
06-06-2012	BBCH stage 37
12-06-2012	BBCH stage 44
19-06-2012	BBCH stage 50
19-06-2012	Biomass 644.8 g/m ² - 100% DM
28-06-2012	BBCH stage 59
28-06-2012	Bell (boscalid + epoxiconazol) - fungi - 1.5 l/ha (epoxiconazol not analysed)
02-07-2012	BBCH stage 61
10-07-2012	BBCH stage 79
10-07-2012	Biomass 1,138.3 g/m ² - 100% DM
24-07-2012	BBCH stage 83
06-08-2012	BBCH stage 86
13-08-2012	BBCH stage 88
13-08-2012	Glyfona 450 Plus (glyphosate) - weeds - 2.4 l/ha (not analysed)
27-08-2012	BBCH stage 89
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 (potassium 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. Final plant number 125/m ² . Sown with rotorharrow combine sowing machine
05-10-2012	BBCH stage 9
10-10-2012	BBCH stage 11
12-10-2012	BBCH stage 12
12-10-2012	Boxer (prosulfocarb) - weeds - 4.0 l/ha

Date	Management practice and growth stages - Tylstrup
22-10-2012	BBCH stage 12
05-11-2012	BBCH stage 13
14-11-2012	BBCH stage 20
26-11-2012	BBCH stage 22
26-11-2012	Biomass 7.0 g/m ² - 100% DM
04-04-2013	Fertilisation - 56.7 N, 8.1 P, 27 K, kg/ha
04-04-2013	BBCH stage 22
02-05-2013	BBCH stage 30-31
02-05-2013	Fertilisation - 71.4 N, 10.2 P, 34 K, kg/ha
07-05-2013	BBCH stage 31
08-05-2013	Starane XL (fluroxypyr) - weeds - 1.2 l/ha
24-05-2013	BBCH stage 50
24-05-2013	Biomass 422.8 g/m ² - 100% DM
28-05-2013	BBCH stage 57
31-05-2013	BBCH stage 59
10-06-2013	BBCH stage 67
18-06-2013	BBCH stage 70
25-06-2013	BBCH stage 72
02-07-2013	Biomass 1,275.2 g/m ² - 100% DM
02-07-2013	BBCH stage 76
09-07-2013	BBCH stage 79
18-07-2013	BBCH stage 81
05-08-2013	BBCH stage 87
13-08-2013	BBCH stage 89
20-08-2013	Harvest of winter rye. Stubbleheight 15 cm, grainyield 77.4 hkg/ha - 85% DM. Straw removed, yield 33.8 hkg/ha - 100% DM
26-02-2014	Potatoes
26-02-2014	Ploughed - depth 23 cm
02-04-2014	Seed bed preparation, 5 cm depth and packed with a roller
03-04-2014	Fertilisation - 175.5 N, kg/ha
03-04-2014	Fertilisation - 100 K, kg/ha
15-04-2014	Maxim 100 FS (fludioxonil) - fungi - 250 ml/ton potatoes ~ 625 ml/ha sprayed on potatoes before the planting
15-04-2014	Seed bed preparation diagonally - depth 20 cm
15-04-2014	Planting of potatoes. cv. Kuras rowdistance 75 cm, plantdistance 25 cm, depth 17 cm, final plant number 4/m ²
16-04-2014	BBCH stage 00
16-04-2014	Command CS (clomazon) - weeds - 0.25 l/ha (not included)
25-04-2014	BBCH stage 01
30-04-2014	BBCH stage 03
05-05-2014	BBCH stage 05
15-05-2014	BBCH stage 08 to 09
15-05-2014	Titus WSB (rimsulfuron) - weeds - 10 g/ha (not included in monitoring)
17-05-2014	BBCH stage 9 – emergence
22-05-2014	Titus WSB (rimsulfuron) + U46 M (MCPA) - weeds - 20 g/ha + 100 ml/ha (not included in monitoring)
22-05-2014	BBCH stage 13
27-05-2014	BBCH stage 15
04-06-2014	BBCH stage 15
10-06-2014	BBCH stage 27
13-06-2014	BBCH stage 45
13-06-2014	Irrigation 24 mm. Started 13/06
18-06-2014	BBCH stage 47
18-06-2014	Biomass tubers 119.0 g Top 233.3 g/m ² - 100% DM
20-06-2014	BBCH stage 53
20-06-2014	Irrigation 24 mm. Started 20/06. Ended 20/06
26-06-2014	BBCH stage 59
26-06-2014	Dithane NT (mancozeb) - fungi - 2.0 l/ha
02-07-2014	Biomass tubers 388.9 g Top 391.2 g/m ² - 100% DM
02-07-2014	BBCH stage 60
03-07-2014	BBCH stage 60
04-07-2014	Irrigation 24 mm. Started 04/07. Ended 04/07
04-07-2014	Dithane NT (mancozeb) - fungi - 2.0 l/ha
14-07-2014	BBCH stage 69
14-07-2014	Dithane NT (mancozeb) - fungi - 2.0 l/ha
23-07-2014	BBCH stage 75?

Date	Management practice and growth stages - Tylstrup
23-07-2014	Irrigation 24 mm. Started 23/07. Ended 23/07
24-07-2014	Dithane NT (mancozeb) - fungi - 2.0 l/ha
24-07-2014	BBCH stage 75?
30-07-2014	Irrigation 30 mm. Started 30/07
02-08-2014	BBCH stage?
02-08-2014	Dithane NT (mancozeb) - fungi - 2.0 l/ha
11-08-2014	BBCH stage 90?
11-08-2014	Dithane NT (mancozeb) - fungi - 2.0 l/ha
13-08-2014	Biomass tubers 1,270.3 g. Top 266.3 g/m ² - 100% DM
13-08-2014	BBCH stage 92
18-08-2014	BBCH stage 92
18-08-2014	Dithane NT (mancozeb) - fungi - 2.0 l/ha
25-08-2014	BBCH stage 92
25-08-2014	Dithane NT (mancozeb) - fungi - 2.0 l/ha
12-09-2014	Harvest of potatoes. Tuber yield 107.1 hkg/ha - 100% DM
15-09-2014	Liming - 4.0 t/ha
20-09-2014	Disk harrowed - depth 10 cm
20-09-2014	Stubble cultivated - depth 25 cm

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

Date	Management practice and growth stages - Jyndeved
07-08-2009	Harvest of spring barley. Seed yield 63.96 hkg/ha - 85% DM, straw yield 19.5 hkg/ha - 100% DM, stubble height 15 cm
14-04-2010	Potatoes
14-04-2010	Ploughed. Depth 24 cm
15-04-2010	Rolled with a concrete roller
21-04-2010	Fertilization 119.9 N, kg/ha
21-04-2010	Fertilization 79.3 N, 17.0 P, 85.1 K, kg/ha
22-04-2010	Seed bed preparation. 9.0 cm depth
22-04-2010	Fertilization 60.0 K, kg/ha
04-05-2010	Ridging
04-05-2010	BBCH stage 0
04-05-2010	Planting of potatoes. cv. Kuras row distance 75 cm, plant distance 33 cm, depth 8 cm, final plant number 4.0/m ²
27-05-2010	BBCH stage 8
27-05-2010	Fenix (aclonifen) - weeds - 1.0 l/ha
27-05-2010	Titus WSB (rimsulfuron) - weeds - 10 g/ha
02-06-2010	BBCH stage 9
08-06-2010	BBCH stage 21
08-06-2010	Titus WSB (rimsulfuron) - weeds - 20 g/ha
21-06-2010	BBCH stage 30
24-06-2010	BBCH stage 32
24-06-2010	Irrigation - 25 mm/ha. Started 24/06. Ended 25/06
28-06-2010	BBCH stage 42
28-06-2010	Ranman (cyazofamid) - fungi - 0.2 l/ha
30-06-2010	BBCH stage 42
30-06-2010	Irrigation - 25 mm/ha. Started 30/06. Ended on 01/07
01-07-2010	BBCH stage 42
01-07-2010	Biomass tubers 509.6 g Top 1,059.9 g/10 m row - 100% DM
06-07-2010	Amistar (azoxystrobin) - fungi - 0.5 l/ha
06-07-2010	BBCH stage 61
07-07-2010	BBCH stage 62
07-07-2010	Ranman (cyazofamid) - fungi - 0.2 l/ha
08-07-2010	BBCH stage 62
08-07-2010	Irrigation - 30 mm/ha. Started 08/07. Ended 09/07
12-07-2010	BBCH stage 63
14-07-2010	BBCH stage 65
14-07-2010	Ranman (cyazofamid) - fungi - 0.2 l/ha
16-07-2010	Karate 2,5 WG (Lambda-cyhalothrin) - 0.3 kg/ha (not analysed)
16-07-2010	BBCH stage 65
19-07-2010	BBCH stage 65
22-07-2010	Biomass tubers 535.9 g. Top 369.7 g/10 m row - 100% DM
25-07-2010	Ridomil Gold MZ Pepite (mancozeb - metalaxyl-M) - fungi - 2.0 kg/ha
25-07-2010	BBCH stage 71
01-08-2010	Ranman (cyazofamid) - fungi - 0.2 l/ha
01-08-2010	BBCH stage 75
02-08-2010	BBCH stage 78
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 - 2.0 l/ha (not analysed)
31-08-2010	Dithane NT (mancozeb) - fungi - 2.0 kg/ha (not analysed)
01-09-2010	BBCH stage 91
10-09-2010	Dithane NT (mancozeb) - fungi - 2.0 kg/ha (not analysed)
13-09-2010	BBCH stage 92
23-09-2010	Shirlan (fluazinam) - fungi - 0.4 l/ha (not analysed)
28-09-2010	BBCH stage 95
19-10-2010	Harvest of potatoes. Yield in tubers 120.6 hkg/ha - 100% DM
22-03-2011	Spring barley
22-03-2011	Ploughed. Depth 24 cm
23-03-2011	BBCH stage 0
23-03-2011	Sowing spring barley cv. Quench, depth 4.0 cm, row distance 12 cm, seed rate 164 kg/ha, final plant number 301/m ² - using a combine drill
24-03-2011	Rolled with a concrete roller
30-03-2011	Fertilization 133.1 N, 18.5 P, 61.6 K, kg/ha
05-04-2011	BBCH stage 9

Date	Management practice and growth stages - Jynde vad
08-04-2011	BBCH stage 10
20-04-2011	BBCH stage 13
26-04-2011	BBCH stage 21-22
26-04-2011	Oxitril CM (bromoxynil + ioxynil) - 0.5 l/ha (not analysed)
26-04-2011	DFF (diflufenican) - 0.25 l/ha- weeds
02-05-2011	BBCH stage 26
02-05-2011	Irrigation - 30 mm/ha. Started 02/05. Ended 03/05
03-05-2011	Biomass 92,8 g/m ² - 100% DM
04-05-2011	BBCH stage 26
04-05-2011	Microcare/Mantrac - 1.0 l/ha - manganese 0.368 kg/ha + N 0.035 kg/ha
18-05-2011	BBCH stage 37
23-05-2011	BBCH stage 40
23-05-2011	Irrigation - 32 mm/ha. Started 23/05. Ended 24/05
26-05-2011	BBCH stage 50
26-05-2011	Biomass 402.0 g/m ² - 100% DM
01-06-2011	BBCH stage 59
30-06-2011	BBCH stage 75
30-06-2011	Biomass 672.6 g/m ² - 100% DM
04-07-2011	BBCH stage 76
04-07-2011	Irrigation - 30 mm/ha. Started 04/07. Ended 05/07
20-07-2011	BBCH stage 82
01-08-2011	BBCH stage 90
23-08-2011	Harvest of spring barley. Seed yield 72.4 hkg/ha - 85% DM, stubble height 15 cm
25-08-2011	Removal of straw, straw yield 30.2 hkg/ha - 100% DM
30-03-2012	Maize
30-03-2012	Ploughed. Depth 22 cm
02-04-2012	Rolled with concrete roller
30-04-2012	Fertilization 120 K, kg/ha
30-04-2012	Fertilization 140 N, 17.7 P, 65.3 K, kg/ha
03-05-2012	Sowing maize - cultivare Atrium - seed distance 12 cm, row distance 75 cm, depth 6 cm. Seedrate 111,000 seeds/ha, final plant number 12.8/m ²
03-05-2012	Fertilization 29.4 N, 14.7 P, kg/ha
07-05-2012	Tracer (potasium bromide), 30.54 kg/ha
17-05-2012	BBCH stage 9 – emergence
22-05-2012	BBCH stage 11
26-05-2012	BBCH stage 14-15
26-05-2012	Fighter 480 (bentazone) - weeds - 1.0 l/ha
30-05-2012	BBCH stage 13
30-05-2012	Biomass 41.7 g/m ² - 100% DM
05-06-2012	BBCH stage 15
05-06-2012	Callisto (mesotrion) - weeds - 1.5 l/ha
06-06-2012	BBCH stage 15
15-06-2012	BBCH stage 16
15-06-2012	Tomahawk 180 EC (fluroxypyr) + Catch (florasulam + 2,4 D) -1.5 l/ha + 0.06 l/ha - weeds - (none analysed)
18-06-2012	BBCH stage 17
25-06-2012	BBCH stage 19
02-07-2012	BBCH stage 31
10-07-2012	BBCH stage 35
17-07-2012	BBCH stage 51
18-07-2012	Biomass 2,182.3 g/m ² - 100% DM
23-07-2012	BBCH stage 53
30-07-2012	BBCH stage 59
05-08-2012	BBCH stage 63
14-08-2012	BBCH stage 66
17-08-2012	BBCH stage 67
17-08-2012	Biomass 8,241.8 g/m ² - 100% DM
20-08-2012	BBCH stage 68
27-08-2012	BBCH stage 72
03-09-2012	BBCH stage 74
13-09-2012	BBCH stage 82
19-09-2012	BBCH stage 83
24-09-2012	BBCH stage 84
24-09-2012	Dry matter content whole plants 25.4%
01-10-2012	BBCH stage 87
01-10-2012	Dry matter content whole plants 27.5%

