The Danish Pesticide Leaching Assessment Programme

Monitoring results May 1999–June 2016

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Preface

In 1998, the Danish Parliament initiated the Danish Pesticide Leaching Assessment Programme (PLAP), which is 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. Additionally, funding for establishing a new test field (with a basal till overlaying chalk) designated to be included in the monitoring programme for 2016-2018 was provided in the Danish National Budget for the fiscal year of 2015. The establishment of said new test field was, however, delayed and not initiated until the autumn of 2016. Therefore, the present report does not include any data from this field. A separate report with the title "Characterization and monitoring design of the Lund PLAP-field" will, however, be published during autumn 2017. In April 2017, PLAP received founding until 2021 via the Pesticide Strategy 2017-2021 set by the Danish Government.

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) at Aarhus University, under the direction of a management group comprising Annette E. Rosenbom (GEUS), Preben Olsen (AGRO), Nora Badawi (GEUS), Eline Bojsen Haarder (GEUS), Lis Wollesen de Jonge (AGRO), Carsten B. Nielsen (BIOS), Steen Marcher (Danish EPA) and Anne Louise Gimsing (Danish EPA).

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This report presents the results for the period May 1999–June 2016. Results including part of the period May 1999–June 2015 have been reported previously (Kjær *et al.*, 2002, Kjær *et al.*, 2003, Kjær *et al.*, 2004, Kjær *et al.*, 2005c, Kjær *et al.*, 2006, Kjær *et al.*, 2007, Kjær *et al.*, 2008, Kjær *et al.*, 2009, Rosenbom *et al.*, 2010b, Kjær *et al.*, 2011, Brüsch *et al.*, 2013a, Brüsch *et al.*, 2013b, Brüsch *et al.*, 2015, Brüsch *et al.*, 2016, Rosenbom *et al.*, 2016). 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 2014-2016.

The report was prepared jointly by Annette E. Rosenbom (GEUS), Eline Bojsen Haarder (GEUS), Nora Badawi (GEUS), Frants von Platten-Hallermund (GEUS), Lasse Gudmundsson (GEUS), Carl H. Hansen (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: Annette E. Rosenbom, Eline Bojsen Haarder and Preben Olsen.
- Agricultural management: Preben Olsen.
- Soil water dynamics and water balances: Annette E. Rosenbom, Finn Plauborg, Eline Bojsen Haarder and Carsten B. Nielsen.
- Pesticide analysis quality assurance: Nora Badawi.

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Annette E. Rosenbom
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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 and/or their degradation products (metabolites) 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.

Compared to earlier PLAP-reports, this report presents the results of the monitoring period July 2014–June 2016 comprising 9921 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 15 pesticides and 28 degradation products after applying the maximum allowed dose of the specific pesticide in connection with a specific crop. The 43 compounds include 12 compounds not evaluated in PLAP previously (marked in red in Table 0.1).

Highlights from the monitoring period July 2014–June 2016:

- **The degradation product of many triazole fungicides, 1,2,4-triazole, is still being detected in groundwater in concentrations above 0.1 µg L^{-1}**
  With indications of 1,2,4-triazole being a threat to the quality of groundwater, the Danish EPA enforced restrictions in 2014 on the use of certain fungicides found to be a source for 1,2,4-triazole in the terrestric environment. Additionally, leaching of the degradation product 1,2,4-triazole was evaluated in PLAP in connection with the use of tebuconazole against fungi in cereals in 2014 on the two sandy fields Tylstrup and Jyndevad and the two clayey till fields Estrup and Faardrup. The results show that 1,2,4-triazole can leach to the groundwater and at Estrup in concentrations of up to 0.26 µg L^{-1}. 38 groundwater samples out of 590 had a 1,2,4-triazole concentration exceeding 0.1 µg L^{-1} (Table 0.1). A general decreasing level of concentration with depth in the groundwater zone indicated a surface near source. With the exception of Faardrup, 1,2,4-triazole was detected in groundwater samples before the spraying with tebuconazole took place. At Estrup some background concentrations were above the regulatory limit of 0.1 µg L^{-1}. Therefore it is not possible to fully relate the detections in the groundwater to the specific application of tebuconazole at the two sandy fields and at Estrup, since the measurements may be influenced by other sources such as prior use of other fungicides or seed dressing. To evaluate the leaching of 1,2,4-triazole, as a result of the application of other parent fungicides, the following fungicides were applied at Jyndevad: i) epoxiconazole to winter wheat in May 2015 ii) prothioconazole to winter wheat in June 2015 and iii) propiconazole in spring barley undersown with clovergrass. At Tylstrup the applications were: i) prothioconazole to winter wheat in May 2015 and ii) prothioconazole to winter wheat in June 2015. At Faardup the applications were: i) prothioconazol to winter wheat in May 2015 and ii) propiconazol to spring barley in June 2016. The 2014-restrictions was not enforced on the use of prothioconazole because prothioconazol only forms minor amounts of 1,2,4-triazole in soil according to the