Date	Management practice and growth stages - Jynde vad
08-10-2012	BBCH stage 88
08-10-2012	Dry matter content whole plants 33.0%
08-10-2012	Harvest of maize. Whole crop yield 151.41 hkg/ha - 100% DM. Stubble height 25 cm
06-04-2013	Pea
06-04-2013	Ploughing - 22 cm depth
12-04-2013	Rolled with concrete roller
14-04-2013	Sowing pea cultivare Alvestra, depth 5 cm, row distance 12 cm, seed rate 235 kg/ha, using a combine drill, final plant number 92/m ²
26-04-2013	BBCH stage 9 – emergence
03-05-2013	BBCH stage 12
07-05-2013	Fighter 480 (bentazon) + Stomp (pendimethalin) 0.4 l/ha + 0.6 l/ha - weeds (pendimethalin not analysed)
07-05-2013	BBCH stage 13-14
13-05-2013	BBCH stage 14
16-05-2013	BBCH stage 14-15
16-05-2013	Bentazon 480 (bentazon) + Stomp (pendimethalin) 0.5 l/ha + 0.6 l/ha - weeds (pendimethalin not analysed)
17-05-2013	Fertilization 16.0 P, 83.2 K, kg/ha
21-05-2013	BBCH stage 25
27-05-2013	BBCH stage 30
03-06-2013	BBCH stage 37
04-06-2013	Biomass 105.7 g/m ² - 100% DM
06-06-2013	BBCH stage 38
06-06-2013	Irrigation - 30 mm/ha. Started on eastside 06/06. Ended on westside 07/06
10-06-2013	BBCH stage 41
17-06-2013	BBCH stage 60
21-06-2013	Biomass 393,5 g/m ² - 100% DM
25-06-2013	BBCH stage 65
01-07-2013	BBCH stage 67
09-07-2013	BBCH stage 68
09-07-2013	Irrigation - 30 mm/ha. Started on eastside 09/07. Ended on westside 10/07
15-07-2013	BBCH stage 69
15-07-2013	Biomass 722,5 g/m ² - 100% DM
16-07-2013	Pirimor G (pirimicarb) - pests - 0.25 kg/ha (not analysed)
22-07-2013	BBCH stage 78
29-07-2013	BBCH stage 81
05-08-2013	Biomass 737.2 g/m ² - 100% DM
05-08-2013	BBCH stage 90
07-08-2013	Harvest of pea - western half of the field - interrupted by rain. Seed yield 38.8 hkg/ha - 86% DM. Straw yield 30.1 hkg/ha - 100% DM, stubble height 10 cm. Straw shredded at harvest
14-08-2013	Harvest of the eastern half of the field - straw shredded at harvest
20-08-2013	Potatoes
20-08-2013	Stubble cultivation - 8,0 cm depth
22-08-2013	Rotor harrowed - 7 cm depth
26-03-2014	Ploughing - 22 cm depth
09-04-2014	Rolled with concrete roller
10-04-2014	Fertilization 180.0 N, 38.6 P, 192.9 K kg/ha
10-04-2014	Fertilization 19.7 N, kg/ha
15-04-2014	Planting potatoes. Cv. Oleva, Row distance 75 cm plant distance 33 cm, depth 7 cm. Final plant number 4/m ²
15-04-2014	Maxim 100 FS (fludioxonil) - fungi - 625 ml/ha sprayed at potatoes when planting
30-04-2014	BBCH stage 05 - 08 (crop not emerged yet)
30-04-2014	Command CS (clomazon) + Glyphogan (glyphosate) - weeds - 0.25 l/ha + 1.5 l/ha
06-05-2014	BBCH stage 08 (crop not emerged yet)
06-05-2014	Titus WSB (rimsulfuron) - weeds - 10 g/ha (not included in monitoring)
14-05-2014	BBCH stage 9 - emergence
26-05-2014	BBCH stage 22
27-05-2014	Titus WSB (rimsulfuron) - weeds - 20 g/ha (not included in monitoring)
02-06-2014	BBCH stage 29
10-06-2014	BBCH stage 38
12-06-2014	BBCH stage 39
12-06-2014	Dithane NT (mancozeb) - fungi - 2.0 l/ha
14-06-2014	BBCH stage 47
14-06-2014	Irrigation - 20 mm/ha. Started on eastside 14/06. Ended on westside 15/06
16-06-2014	BBCH stage 48
18-06-2014	BBCH stage 50

Date	Management practice and growth stages - Jynde vad
18-06-2014	Dithane NT (mancozeb) - fungi - 2.0 l/ha + Mospilan SG (acetamiprid) - pests - 150 g/ha (not included)
18-06-2014	Microcare - 1.0 l/ha - manganese 0.368 kg/ha + N 0.035 kg/ha
19-06-2014	BBCH stage 50
19-06-2014	Irrigation - 25 mm/ha. Started on eastside 19/06. Ended on westside 20/06
20-06-2014	Biomass tubers 195.3 g/m ² - 100% DM. Top 299.5 g/m ² row - 100% DM
23-06-2014	BBCH stage 50
27-06-2014	Dithane NT (mancozeb) - fungi - 2.0 l/ha + Mospilan SG (acetamiprid) - pests - 150 g/ha (not included)
27-06-2014	BBCH stage 65
30-06-2014	BBCH stage 66
01-07-2014	Biomass knolde 91.3 g/m ² - 100% DM. Top 395.3 g/m ² row - 100% DM
04-07-2014	BBCH stage 69
04-07-2014	Dithane NT (mancozeb) - fungi - 2.0 l/ha
08-07-2014	BBCH stage 69
12-07-2014	Dithane NT (mancozeb) - fungi - 2.0 l/ha
12-07-2014	BBCH stage 70
18-07-2014	BBCH stage 72
18-07-2014	Dithane NT (mancozeb) - fungi - 2.0 l/ha
18-07-2014	Microcare - 1.0 l/ha - manganese 0.368 kg/ha + N 0.035 kg/ha
21-07-2014	BBCH stage 79
21-07-2014	Irrigation - 25 mm/ha. Started on eastside 21/07. Ended on westside 22/07
24-07-2014	BBCH stage 81
24-07-2014	Dithane NT (mancozeb) - fungi - 2.0 l/ha
29-07-2014	BBCH stage 82
29-07-2014	Irrigation - 25 mm/ha. Started on eastside 29/07. Ended on westside 30/07
30-07-2014	Ranman (cyazofamid) - fungi - 0.2 l/ha
30-07-2014	BBCH stage 85
04-08-2014	BBCH stage 86
04-08-2014	Irrigation - 25 mm/ha. Started on eastside 04/08. Ended on westside 05/08
07-08-2014	BBCH stage 86
07-08-2014	Ranman (cyazofamid) - fungi - 0.2 l/ha
11-08-2014	BBCH stage 93
12-08-2014	Biomass tubers 1,881.1 g/m ² - 100% DM. Top 211.5 g/m ² row - 100% DM
14-08-2014	BBCH stage 93
14-08-2014	Dithane NT (mancozeb) - fungi - 2.0 l/ha
01-09-2014	Winter wheat
01-09-2014	Rotor harrowed – depth 6 cm
16-09-2014	Harrowed diagonally - depth 6 cm
18-09-2014	Winterwheat drilled directly in the potato stuble
28-08-2015	Harvest of potatoes. Yield in tubers 144.4 hkg - 100% DM/ha

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 and growth stages - Silstrup
30-03-2009	Harrowed two times across - depth 5 cm
02-04-2009	Pig slurry application - injected approx. 10 cm - 41.0 t/ha - 190.7 Total-N, 121.0 NH ₄ -N, 54.53 P, 72.6 K, kg/ha
02-04-2009	Tracer (potassium 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 plant number 263/m ² . Undersown red fescue cv. Jasperina, broadcast, seeding rate 8.8 kg/ha
11-04-2009	Rolled with a Cambridge roller
20-04-2009	BBCH stage 09 emergence
29-04-2009	BBCH stage 12
11-05-2009	BBCH stage 22
11-05-2009	Biomass 31.8 g/m ² - 100% DM
19-05-2009	BBCH stage 24
19-05-2009	Fighter 480 (bentazone) - weeds - 1.25 l/ha
28-05-2009	BBCH stage 31
03-06-2009	BBCH stage 45
08-06-2009	Biomass 546.3 g/m ² - 100% DM
08-06-2009	BBCH stage 50
19-06-2009	BBCH stage 55
24-06-2009	Amistar (azoxystrobin) - fungi - 1.0 l/ha
24-06-2009	BBCH stage 59
06-07-2009	BBCH stage 77
08-07-2009	Biomass 1,233.4 g/m ² - 100% DM
16-07-2009	BBCH stage 85
16-07-2009	Whole crop harvest, 94.6 hkg/ha - 100% DM stubble height 15 cm
17-07-2009	Red fescue
17-07-2009	Fertilization 49.5 N, kg/ha
14-08-2009	Trimming of grass - 3-4 cm height
24-08-2009	BBCH stage 24
24-08-2009	Hussar OD (iodosulfuron-methyl) - weeds - 0.020 l/ha
03-09-2009	BBCH stage 24
03-09-2009	Biomass 62.9 g/m ² - 100% DM
09-09-2009	Fox 480 SC (bifenox) - weeds - 1.5 l/ha
09-09-2009	BBCH stage 25
15-09-2009	Pig slurry application - injected approx. 4-5 cm - 12.8 t/ha - 75.8 Total-N, 52.9 NH ₄ -N, 16.8 P, 33.7 K, kg/ha
07-10-2009	Trimming of grass - 8-9 cm height
07-04-2010	BBCH stage 25
07-04-2010	Fertilization 58.0 N, kg/ha
21-04-2010	BBCH stage 29
02-05-2010	BBCH stage 30
02-05-2010	Fusilade Max (fluazifop-P-butyl) - weeds - 1.5 l/ha
05-05-2010	BBCH stage 31
05-05-2010	Hussar OD (iodosulfuron) - weeds - 0.1 l/ha
05-05-2010	SweDane MCPA 750 0.7 l/ha
26-05-2010	Biomass 412.2 g/m ² - 100% DM
26-05-2010	BBCH stage 55
09-06-2010	BBCH stage 60
21-06-2010	BBCH stage 69
30-06-2010	Biomass 849.5 g/m ² - 100% DM
30-06-2010	BBCH stage 75
14-07-2010	BBCH stage 89
20-07-2010	BBCH stage 93
21-07-2010	Straw burned, 69.3 hkg/ha - 100% DM
21-07-2010	Harvest of grass seed. Yield 16.5 hkg/ha - 87% DM, stubble height 15 cm
21-07-2010	BBCH stage 99
22-07-2010	Red fescue - 2. season
16-03-2011	Fertilization 50 N, 7 P, 24 K, kg/ha
15-04-2011	Hussar OD (iodosulfuron) - weeds - 0.05 l/ha (not analysed)
15-04-2011	BBCH stage 20-25
19-04-2011	BBCH stage 25
19-04-2011	Biomass 185.6 g/m ² - 100% DM
26-04-2011	BBCH stage 25
26-04-2011	Fusilade Max (fluazifop-P-butyl) - weeds - 1.5 l/ha
04-05-2011	BBCH stage 35

Date	Management practice and growth stages - Silstrup
13-05-2011	Biomass 507.9 g/m ² - 100% DM
13-05-2011	BBCH stage 53
07-06-2011	BBCH stage 59
23-06-2011	BBCH stage 68
04-07-2011	BBCH stage 85
04-07-2011	Biomass 1,022.7 g/m ² - 100% DM
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
17-08-2011	Trimming of grass - 4-5 cm height
16-09-2011	BBCH stage 20
16-09-2011	Fox 480 SC (bifenox) - weeds - 1.5 l/ha
29-09-2011	Trimming of grass - 5-6 cm height
05-10-2011	Pig slurry application - surface applied - 29.0 t/ha - 122,1 Total-N, 72.8 NH ₄ -N, 30.2 P, 52.2 K, 14,9 Mg, kg/ha, 908 g/ha CU, (VAP no. 36552)
15-03-2012	Fertilization 60 N, 32 S kg/ha
13-04-2012	DFF (diflufenican) - weeds - 0.15 l/ha
13-04-2012	BBCH stage 25
13-04-2012	Biomass 176.5 g/m ² - 100% DM
19-04-2012	BBCH stage 25
19-04-2012	Fusilade Max (fluazifop-P-butyl) - weeds - 1.5 l/ha
10-05-2012	BBCH stage 41
15-05-2012	BBCH stage 51
18-05-2012	BBCH stage 52
18-05-2012	Folicur (tebuconazol) - fungi - 1.0 l/ha
22-05-2012	Biomass 441.9 g/m ² - 100% DM
22-05-2012	BBCH stage 57
07-06-2012	BBCH stage 60
22-06-2012	BBCH stage 67
03-07-2012	BBCH stage 85
05-07-2012	BBCH stage 85
05-07-2012	Biomass 915.3 g/m ² - 100% DM
25-07-2012	Harvest of grass seed. Yield 14.16 hkg/ha - 87% DM
25-07-2012	Straw removed - straw yield 48.3 hkg/ha - 100% DM, stubble height 12 cm
25-07-2012	BBCH stage 89
10-09-2012	Tracer (potassium 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
17-10-2012	BBCH stage 5
24-10-2012	BBCH stage 9
24-10-2012	BBCH stage 9
31-10-2012	BBCH stage 10
09-11-2012	BBCH stage 10
09-11-2012	DFF (diflufenican) + Oxitril CM (ioxynil+bromoxynil - not analysed) - weeds - 0.12 g/ha + 0.2 l/ha
14-11-2012	BBCH stage 11
28-11-2012	BBCH stage 12
08-01-2013	BBCH stage 12
22-02-2013	BBCH stage 12
22-02-2013	Fertilization 52.5 N, 7.5 P, 25.0 K kg/ha
03-05-2013	Spring barley
03-05-2013	Sowing spring barley 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	The remaining winter wheat plants incorporated at the sowing of spring barley
04-05-2013	Fertilization 67.2 N, 9.6 P, 32.0 K kg/ha
14-05-2013	BBCH stage 8
16-05-2013	BBCH stage 9
22-05-2013	BBCH stage 12
29-05-2013	BBCH stage 22
29-05-2013	Biomass 23.3 g/m ² - 100% DM
30-05-2013	BBCH stage 22
30-05-2013	Duotril 400 EC (ioxynil+bromoxynil) - weeds - 0.6 l/ha
11-06-2013	BBCH stage 30
25-06-2013	BBCH stage 47

Date	Management practice and growth stages - Silstrup
25-06-2013	Amistar (azoxystrobin) - fungi - 1.0 l/ha
01-07-2013	Folicur 250 EC (tebuconazol) - fungi - 1.0 l/ha
01-07-2013	BBCH stage 50
01-07-2013	Biomass 537.0 g/m ² - 100% DM
09-07-2013	BBCH stage 58
19-07-2013	BBCH stage 70
06-08-2013	BBCH stage 80
06-08-2013	Biomass 1,332.1 g/m ² - 100% DM
14-08-2013	BBCH stage 86
20-08-2013	Glyfonova 450 Plus (glyphosate) - weeds (killing the grass) - 2.4 l/ha
20-08-2013	BBCH stage 87
30-08-2013	BBCH stage 89
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
23-09-2013	Ploughed - depth 24 cm – packed
25-09-2013	Sowing winter wheat cv. Hereford. Depth 4 cm, seeding rate 190 kg/ha, final plant number 346/m ² , row distance 15.0 cm using a Horch Pronto 6 DC
01-10-2013	BBCH stage 6
07-10-2013	BBCH stage 9 – emergence
16-10-2013	BBCH stage 10
16-10-2013	Oxiril CM (bromoxynil + ioxynil) + DFF (diflufenican) - weeds - 0,08 l/ha + 0.2 l/ha (bromoxynil and ioxynil not included)
30-10-2013	BBCH stage 12
05-11-2013	BBCH stage 13
20-11-2013	BBCH stage 13
04-12-2013	BBCH stage 13
07-04-2014	Fertilization 170.5 N, 23.3 P, 77.5 K kg/ha
07-04-2014	BBCH stage 13
15-04-2014	BBCH stage 20
25-04-2014	BBCH stage 30
25-04-2014	Biomass 94.0 g/m ² - 100% DM
30-04-2014	BBCH stage 30
15-05-2014	BBCH stage 32
21-05-2014	BBCH stage 34
27-05-2014	BBCH stage 41
02-06-2014	Biomass 962.0 g/m ² - 100% DM
02-06-2014	BBCH stage 51
03-06-2014	BBCH stage 53
04-06-2014	Amistar (azoxystrobin) - fungi - 1.0 l/ha
18-06-2014	BBCH stage 63
23-06-2014	BBCH stage 68
02-07-2014	Biomass 1,776.5 g/m ² - 100% DM
02-07-2014	BBCH stage 75
08-07-2014	BBCH stage 76
16-07-2014	BBCH stage 79
22-07-2014	BBCH stage 83
25-07-2014	BBCH stage 87
25-07-2014	Glyfonova 450 Plus (glyphosate) - weeds - 2.4 l/ha
15-08-2014	BBCH stage 90
16-08-2014	Harvest of winter wheat. Grain yield 83.5 hkg/ha - 85% DM, straw yield 113.8 hkg/ha - 100% DM, stubbleheight 14 cm. Straw shredded (left in field) at harvest
19-09-2014	Stubble harrowed, disk harrow (Heva Disc Roller) - depth 5-8 cm (incorporation of straw)

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 and growth stages - Estrup
04-04-2009	Fertilization 110 N, 15 P, 40 K, kg/ha
05-04-2009	Seed bed preparation - depth 6 cm
05-04-2009	Sowing sugar beet cv. Palace. Depth 3.0 cm, row distance 50.0 cm, plant distance 20 cm, seeding rate 100,000 seeds/ha. Final plant number 8.5/m ²
16-04-2009	BBCH stage 9
24-04-2009	Betanal (phenmedipham) - weeds - 1.5 l/ha
24-04-2009	Goliath (metamitron) - 1.0 l/ha
24-04-2009	BBCH stage 10
30-04-2009	Safari (triflurosulfuron-methyl) - weeds - 10 g/ha
30-04-2009	Ethosan (ethofumesate) - 0.07 l/ha
30-04-2009	Betanal (phenmedipham) - 1.5 l/ha
30-04-2009	BBCH stage 11
30-04-2009	Goliath (metamitron) - 1.0 l/ha
11-05-2009	BBCH stage 14
11-05-2009	Safari (triflurosulfuron-methyl) - weeds - 10 g/ha
11-05-2009	Betanal (phenmedipham) - 1.5 l/ha
11-05-2009	Goliath (metamitron) - 1.0 l/ha
11-05-2009	Ethosan (ethofumesate) - 0.07 l/ha
14-05-2009	BBCH stage 15
14-05-2009	Focus Ultra (cycloxydim) - weeds - 1.0 l/ha
18-05-2009	BBCH stage 16
26-05-2009	BBCH stage 18
03-06-2009	BBCH stage 19
09-06-2009	BBCH stage 19-31
09-06-2009	Biomass 100.0 root and 347.6 top, g/10 m of row - 100% DM
17-06-2009	BBCH stage 31-34
17-06-2009	Focus Ultra (cycloxydim) - weeds - 1.0 l/ha
22-06-2009	BBCH stage 34-36
22-06-2009	Biomass 568.4 root and 1,030.3 top, g/10 m of row - 100% DM
01-07-2009	BBCH stage 37-39
02-07-2009	Biomass 1,292.3 root and 1,284.7 top, g/10 m of row - 100% DM
05-10-2009	BBCH stage 49
06-10-2009	Harvest of sugar beet. 147.9 hkg/ha - 100% root DM and 40.1 hkg/ha - 100% top DM
01-11-2009	Spring barley and red fescue
01-11-2009	Ploughing - depth 20 cm
07-04-2010	Seed bed preparation - depth 6 cm
15-04-2010	Fertilization 120 N, 9 P, 32 K, kg/ha
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
01-05-2010	BBCH stage 9
06-05-2010	BBCH stage 10
17-05-2010	BBCH stage 12-20
24-05-2010	BBCH stage 22-24
01-06-2010	BBCH stage 24-26
01-06-2010	Fighter 480 (bentazone) - weeds - 1.25 l/ha
09-06-2010	Biomass 149.4 g/m ² - 100% DM
09-06-2010	BBCH stage 31
18-06-2010	BBCH stage 37
02-07-2010	Amistar (azoxystrobin) - fungi - 1.0 l/ha (not analysed)
02-07-2010	BBCH stage 52
02-07-2010	Biomass 934.8 g/m ² - 100% DM
20-07-2010	BBCH stage 75
27-07-2010	BBCH stage 83
27-07-2010	Biomass 1,454.6 g/m ² - 100% DM
02-08-2010	BBCH stage 87
17-08-2010	BBCH stage 89
21-08-2010	Straw removed. Straw yield 27.5 hkg/ha - 100% DM. Stubble height 10 cm
21-08-2010	Harvest of spring barley. Grain yield 58.5 hkg - 85% DM
22-08-2010	Red fescue
06-09-2010	Fertilization 58.5 N, 4.5 P, 15.8 K, kg/ha
06-09-2010	BBCH stage 24-29
25-10-2010	Fox 480 SC (bifenox) - weeds - 1.5 l/ha
25-10-2010	BBCH stage 24-29

Date	Management practice and growth stages - Estrup
07-03-2011	BBCH stage 26-27
07-03-2011	Fertilization 104 N, 8 P, 28 K, kg/ha
15-03-2011	BBCH stage 25-29
01-04-2011	BBCH stage 25-29
09-04-2011	BBCH stage 29-30
19-04-2011	BBCH stage 29-30
02-05-2011	BBCH stage 29-31
12-05-2011	BBCH stage 30-32
12-05-2011	Biomass 423.0 g/m ² - 100% DM
19-05-2011	BBCH stage 30-55
21-05-2011	BBCH stage 37-59
21-05-2011	Fusilade Max (fluazifop-P-butyl) - weeds - 1.5 l/ha
24-05-2011	BBCH stage 51-57
24-05-2011	Biomass 725.8 g/m ² - 100% DM
01-06-2011	BBCH stage 54-59
08-06-2011	BBCH stage 55-59
17-06-2011	BBCH stage 59
24-06-2011	BBCH stage 73-75
24-06-2011	Biomass 710.6 g/m ² - 100% DM
01-07-2011	BBCH stage 77-82
05-07-2011	Windrowing. Stubble height 5 cm
20-07-2011	Straw removed. Straw yield 21.1 hkg/ha
20-07-2011	Threshing of grass seed. Yield 7.2 hkg/ha - 87% DM, stubble height 5 cm
03-10-2011	BBCH stage 29
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 . Undersown white clover cv. Liflex, seeding rate 2.0 kg/ha, depth 2-3 cm, row distance 13 cm
04-04-2012	Tracer (potassium bromide) 30 kg/ha
19-04-2012	BBCH 9 - emergence of spring barley
23-04-2012	BBCH stage 10
24-04-2012	BBCH 9 - emergence of white clover
03-05-2012	BBCH stage 13-21
16-05-2012	BBCH stage 23-27
18-05-2012	BBCH stage 24-29
18-05-2012	Fighter 480 (bentazone) - weeds - 1.25 l/ha
23-05-2012	BBCH stage 29-31
23-05-2012	Biomass 112.7 g/m ² - 100% DM
01-06-2012	BBCH stage 33-37
06-06-2012	BBCH stage 39
06-06-2012	Flexity (metrafenon) - fungi - 0.5 l/ha
11-06-2012	BBCH stage 45-51
11-06-2012	Biomass 592.5 g/m ² - 100% DM
21-06-2012	BBCH stage 55-57
05-07-2012	BBCH stage 71
23-07-2012	BBCH stage 83
23-07-2012	Biomass 1,321.7 g/m ² - 100% DM
30-07-2012	BBCH stage 85
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
27-08-2012	BBCH stage 22-29 clover vegetative growth - formation of side shoots
29-08-2012	Trimming of stubble
26-01-2013	Kerb 400 SC (propyzamid) - fungi - 1.0 l/ha
13-05-2013	Biomass 298.2 g/m ² - 100% DM
14-05-2013	Fighter 480 (bentazone) - weeds - 3.0 l/ha
22-05-2013	Rolled with a concrete roller
29-05-2013	Biomass 402.9 g/m ² - 100% DM
31-05-2013	Karate (Lambda-cyhalothrin) - pest - 0.3 l/ha (not analysed)
12-06-2013	Karate (Lambda-cyhalothrin) - pest - 0.3 l/ha (not analysed)
25-06-2013	Biomass 698.3 g/m ² - 100% DM
22-07-2013	Windrowing. Stubble height 8.0 cm

Date	Management practice and growth stages - Estrup
28-07-2013	Threshing of white clover. Seed yield fresh 1,560 hkg/ha. Straw yield fresh 0.96 hkg/ha
07-10-2013	Winter wheat
07-10-2013	Ploughed and packed - depth 14 cm
07-10-2013	Rotor harrowed at the time of sowing the winter wheat, cv. Mariboss - depth 4 cm, row distance 11 cm, seeding rate 200 kg/ha - final plant number 320/m ²
18-10-2013	BBCH 09 – emergence
13-03-2014	BBCH 23
13-03-2014	Fertilization 81 N, 16 P, 61 K, kg/ha
09-04-2014	Fertilization 81 N, 16 P, 61 K, kg/ha
09-04-2014	BBCH 25
15-04-2014	BBCH 24
28-04-2014	Briotril (ioxynil+ bromoxynil) - weeds - 0.6 l/ha + Tomahawk 180 EC (fluroxypyr) - weeds - 0.8 l/ha (neither included)
28-04-2014	BBCH 24
30-04-2014	BBCH 30
15-05-2014	BBCH 32
15-05-2014	Amistar (azoxystrobin) - fungi - 1.0 l/ha (not included)
04-06-2014	Biomass 1,321 g/m ² - 100% DM
04-06-2014	BBCH 55
12-06-2014	BBCH 59
20-07-2014	BBCH 83
20-07-2014	Biomass 1,995 g/m ² - 100% DM
25-07-2014	BBCH 87
30-07-2014	Harvest of winter wheat. Grain yield 56.6 hkg - 85% DM, stubbleheight 12 cm
26-08-2014	Glyfonova Plus (glyphosate) - weeds - 4.0 l/ha (not included)
23-09-2014	Ploughing - 14 cm depth - straw 70 hkg/ha (fresh weight) incorporated