EFSA (2007) Conclusion on the peer review of prothioconazole. Prothioconazole is tested in PLAP to confirm that 1,2,4-triazole is not formed by degradation of prothioconazole. Following the epoxiconazole and prothioconazole application in 2015, an increase in the concentration of 1,2,4-triazole in water collected from 1 m depth and groundwater monitoring wells was detected. At Faardrup only one detection (0.01 µg/L) was found following the period September 2015 to May 2016 during which monitoring was temporarily stopped due to analysis expenses. At Jyndevad the applications in 2015 resulted in a concentration level at 1 m depth exceeding 0.1 µg L^{-1} (Figure 3.8). The outcome reveals that 1,2,4-triazole is present in the variably saturated zone (1 m depth) at both of the sandy fields but also at the two clayey till fields.

- **Repeated application of azoxystrobin cause increase in CyPM detections exceeding 0.1 µg L^{-1} in the groundwater**
  CyPM is a degradation product of azoxystrobin, which is used against fungi. In the period June 2004 – June 2014 azoxystrobin was applied five times at Silstrup and six times at Estrup. At both fields groundwater samples collected following each application have revealed a concentration pulse of CyPM moving into the groundwater increasing in both maximum concentration and duration after each application. Detections in water samples taken from a horisontal well installed in 2 m depth, which became operational at both fields in early 2012, underlines this pattern. Possible underlying relationships to these findings are under evaluation in PLAP.

- **Flupyrsulfuron-methyl and three of its degradation products have not been detected in the groundwater**
  Flupyrsulfuron-methyl was applied to winter wheat at Jyndevad (October 2014 and March 2015) and Faardrup (November 2014 and April 2015). Following these applications, flupyrsulfuron-methyl and its three degradation products IN-JV460, IN-KC576 and IN-KY374 were included in the monitoring programme. None of the compounds were detected in the groundwater. Only IN-KY374 was detected in the variably-saturated zone at Jyndevad in four samples.

- **Snowmelt once again caused detection of glyphosate exceeding 0.1 µg L^{-1} in the groundwater**
  As in the beginning of 2013, snowmelt at Estrup seems to cause one detection of glyphosate exceeding 0.1 µg L^{-1} in the groundwater in March 2016, i.e. more than two years after application. Also, heavy rain events in August-September 2015 triggered a detection in the groundwater of 0.09 µg L^{-1}. Even though such events trigger detections of high concentrations in the groundwater and the fact that glyphosate and its degradation product AMPA have been detected in relatively high concentrations through the variably-saturated zone, the two compounds still do not seem to pose a constant threat to the quality of the groundwater.

- **A split application of mesotrione triggers short-term leaching resulting in a mesotrione detection exceeding 0.1 µg L^{-1} in the groundwater**
  The herbicide mesotrione was applied in maize two-fold in May-June 2015 at Estrup and in June 2015 at Silstrup. These two applications triggered more or less immediate detections of high concentrations of both mesotrione and its degradation product MNBA in drainage (1 m depth). The application at Estrup

further resulted in mesotrione and MNBA being detected in groundwater 11 days after the second application with water from 3.5 m depth having a mesotrione concentration above 0.1 µg L^{-1}. In all there were three detections of mesotrione in groundwater.