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 and growth stages - Faardrup
04-04-2009	Fertilization 110 N, 15 P, 40 K, kg/ha
05-04-2009	Seed bed preparation - depth 6 cm
05-04-2009	Sowing sugar beet cv. Palace. depth 3.0 cm, row distance 50.0 cm, plant distance 20 cm, seeding rate 100,000 seeds/ha. Final plant number 8.5/m ²
16-04-2009	BBCH stage 9
24-04-2009	Betanal (phenmedipham) - weeds - 1.5 l/ha
24-04-2009	Goliath (metamitron) - 1.0 l/ha
24-04-2009	BBCH stage 10
30-04-2009	Safari (triflusaluron-methyl) - weeds - 10 g/ha
30-04-2009	Ethosan (ethofumesate) - 0.07 l/ha
30-04-2009	Betanal (phenmedipham) - 1.5 l/ha
30-04-2009	BBCH stage 11
30-04-2009	Goliath (metamitron) - 1.0 l/ha
11-05-2009	BBCH stage 14
11-05-2009	Safari (triflusaluron-methyl) - weeds - 10 g/ha
11-05-2009	Betanal (phenmedipham) - 1.5 l/ha
11-05-2009	Goliath (metamitron) - 1.0 l/ha
11-05-2009	Ethosan (ethofumesate) - 0.07 l/ha
14-05-2009	BBCH stage 15
14-05-2009	Focus Ultra (cycloxydim) - weeds -1.0 l/ha
18-05-2009	BBCH stage 16
26-05-2009	BBCH stage 18
03-06-2009	BBCH stage 19
09-06-2009	BBCH stage 19-31
09-06-2009	Biomass 100.0 root and 347.6 top, g/10 m of row - 100% DM
17-06-2009	BBCH stage 31-34
17-06-2009	Focus Ultra (cycloxydim) - weeds -1.0 l/ha
22-06-2009	BBCH stage 34-36
22-06-2009	Biomass 568.4 root and 1,030.3 top, g/10 m of row - 100% DM
01-07-2009	BBCH stage 37-39
02-07-2009	Biomass 1,292.3 root and 1,284.7 top, g/10 m of row - 100% DM
05-10-2009	BBCH stage 49
06-10-2009	Harvest of sugar beet. 147.9 hkg/ha - 100% root DM and 40.1 hkg/ha - 100% top DM
01-11-2009	Spring barley and red fescue
01-11-2009	Ploughing - depth 20 cm
07-04-2010	Seed bed preparation - depth 6 cm
15-04-2010	Fertilization 120 N, 9 P, 32 K, kg/ha
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
01-05-2010	BBCH stage 9
06-05-2010	BBCH stage 10
17-05-2010	BBCH stage 12-20
24-05-2010	BBCH stage 22-24
01-06-2010	BBCH stage 24-26
01-06-2010	Fighter 480 (bentazone) - weeds - 1.25 l/ha
09-06-2010	Biomass 149,4 g/m ² - 100% DM
09-06-2010	BBCH stage 31
18-06-2010	BBCH stage 37
02-07-2010	Amistar (azoxystrobin) - fungi - 1.0 l/ha (not analysed)
02-07-2010	BBCH stage 52
02-07-2010	Biomass 934,8 g/m ² - 100% DM
20-07-2010	BBCH stage 75
27-07-2010	BBCH stage 83
27-07-2010	Biomass 1,454.6 g/m ² - 100% DM
02-08-2010	BBCH stage 87
17-08-2010	BBCH stage 89
21-08-2010	Straw removed. Straw yield 27.5 hkg/ha - 100% DM. Stubble height 10 cm
21-08-2010	Harvest of spring barley. Grain yield 58.5 hkg - 85% DM
22-08-2010	Red fescue
06-09-2010	Fertilization 58.5 N, 4.5 P, 15.8 K, kg/ha
06-09-2010	BBCH stage 24-29
25-10-2010	Fox 480 SC (bifenox) - weeds - 1.5 l/ha
25-10-2010	BBCH stage 24-29

Date	Management practice and growth stages - Faardrup
07-03-2011	BBCH stage 26-27
07-03-2011	Fertilization 104 N, 8 P, 28 K, kg/ha
15-03-2011	BBCH stage 25-29
01-04-2011	BBCH stage 25-29
09-04-2011	BBCH stage 29-30
19-04-2011	BBCH stage 29-30
02-05-2011	BBCH stage 29-31
12-05-2011	BBCH stage 30-32
12-05-2011	Biomass 423.0 g/m ² - 100% DM
19-05-2011	BBCH stage 30-55
21-05-2011	BBCH stage 37-59
21-05-2011	Fusilade Max (fluazifop-P-butyl) - weeds - 1.5 l/ha
24-05-2011	BBCH stage 51-57
24-05-2011	Biomass 725.8 g/m ² - 100% DM
01-06-2011	BBCH stage 54-59
08-06-2011	BBCH stage 55-59
17-06-2011	BBCH stage 59
24-06-2011	BBCH stage 73-75
24-06-2011	Biomass 710.6 g/m ² - 100% DM
01-07-2011	BBCH stage 77-82
05-07-2011	Windrowing. Stubble height 5 cm
20-07-2011	Straw removed. Straw yield 21.1 hkg/ha
20-07-2011	Threshing of grass seed. Yield 7.2 hkg/ha - 87% DM, stubble height 5 cm
03-10-2011	BBCH stage 29
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 . Undersown 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
19-04-2012	BBCH 9 - emergence of spring barley
23-04-2012	BBCH stage 10
24-04-2012	BBCH 9 - emergence of white clover
03-05-2012	BBCH stage 13-21
16-05-2012	BBCH stage 23-27
18-05-2012	BBCH stage 24-29
18-05-2012	Fighter 480 (bentazone) - weeds - 1.25 l/ha
23-05-2012	BBCH stage 29-31
23-05-2012	Biomass 112.7 g/m ² - 100% DM
01-06-2012	BBCH stage 33-37
06-06-2012	BBCH stage 39
06-06-2012	Flexity (metrafenon) - fungi - 0.5 l/ha
11-06-2012	BBCH stage 45-51
11-06-2012	Biomass 592.5 g/m ² - 100% DM
21-06-2012	BBCH stage 55-57
05-07-2012	BBCH stage 71
23-07-2012	BBCH stage 83
23-07-2012	Biomass 1,321.7 g/m ² - 100% DM
30-07-2012	BBCH stage 85
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
27-08-2012	BBCH stage 22-29 clover vegetative growth - formation of side shoots
29-08-2012	Trimming of stubble
26-01-2013	Kerb 400 SC (propyzamid) - fungi - 1.0 l/ha
13-05-2013	Biomass 298.2 g/m ² - 100% DM
14-05-2013	Fighter 480 (bentazone) - weeds - 3.0 l/ha
22-05-2013	Rolled with a concrete roller
29-05-2013	Biomass 402.9 g/m ² - 100% DM
31-05-2013	Karate (Lambda-cyhalothrin) - pest - 0.3 l/ha (not analysed)
12-06-2013	Karate (Lambda-cyhalothrin) - pest - 0.3 l/ha (not analysed)
25-06-2013	Biomass 698.3 g/m ² - 100% DM
22-07-2013	Windrowing. Stubble height 8.0 cm

Date	Management practice and growth stages - Faardrup
28-07-2013	Threshing of white clover. Seed yield fresh 1,560 hkg/ha. Straw yield fresh 0.96 hkg/ha
07-10-2013	Winter wheat
07-10-2013	Ploughed and packed - depth 14 cm
07-10-2013	Rotor harrowed at the time of sowing the winter wheat, cv. Mariboss - depth 4 cm, row distance 11 cm, seeding rate 200 kg/ha - final plant number 320/m ²
18-10-2013	BBCH 09 – emergence
13-03-2014	BBCH 23
13-03-2014	Fertilization 81 N, 16 P, 61 K, kg/ha
09-04-2014	Fertilization 81 N, 16 P, 61 K, kg/ha
09-04-2014	BBCH 25
15-04-2014	BBCH 24
28-04-2014	Briotril (ioxynil+ bromoxynil) - weeds - 0.6 l/ha + Tomahawk 180 EC (fluroxypyr) - weeds - 0.8 l/ha (neither included)
28-04-2014	BBCH 24
30-04-2014	BBCH 30
15-05-2014	BBCH 32
15-05-2014	Amistar (azoxystrobin) - fungi - 1.0 l/ha (not included)
04-06-2014	Biomass 1,321 g/m ² - 100% DM
04-06-2014	BBCH 55
12-06-2014	BBCH 59
20-07-2014	BBCH 83
20-07-2014	Biomass 1,995 g/m ² - 100% DM
25-07-2014	BBCH 87
30-07-2014	Harvest of winter wheat. Grain yield 56.6 hkg - 85% DM. Stubble height 12 cm
26-08-2014	Glyfonova Plus (glyphosate) - weeds - 4.0 l/ha (not included)
23-09-2014	Ploughing - 14 cm depth - straw 70 hkg/ha (fresh weight) incorporated

Appendix 4

Precipitation data for the PLAP sites

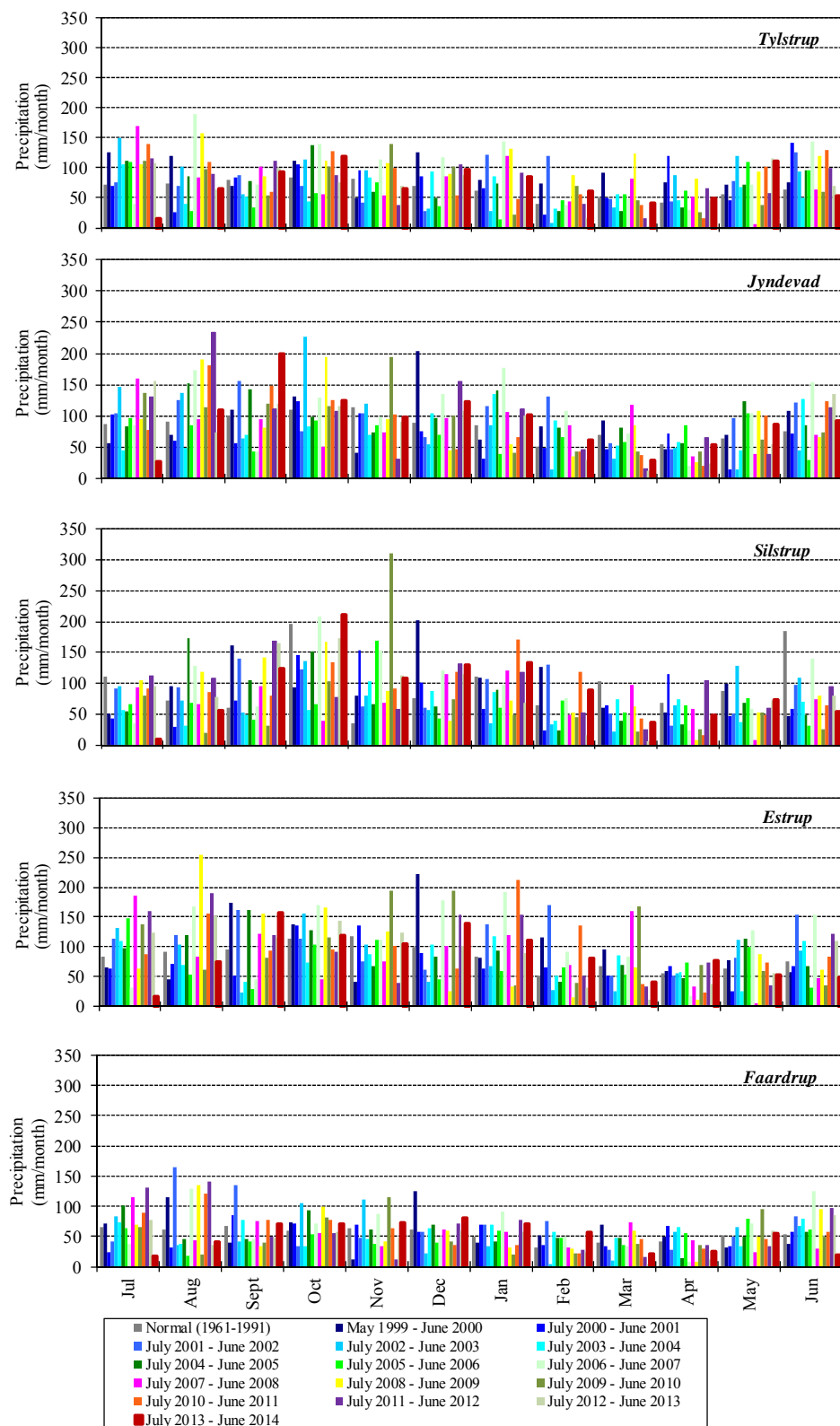


Figure A4.1. Monthly precipitation at all localities for the monitoring period July 2000–June 2014. Normal values (1961–1990) are included for comparison.

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 monitoring period up to August 2014. All samples included.

Tylstrup		Horizontal			Vertical			Suction cups		
Parent	Compound	nd	≤ 0.1	> 0.1	nd	≤ 0.1	> 0.1	nd	≤ 0.1	> 0.1
Aclonifen	Aclonifen									
Aminopyralid	Aminopyralid	22	-	-	134	-	-	71	-	-
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	-	-			
Fludioxonil	CGA 192155	4	-	-	30	-	-	11	-	-
	CGA 339833	4	-	-	30	-	-	11	-	-
Fluroxypyr	Fluroxypyr				194	-	-	70	-	-
Ioxynil	Ioxynil				198	-	-	72	-	-
Linuron	Linuron				271	-	-	67	-	-
Mancozeb	EBIS	3	-	-	19	-	-	7	-	-
	ETU				198	2	-	37	7	-
Metalaxyl-M	CGA 108906	2	21	-	50	178	45	18	80	35
	CGA 62826	22	1	-	257	16	-	101	28	5
	Metalaxyl-M	23	-	-	256	17	-	131	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	-	-
	RH-24644				221	-	-	82	-	-
	RH-24655				157	-	-	58	-	-
Prosulfocarb	Prosulfocarb	15	-	-	93	4	-	52	1	-
Rimsulfuron	PPU	9	-	-	589	58	-	74	191	3
	PPU-desamino	9	-	-	638	9	-	205	63	-
	Rimsulfuron				178	-	-	65	-	-
Tebuconazole	Tebuconazole				195	1	-	77	-	-

Tylstrup		Horizontal			Vertical			Suction cups		
Parent	Compound	nd	≤ 0.1	> 0.1	nd	≤ 0.1	> 0.1	nd	≤ 0.1	> 0.1
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 0.1µg/L ($\leq 0.1 \mu\text{g/L}$) or detected in concentrations above 0.1 µg/L ($> 0.1 \mu\text{g/L}$) at **Jynde vad**. Numbers are accumulated for the monitoring period up to August 2014. All samples included.

Jynde vad		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	-	-	43	-	-
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	20	1	-	580	-	-	98	62	14
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	4	-	-	28	-	-	10	-	-
	FMC 65317	4	-	-	29	-	-	10	-	-
Cyazofamid	Cyazofamid	4	-	-	131	-	-	32	-	-
Diflufenican	AE-05422291	12	-	-	140	-	-	38	-	-
	AE-B107137	12	-	-	140	-	-	52	-	-
	Diflufenican	12	-	-	140	-	-	38	-	-
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	-	-			
Fludioxonil	CGA 192155	4	-	-	34	-	-	3	-	-
	CGA 339833	4	-	-	34	-	-	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	-	-
Mancozeb	EBIS	3	-	-	24	-	-	3	-	-
Mesosulfuron-methyl	Mesosulfuron				12	-	-	45	-	-
	Mesosulfuron-methyl				285	-	-	78	-	-
Mesotrione	AMBA	21	-	-	144	-	-	54	-	-
	MNBA	21	-	-	144	-	-	54	-	-
	Mesotrione	21	-	-	144	-	-	54	-	-
Metalaxyl-M	CGA 108906	-	16	6	82	145	72	25	33	34
	CGA 62826	-	13	9	184	115	-	24	48	20
	Metalaxyl-M	9	8	5	243	38	17	71	11	-
Metribuzin	Desamino-diketo-metribuzin				6	7	13	6	-	-
	Desamino-metribuzin				26	-	-	4	-	-
	Diketo-metribuzin				-	7	19	3	3	-
	Metribuzin				26	-	-	6	-	-
Pendimethalin	Pendimethalin				257	-	-	71	-	-
Picolinafen	CL153815				35	-	-	36	-	-
	Picolinafen				35	-	-	35	1	-
Pirimicarb	Pirimicarb				251	-	-	69	-	-
	Pirimicarb-desmethyl				251	-	-	68	1	-
	Pirimicarb-desmethyl-formamido				251	-	-	69	-	-
Propiconazole	Propiconazole				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

Jynde vad		Horizontal			Vertical			Suction cups		
Parent	Compound	nd	≤ 0.1	>0.1	nd	≤0.1	>0.1	nd	≤0.1	>0.1
	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 0.1µg/L (> = 0.1) at **Silstrup**. Numbers are accumulated for the monitoring period up to August 2014. All samples included.

Silstrup		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	110	12	1	158	-	-	292	1	-			
	CyPM	50	81	15	176	18	1	337	29	2			
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	25	-	-	36	-	-	59	-	-			
Chlormequat	Chlormequat	20	1	-	36	-	-	66	-	-			
Clopyralid	Clopyralid	44	-	-	67	-	-	124	-	-			
Desmedipham	Desmedipham	101	-	-	107	1	-	240	-	-	58	-	-
	EHPC	74	-	-	68	-	-	139	-	-	26	-	-
Diffenican	AE-05422291	43	-	-	53	-	-	84	-	-			
	AE-B107137	35	4	1	53	-	-	84	-	-			
	Diffenican	32	10	1	53	-	-	83	-	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	56	30	23	107	23	2	177	48	14			
Fluroxypyr	Fluroxypyr	50	-	-	74	-	-	142	-	-			
Glyphosate	AMPA	35	133	17	165	8	-	293	16	-	8	-	-
	Glyphosate	97	67	20	170	3	-	285	24	-	8	-	-
Iodosulfuron-methyl	Iodosulfuron-methyl	60	-	-	85	-	-	165	-	-			
	Metsulfuron-methyl	60	-	-	85	-	-	165	-	-			
Ioxynil	Ioxynil	25	-	-	36	-	-	59	-	-			
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	-	-
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	-	-			

Silstrup		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
Terbuthylazine	2-hydroxy-desethyl- terbuthylazine	43	27	1	84	-	-	151	1	-	27	-	-
	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	-	-			
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 monitoring period up to August 2014. All samples included.

Estrup		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	68	-	-	50	-	-	67	-	-			
Azoxystrobin	Azoxystrobin	202	112	15	173	1	-	446	1	-			
	CyPM	38	166	125	160	13	1	442	5	-			
Bentazone	2-amino-N-isopropyl-benzamide	237	1	-	79	1	-	271	-	-	5	-	-
	Bentazone	177	175	14	141	28	-	472	2	-	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	32	-	-	30	-	-	34	-	-			
	FMC 65317	32	-	-	30	-	-	34	-	-			
Clopyralid	Clopyralid	1	-	-									
Diiflufenican	AE-05422291	29	-	-	16	-	-	28	-	-			
	AE-B107137	16	14	-	22	1	-	30	-	-			
	Diiflufenican	8	9	12	16	-	-	28	-	-			
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	71	328	111	243	1	-	667	7	-	23	-	-
	Glyphosate	193	210	107	238	4	1	632	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	72	20	-	59	-	-	102	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	1,2,4-triazol				-	6	-	2	1	1			
	Tebuconazole	40	24	17	39	-	-	118	3	2			
Terbuthylazine	2-hydroxy-desethyl-terbuthylazine	44	63	24	50	-	-	180	-	-			
	Desethyl-terbuthylazine	18	111	35	59	7	-	232	-	-			
	Desisopropylatrazine	90	70	1	62	1	-	197	26	-			
	Hydroxy-terbuthylazine	43	72	16	50	-	-	180	-	-			
	Terbuthylazine	49	78	34	63	-	-	222	1	-			

Estrup 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
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	-	-

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 monitoring period up to August 2014. All samples included.

Faardrup		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
Parrent	compound	106	-	-	92	-	-	194	-	-			
Azoxystrobin	Azoxystrobin												
	CyPM	102	4	-	92	-	-	194	-	-			
Bentazone	2-amino-N-isopropyl-benzamide	67	1	-	61	-	-	132	-	-			
	Bentazone	149	22	6	126	7	1	289	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	76	-	-	61	-	-	131	-	-			
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	44	-	-	39	-	-	83	-	-			
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	105	2	2	98	1	-	215	-	-			
	RH-24580	109	-	-	99	-	-	215	-	-			
	RH-24644	105	4	-	99	-	-	215	-	-			
	RH-24655	108	1	-	99	-	-	215	-	-			
Prosulfocarb	Prosulfocarb	78	-	-	61	-	-	126	-	-			
Tebuconazole	1,2,4-triazol				4	-	-	12	1	-			
	Tebuconazole	50	4	-	53	-	-	120	1	-			
Terbuthylazine	2-hydroxy-desethyl-terbuthylazine	60	7	1	60	1	-	126	6	-			
	Desethyl-terbuthylazine	21	82	7	68	21	-	149	15	30			
	Desisopropylatrazine	85	24	1	57	32	-	166	28	-			
	Hydroxy-terbuthylazine	89	20	1	85	4	-	164	30	-			
	Terbuthylazine	69	30	11	83	5	1	149	25	20			
Thiamethoxam	CGA 322704	68	-	-	58	-	-	126	-	-			

Faardrup		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
Tribenuron-methyl Triflusulfuron-methyl	Thiamethoxam	68	-	-	58	-	-	126	-	-			
	Triazinamin-methyl	77	-	-	57	-	-	148	-	-			
	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

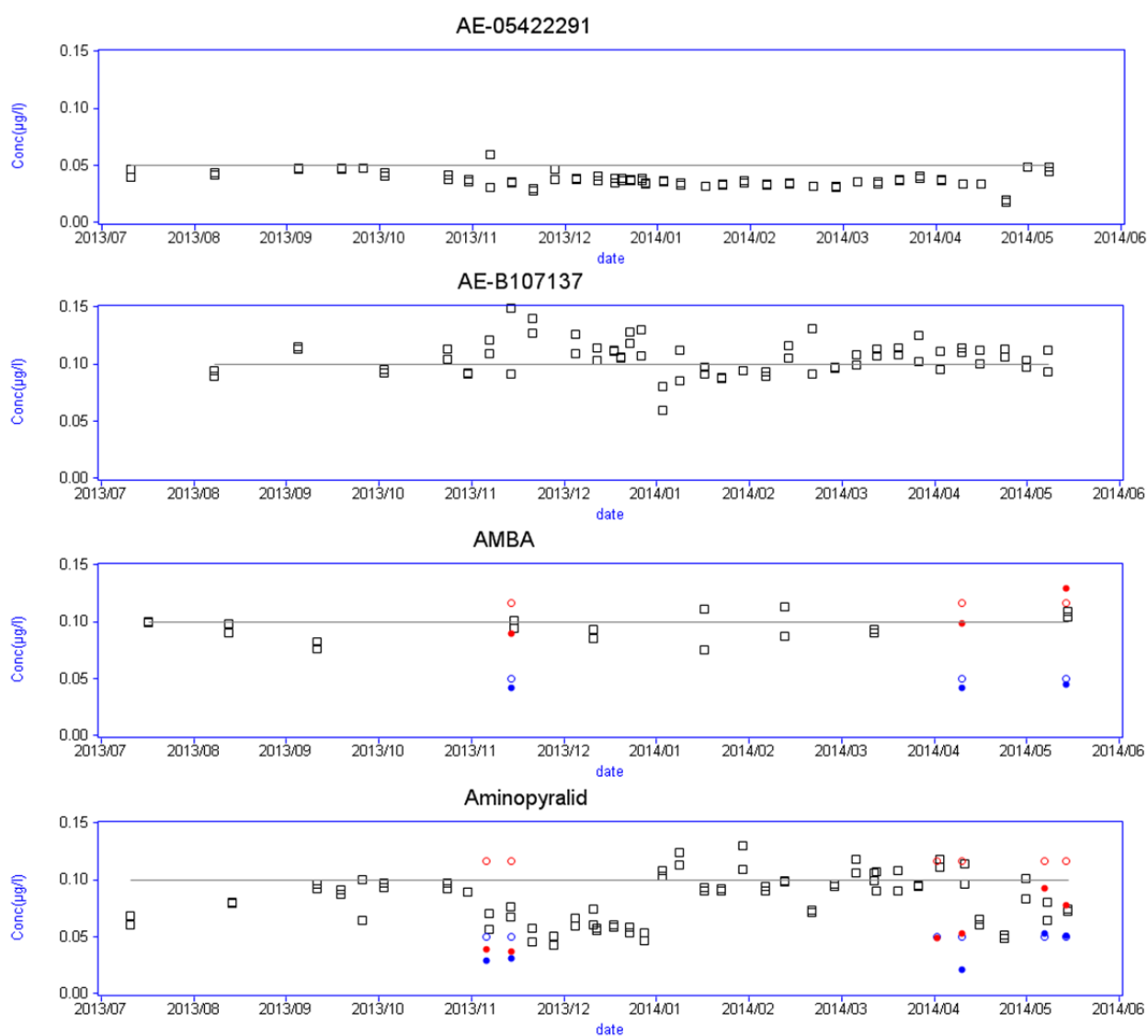


Figure A6.1. Quality control data for pesticide analysis by laboratory 1. Internal laboratory control (IQ) samples are indicated by square symbols and the nominal level is indicated by the solid grey line (\square IQ measured, $—$ IQ nominal concentration). External control (EQ) samples are indicated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

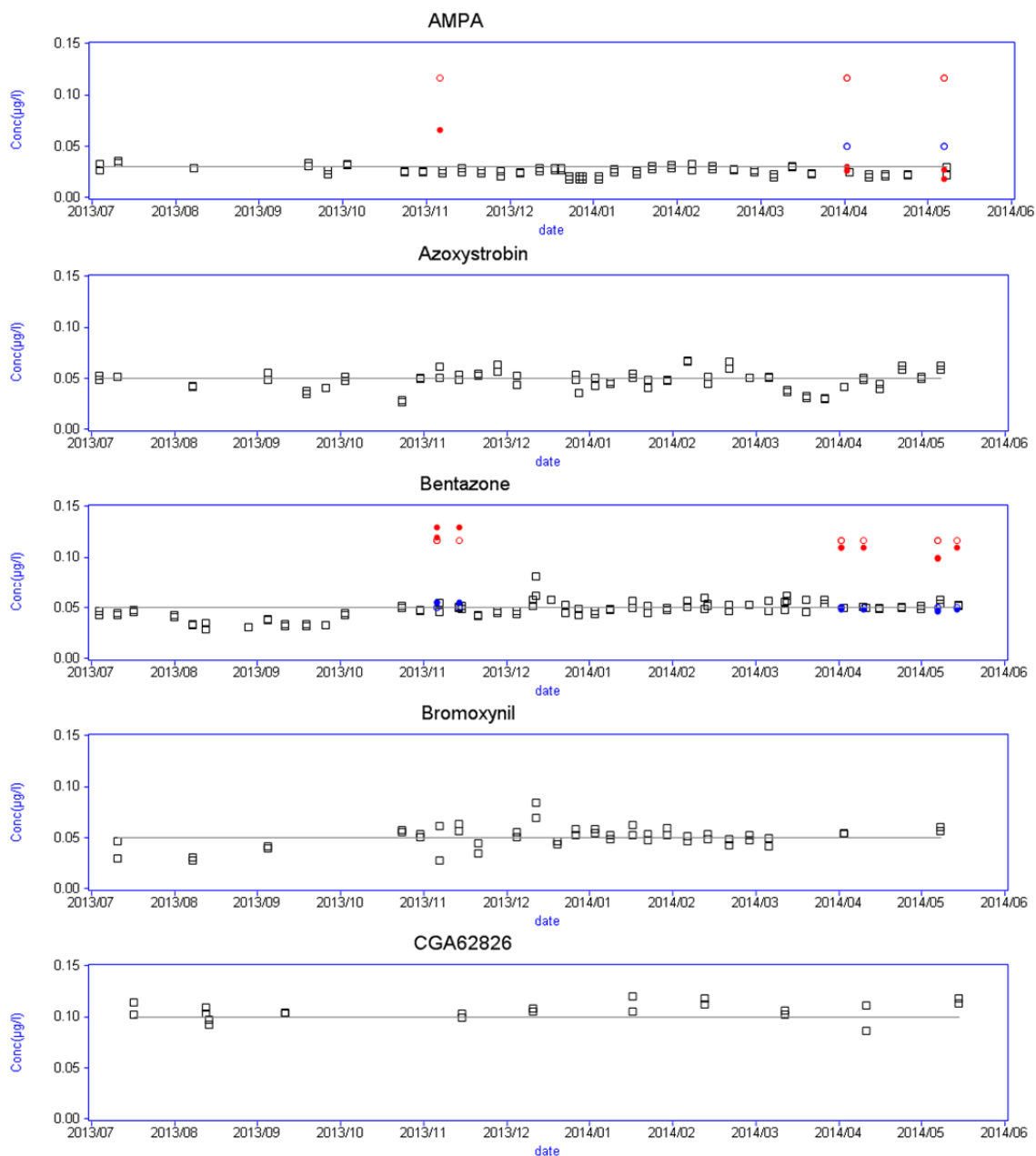


Figure A6.1 continued. Quality control data for pesticide analysis by laboratory 1. Internal laboratory control (IQ) samples are indicated by square symbols and the nominal level is indicated by the solid grey line (□ IQ measured, — IQ nominal concentration). External control (EQ) samples are indicated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

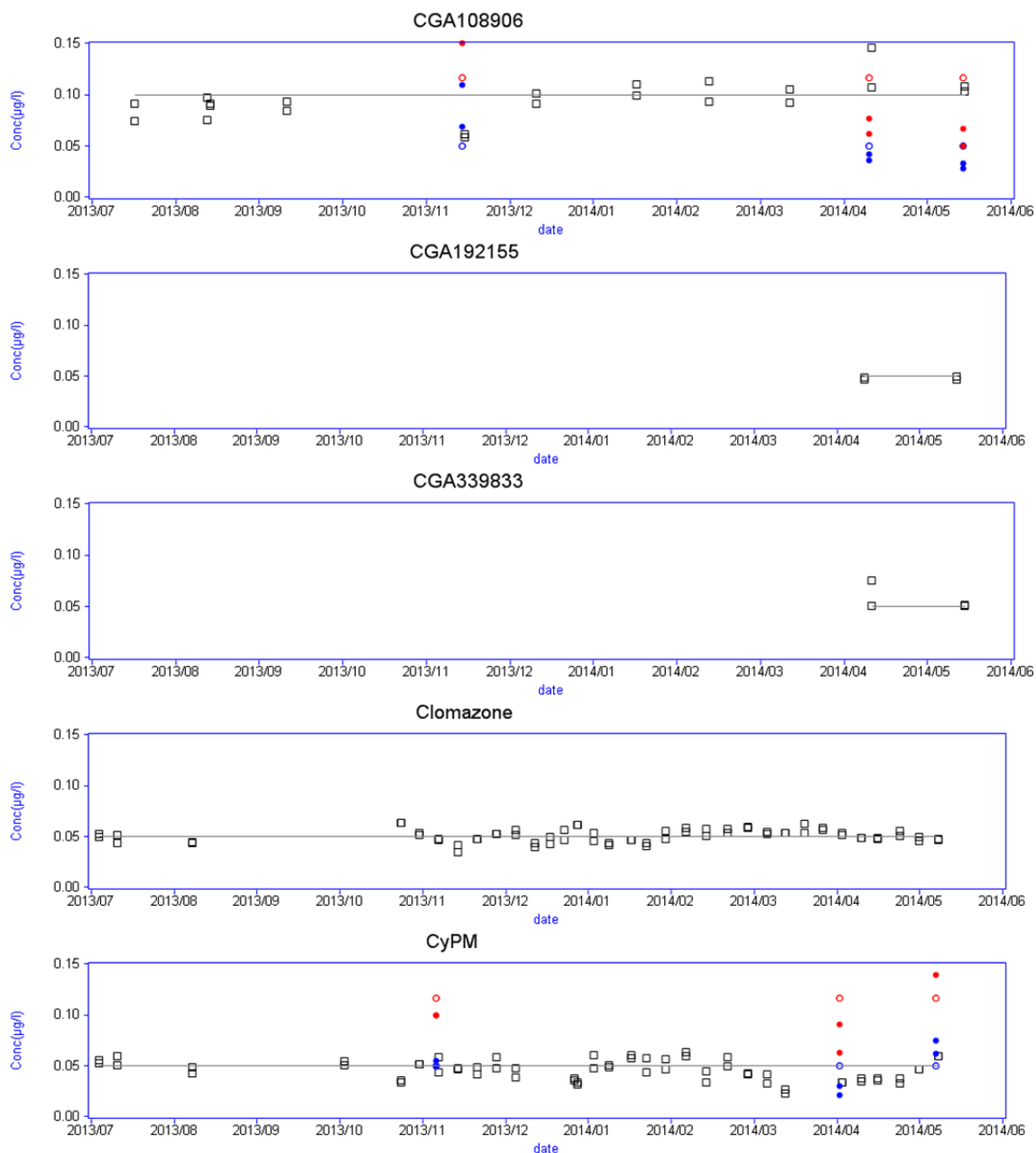


Figure A6.1 continued. Quality control data for pesticide analysis by laboratory 1. Internal laboratory control (IQ) samples are indicated by square symbols and the nominal level is indicated by the solid grey line (□ IQ measured, — IQ nominal concentration). External control (EQ) samples are indicated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

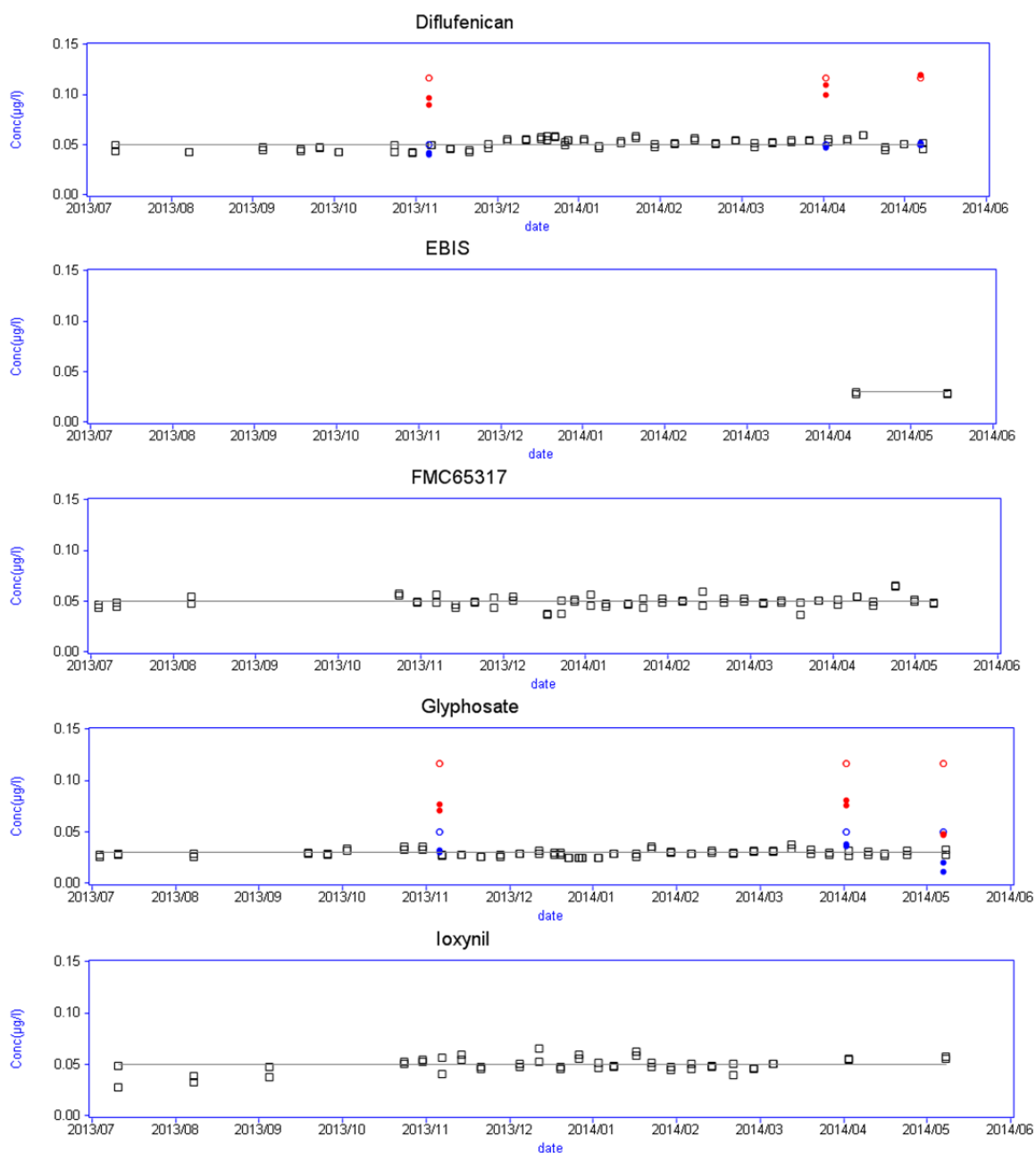


Figure A6.1 continued. Quality control data for pesticide analysis by laboratory 1. Internal laboratory control (IQ) samples are indicated by square symbols and the nominal level is indicated by the solid grey line (□ IQ measured, — IQ nominal concentration). External control (EQ) samples are indicated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

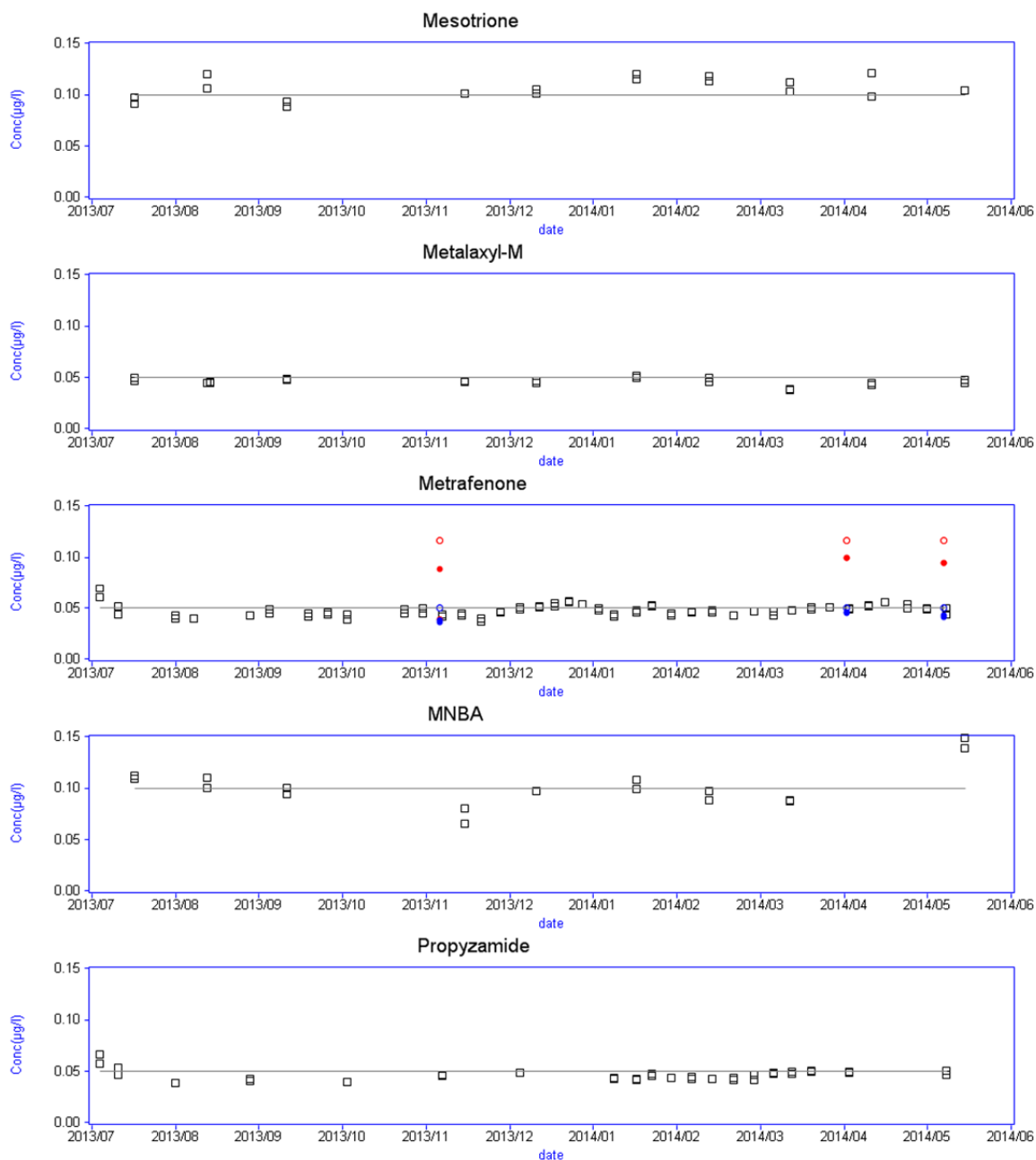


Figure A6.1 continued. Quality control data for pesticide analysis by laboratory 1. Internal laboratory control (IQ) samples are indicated by square symbols and the nominal level is indicated by the solid grey line (□ IQ measured, — IQ nominal concentration). External control (EQ) samples are indicated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

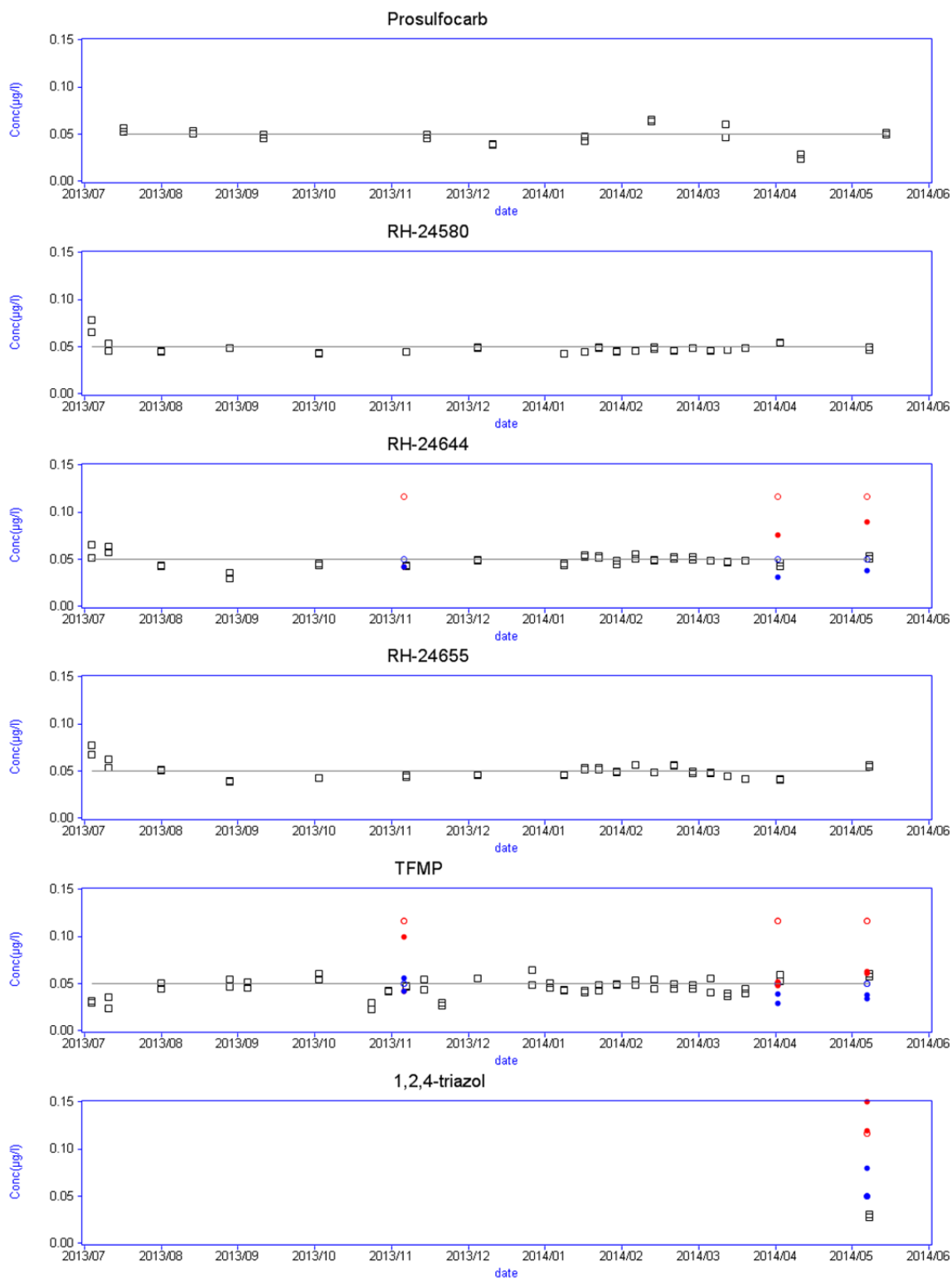


Figure A6.1 continued. Quality control data for pesticide analysis by laboratory 1. Internal laboratory control (IQ) samples are indicated by square symbols and the nominal level is indicated by the solid grey line (□ IQ measured, — IQ nominal concentration). External control (EQ) samples are indicated 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 analysed at five PLAP sites in the period up to 2006/2008

Table A7.1. Pesticides analysed at **Tylstrup** with the products used shown in parentheses. Degradation products are in italics. Precipitation (prec.) and percolation (perc.) are accumulated from the date of first application until the end of monitoring. 1st month perc. refers to accumulated percolation within the first month after the application. C_{mean} refers to average leachate concentration at 1 m b.g.s. the first year after application. (See Appendix 2 for calculation method).

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

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

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

Crop and analysed pesticides	Application date	End of monitoring	Prec. (mm)	Perc. (mm)	1 st month perc. (mm)	C _{mean} (µg/L)
Winter rye 2000						
Glyphosate (Roundup 2000)	Sep 99	Apr 02	2759	1607	139	<0.01
- <i>AMPA</i>						<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
- <i>fenpropimorphic acid</i>						<0.01
Maize 2001						
Terbuthylazine (Lido 410 SC)	May 01	Apr 04	3118	1809	4	<0.01
- <i>desethyl-terbuthylazine</i>	May 01	Apr 07	6742	3826	4	<0.01-0.02
PHCP ²⁾ (Lido 410 SC)	May 01	Jul 03	2413	1366	4	<0.02
Potatoes 2002						
- <i>PPU</i> (Titus) ³⁾	May 02	Jul 10 [†]	9389	5126	11	0.06 ⁴⁾ -0.13
- <i>PPU-desamino</i> (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
- <i>4-chlor,2-methylphenol</i>						<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
- <i>AIBA</i>						<0.01
Pendimethalin (Stomp SC)	May 04	Apr 07	3557	1996	4	<0.01
Pirimicarb (Pirimor G)	Jun 04	Apr 07	3493	1993	27	<0.01
- <i>Pirimicarb-desmethyl</i>						<0.01
- <i>Pirimicarb-desmethyl-formamido</i>						<0.02
- <i>fluazifop-P(free acid)</i> ⁵⁾	Jun 04	Jul 06	2395	1233	27	<0.01
(Fusilade X-tra)						
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
- <i>CyPM</i>						<0.02
Spring barley 2006						
Florasulam (Primus)	May 06	Jul 08	2779	1487	34	<0.01
- <i>florasulam-desmethyl</i>						<0.03
Epoxiconazole (Opus)	Jun 06	Dec 09	4698	2592	31	<0.01

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

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

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

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

⁴⁾ Leaching increased the second year after application.

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

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

Table A7.3. Pesticides analysed at **Silstrup** with the product used shown in parentheses. Degradation products are in italics. Precipitation (prec.) and percolation (perc.) are accumulated from date of first application until end of monitoring. 1st month perc. refers to accumulated percolation within the first month after application. C_{mean} refers to average leachate concentration in the drainage water within the first drainage season after application. (See Appendix 2 for calculation methods).

Crop and analysed pesticides	Application date	End of monitoring	Prec. (mm)	Perc. (mm)	1 st month perc. (mm)	C _{mean} (µg/L)
Fodder beet 2000						
Metamitron (Goltix WG)	May 00	Apr 03	2634	1328	53	0.05
- <i>metamitron-desamino</i>						0.06
Ethofumesate (Betanal Optima)	May 00	Apr 03	2634	1328	53	0.03
Desmedipham (Betanal Optima)	May 00	Apr 03	2634	1328	53	<0.01
- <i>EHPC</i>						<0.02
Phenmedipham (Betanal Optima)	May 00	Apr 03	2634	1328	53	<0.01
- <i>MHPC</i>						<0.02
- <i>3-aminophenol</i>						<0.02
Fluazifop-P-butyl (Fusilade X-tra)	Jun 00	Jul 02	1953	1019	5	<0.01
- <i>fluazifop (free acid)</i>						<0.02
Pirimicarb (Pirimor G)	Jul 00	Jul 07	6452	2825	1	<0.01
- <i>pirimicarb-desmethyl</i>						<0.01
- <i>pirimicarb-desmethyl-formamido</i>						<0.02
Spring barley 2001						
<i>Triazinamin-methyl</i> 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
- <i>flamprop (free acid)</i>						<0.01
Propiconazole (Tilt Top)	Jun 01	Jul 03	1928	944	3	<0.01
Fenpropimorph (Tilt Top)	Jun 01	Jul 03	1928	944	3	<0.01
- <i>fenpropimorphic acid</i>						<0.01
Dimethoate (Perfekthion 500 S)	Jul 01	Jul 03	1882	937	3	0.02
Maize 2002						
Glyphosate (Roundup Bio)	Oct 01	Apr 06	3802	1694	44	0.13
- <i>AMPA</i>						0.06
<i>PHCP</i> 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
- <i>desethyl-terbuthylazine</i>		Apr 05				0.15
- <i>2-hydroxy-terbuthylazine</i>		Apr 05				³⁾
- <i>2-hydroxy-desethyl-terbuthylazine</i>		Apr 05				³⁾
- <i>desisopropyl-atrazine</i>		Apr 05				³⁾
Peas 2003						
Bentazone (Basagran 480)	May 03	Jul 06	2634	1055	44	0.26
- <i>AIBA</i>						<0.01
Pendimethalin (Storm SC)	May 03	Apr 06	2634	1055	44	<0.01
Glyphosate (Roundup Bio)	Sep 03	Apr 06	2207	971	0	<0.01
- <i>AMBA</i>						0.02
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
- <i>4-chlor,2-methylphenol</i>						<0.01
Azoxystrobin (Amistar)	Jun 04	Jul 06	1781	706	0	0.01
- <i>CyPM</i>		Jul 07	2931	1202	0	0.09
Pirimicarb (Pirimor G)	Jul 04	Jul 07	2818	1205	0	<0.01
- <i>Pirimicarb-desmethyl</i>						<0.01
- <i>Pirimicarb-desmethyl-formamido</i>						<0.02
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
- <i>CyPM</i>	Jun 05	Jul 07	2012	828	10	0.02
Pirimicarb (Pirimor G)	Jul 05	Jul 07	1933	818	0	<0.01
- <i>Pirimicarb-desmethyl</i>						<0.01
- <i>Pirimicarb-desmethyl-formamido</i>						<0.01

Table A7.3 continued. Pesticides analysed at **Silstrup** with the product used shown in parentheses. Degradation products are in italics. Precipitation (prec.) and percolation (perc.) are accumulated from date of first application until end of monitoring. 1st month perc. refers to accumulated percolation within the first month after application. C_{mean} refers to average leachate concentration in the drainage water within the first drainage season after application. (See Appendix 2 for calculation methods).

Crop and analysed pesticides	Application date	End of monitoring	Prec. (mm)	Perc. (mm)	1 st month perc. (mm)	C _{mean} (µg/L)
Winter rape 2006						
Propyzamide (Kerb 500 SC)	Nov 05	Apr 08	2345	1115	75	0.22 ⁴⁾
- <i>RH-24644</i>						0.01 ⁴⁾
- <i>RH-24580</i>						<0.01 ⁴⁾
- <i>RH-24655</i>						<0.01 ⁴⁾
Clopyralid (Matrigon)	Apr 06	Apr 08	2009	859	8	<0.01
Winter wheat 2007						
Chlormequat (Cycocel 750)	Apr 07	Jun 08	966	382	3	<0.01
Iodosulfuron-methyl (Hussar OD)	Apr 07	Oct 10	966	382	3	<0.01
Metsulfuron-methyl (Hussar OD)	Apr 07	Oct 10	966	382	3	<0.01
Epoxiconazole (Opus)	Jun 07	Apr 09	947	407	0	<0.01
Pendimethalin (Stomp Pentagon)	Sep 06	Apr 08	1166	508	0	0.04
Fodder beet 2008						
- <i>Fluazifop-P</i> (Fusilade Max)	Jul 08	Jun 12 [*]	985	494	21	<0.01
- <i>TFMP</i> (Fusilade Max)	Jul 08	Jun 12 [*]	985	494	21	0.24
Metamitron (Goliath)	May 08	Dec 10	969	498	4	0.01
- <i>Desamino-metamitron</i>	May 08	Dec 10	969	498	4	0.02
Triflurosulfuron-methyl (Safari)	May 08	Jun 10	969	498	4	<0.01
- <i>IN-D8526</i>	May 08	Jun 10	969	498	4	<0.01
- <i>IN-E7710</i>	May 08	Jun 10	969	498	4	<0.01
- <i>IN-M7222</i>	May 08	Jun 10	969	498	4	<0.02
Ethofumesate (Tramat 500 SC)	May 08	Dec 10	969	497	3	<0.01

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

Crop and analysed pesticides	Application date	End of monitoring	Prec. (mm)	Perc. (mm)	1 st month perc. (mm)	C _{mean} (µg/L)
Spring barley 2000						
Metsulfuron-methyl (Ally)	May 00	Apr 03	2990	1456	29	<0.01
- <i>triazinamin</i>						<0.02
Flamprop-M-isopropyl (Barnon Plus 3)	May 00	Apr 03	2914	1434	2	0.02
- <i>flamprop (free acid)</i>						0.01
Propiconazole (Tilt Top)	Jun 00	Apr 05	4938	2294	0	0.01
Fenpropimorph (Tilt Top)	Jun 00	Jul 02	2211	1048	0	<0.01
- <i>fenpropimorphic acid</i>						<0.02
Dimethoate (Perfekthion 500 S)	Jun 00	Jul 02	2211	1048	0	<0.01
Pea 2001						
Glyphosate (Roundup Bio)	Oct 00	Jul 14 [†]	10484	4977	123	0.54
- <i>AMPA</i>						0.17
Bentazone (Basagran 480)	May 01	Jul 08	7629	3621	9	0.03
- <i>AIBA</i>						<0.01
Pendimethalin (Stomp SC)	May 01	Jul 03	2208	1096	9	<0.01
Pirimicarb (Pirimor G)	Jun 01	Jul 05	4251	1995	10	0.01
- <i>pirimicarb-desmethyl</i>						<0.02
- <i>pirimicarb-desmethyl-formamido</i>						<0.02
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
- <i>4-chlor,2-methylphenol</i>						<0.01
Propiconazole (Tilt 250 EC)	May 02	Apr 05	2920	1336	39	0.02
Pirimicarb (Pirimor G)	Jun 02	Jul 05	2982	1403	58	0.01
- <i>pirimicarb-desmethyl</i>						<0.02
- <i>pirimicarb-desmethyl-formamido</i>		Apr 06				<0.02
Fodder beet 2003						
Glyphosate (Roundup Bio)	Sep 02	Jul 14	8289	3900	0	0.43
- <i>AMPA</i>						0.19
Ethofumesate (Betanal Optima)	May 03	Apr 06	2901	1371	50	0.11
Metamitron (Goltix WG)	May 03	Apr 06	2901	1371	50	1.1
- <i>metamitron-desamino</i>						0.21
Pirimicarb (Pirimor G)	Jul 03	Jul 05	2071	939	0	<0.01
- <i>pirimicarb-desmethyl</i>		Jul 05				<0.01
- <i>pirimicarb-desmethyl-formamido</i>		Apr 06				0.12
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
- <i>CyPM</i>						0.23
Maize 2005						
Terbuthylazine (Inter-Terbuthylazin)	May 05	Apr 09	4247	2042	32	0.48
- <i>desethyl-terbuthylazine</i>		Jul 09	4406	2051	32	0.31
- <i>2-hydroxy-terbuthylazine</i>		Jul 08	3338	1628	32	0.11
- <i>desisopropyl-atrazine</i>		Apr 09	4247	2042	32	0.02
- <i>2-hydroxy-desethyl-terbuthylazine</i>		Jul 08	3338	1628	32	0.24
Bentazone (Laddok TE)	Jun 05	Jul 08	3338	1628	10	0.18
- <i>AIBA</i>						<0.01
Glyphosate (Roundup Bio)	Nov 05	Jul 14	5191	2460	68	4.04 ¹⁾
- <i>AMPA</i>						0.42 ¹⁾
Spring barley 2006						
Florasulam (Primus)	Jun 06	Jul 08	2442	1163	0	<0.01
- <i>florasulam-desmethyl</i>						<0.03
Azoxystrobin (Amistar)	Jun 06	Jul 08	2414	1170	0	0.03
- <i>CyPM</i>						0.13

Table A7.4 continued. Pesticides analysed at **Estrup** with the product used shown in parentheses. Degradation products are in *italics*. Precipitation (prec.) and percolation (perc.) are accumulated from the date of first application until the end of monitoring. 1st month perc. refers to accumulated percolation within the first month after application. C_{mean} refers to average leachate concentration in the drainage water within the first drainage season after application. (See Appendix 2 for calculation methods).

Crop and analysed pesticides	Application date	End of monitoring	Prec. (mm)	Perc. (mm)	1 st month perc. (mm)	C _{mean} (µg/L)
Winter wheat 2007						
Mesosulfuron-methyl (Atlantis WG)	Oct 06	Jul 08	1420	305	29	0.01
- <i>Mesosulfuron</i>	Oct 06	Jul 08	1420	305	29	<0.02
Chlormequat (Cycocel 750)	Apr 07	Jul 08	1261	287	0	<0.01
Epoxiconazole (Opus)	May 07	Jul 08	1154	299	29	0.02

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

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

Crop and analysed pesticides	Application date	End of monitoring	Prec. (mm)	Perc. (mm)	1 st month perc. (mm)	C _{mean} (µg/L)
Winter wheat 1999						
Glyphosate (Roundup 2000)	Aug 99	Apr 03	2526	947	0	<0.01
- <i>AMPA</i>						<0.01
Bromoxynil (Briotril)	Oct 99	Apr 02	1738	751	35	<0.01
Ioxynil (Briotril)	Oct 99	Apr 02	1738	751	35	<0.01
Fluroxypyr (Starane 180)	Apr 00	Apr 02	1408	494	7	<0.01
Propiconazole (Tilt Top)	May 00	Jul 03	2151	669	0	<0.01
Fenpropimorph (Tilt Top)	May 00	Jul 02	1518	491	0	<0.01
- <i>fenpropimorphic acid</i>						<0.01
Pirimicarb (Pirimor G)	Jun 00	Jul 03	2066	684	0	<0.01
- <i>pirimicarb-desmethyl</i>						<0.01
- <i>pirimicarb-desmethyl-formamido</i>						<0.02
Sugar beet 2001						
Glyphosate (Roundup 2000)	Oct 00	Jul 03	1747	709	0	<0.01
- <i>AMPA</i>						0.01
Metamitron (Goltix WG)	May 01	Jul 03	1512	507	4	0.01
- <i>metamitron-desamino</i>						0.01
Ethofumesate (Betanal Optima)	May 01	Jul 03	1512	507	4	0.06
Desmedipham (Betanal Optima)	May 01	Jul 03	1512	507	4	<0.01
- <i>EHPC</i>						<0.02
Phenmedipham (Betanal Optima)	May 01	Jul 03	1512	507	4	<0.01
- <i>MHPC</i>						<0.02
Fluazifop-P-butyl (Fusilade X-tra)	Jun 01	Jul 03	1460	503	0	<0.01
- <i>fluazifop-P (free acid)</i>						0.02
Pirimicarb (Pirimor G)	Jul 01	Jul 03	1460	503	1	<0.01
- <i>pirimicarb-desmethyl</i>						<0.01
- <i>pirimicarb-desmethyl-formamido</i>						<0.02
Spring barley 2002						
Flamprop-M-isopropyl (Barnon Plus 3)	May 02	Jul 04	1337	333	0	<0.01
- <i>flamprop-M (free acid)</i>						<0.01
MCPA (Metaxon)	May 02	Jul 04	1358	337	4	<0.01
- <i>4-chlor-2-methylphenol</i>						<0.02
- <i>triazinamin-methyl¹⁾</i> (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
- <i>FM65317 (propanamide-clomazon)</i>						<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
- <i>4-chlor,2-methylphenol</i>						<0.01
Azoxystrobin (Amistar)	Jun 04	Jul 07	2098	636	0	<0.01
- <i>CyPM</i>						<0.01
Maize 2005						
Terbuthylazine (Inter-Terbutylazin)	May 05	Jul 08	2078	666	4	0.67
- <i>desethyl-terbuthylazine</i>	May 05	Jul 08	2078	666		0.59
- <i>2-hydroxy-terbuthylazine</i>	May 05	Jul 08	2078	666		0.04
- <i>desisopropyl-atrazine</i>	May 05	Jul 08	2078	666		0.03
- <i>2- hydroxy-desethyl-terbuthylazine</i>	May 05	Jul 07	1428	465	4	0.07
Bentazone (Laddok TE)	May 05	Jul 07	1408	464	6	2.82
- <i>AIBA</i>						<0.01
Spring barley 2006						
Fluroxypyr (Starane 180 S)	May 06	Jul 08	1496	524	17	<0.02
Epoxiconazole (Opus)	Jun 06	Jul 08	1441	507	3	<0.01

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

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

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

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) installed 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 Rotamole™, 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, respectively.

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 ($^3\text{H}/^3\text{He}$), 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 Jynde vad and Tylstrup.

The other sites were discounted because 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 Jynde vad 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 Jynde vad 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
Jynde vad	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 analysed according to Sültenfuß et al. (2009). The age of water was determined from the ratio between tritium (^3H), half-life 12.5 yr., and its daughter product helium-3 (^3He) 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.

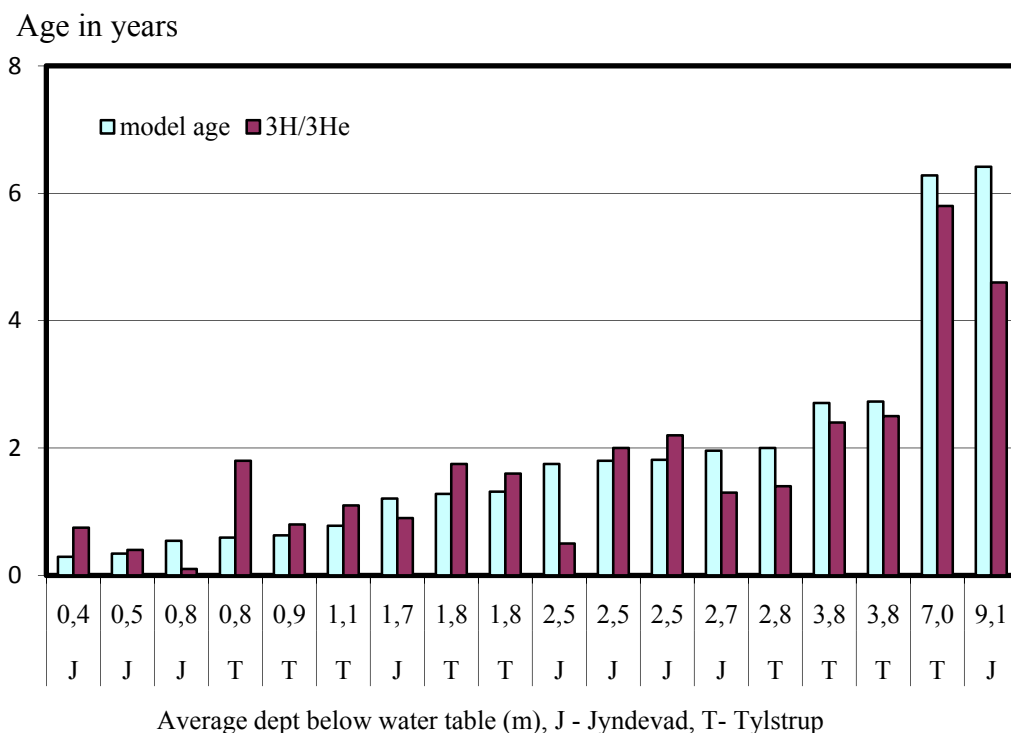


Figure A9.1. Groundwater age at Jynde vad and Tylstrup. Recharge model age assumes water velocity of 1.4 m/yr, except for the Tylstrup deep filter (1.1 m/yr).

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 consistent.