- **Long-term leaching of the degradation product CGA 108906 generates further assessment in the National Groundwater Monitoring (GRUMO) and the Waterworks Drilling Control**
  CGA 108906 is a degradation product of metalaxyl-M, which was used against fungus (blight) in potatoes in 2010 on the two sandy PLAP-fields. CGA 108906 is still being detected in groundwater samples from these fields in concentrations up to 0.34 µg L^{-1} (Table 0.1). Metalaxyl-M and its two degradation products CGA 62826 and CGA 108906 were included in PLAP because the EU-admission directive for metalaxyl-M from 2002 presented material revealing pronounced leaching of the two degradation products. At the national approval of metalaxyl-M in Denmark in 2007 the Danish EPA was aware of the degradation products and asked for test in potatoes in PLAP as soon as possible with regard to the planned crop rotation. After the first years of detections in PLAP, metalaxyl-M was banned in Denmark in December 2013 and was recently included in the revised analysis program of the National Groundwater Monitoring and for drinking water wells in the Waterworks Drilling Control. In the latter, CGA 108906 is already the second-most frequently detected compound. Results from PLAP were also sent to EFSA in connection with the re-evaluation of metalaxyl-M in EU.

- **Initial results indicate no leaching of three degradation products of bentazone through sandy soils**
  The degradation products of bentazone, 6-hydroxy-bentazone, 8-hydroxy-bentazone and N-methyl-bentazone were included in the monitoring programme at the two sandy fields Tylstrup and Jyndevad following the application of bentazone to spring barley in May 2016. None of the compounds have yet been detected even though bentazone has leached in high concentrations to 1 m depth within two months after earlier applications at Jyndevad. Bentazone has, however, never been detected in concentrations exceeding 0.1 µg L^{-1} in any groundwater samples from the two sandy soils. Results after a full two-year monitoring period will reveal, whether the degradation products appear at 1 m depth and groundwater in the longer term.

Throughout the monitoring period (1999-2016) 115 pesticides and/or degradation products (51 pesticides and 64 degradation products) have been analysed in the PLAP, which comprises five fields (1.2 to 2.4 ha) grown with different agricultural crops. The 64 degradation products originate from 37 pesticides of which three have not themselves been analysed in PLAP (fludioxonil, mancozeb and tribenuron-methyl). Of the 54 pesticides (51+3), 17 resulted in detections of the pesticide or its degradation product in groundwater samples in concentrations exceeding 0.1 µg L^{-1}. 16 of these 17 pesticides resulted in detections of the pesticide and/or its degradation product(s) in samples from 1 m depth (from drains or suction cups) exceeding 0.1 µg L^{-1}. Only 4 of the 17 pesticides resulted in detections indicating a relatively high long-term leaching risk through sandy soils (metalaxyl-M, metribuzin, rimsulfuron and tebuconazole), whereas 11 others plus tebuconazole revealed a certain leaching risk through fractured clayey tills (azoxystrobin, bentazone, bifenox, ethofumesate, fluazifop-P-butyl, glyphosate, mesotrione, metamitron, propyzamide, pyridate, terbuthylazine). Here it should be emphasised that 1,2,4-triazol causing the presented leaching risk for tebuconazole at both sandy soils and fractured clayey tills can be the outcome of other applied fungicides and seed dressing. This is evaluted further in PLAP and a 1,2,4-triazol screening is initiated in Danish National Groundwater Monitoring Programme (GRUMO). The following 11 pesticides did not result in any detection in water samples collected from the variably-saturated zone (via drains and suction cups) or saturated zone (via groundwater well screens situated at 1.5-4.5 m depth): Aclonifen, boscalid, chlormequat, cyazofamid, florasulam, iodosulfuron-methyl, linuron, metsulfuron-methyl, thiacloprid, thiamethoxam and tribenuron-methyl. Additionally, 12 pesticides resulted in detections in water samples from 1 m depth (drains or suction cups) in yearly average concentrations not exceeding 0.1 µg L^{-1} and from groundwater but in lower concentrations.

Table 0.1 ***(Same as Table 8.5)*** 15 pesticides and 28 *degradation products* have been analysed in PLAP in the period July 2014-June 2016 of which 12 compounds have not been evaluated in PLAP before (in red). The number of water samples analysed collected from the Variably-saturated Zone (VZ; drains and suction cups), Saturated Zone (SZ; groundwater screens) and irrigated water (Irrigation) are presented together with the results of analysis on samples from VZ and SZ given as number of detections (Det.), detections >0.1 µg L^{-1} and maximum concentration (Max conc). For water used for irrigation, the detected concentration in µg L^{-1} is presented in brackets. (-) indicate no detections.

Pesticide	Analyte	Number of samples from:			Results of analysis					
					VZ			SZ		
		VZ	SZ	Irrigation	Det.	>0.1 µg L^{-1}	Max conc.	Det.	>0.1 µg L^{-1}	Max conc.
Aminopyralid	Aminopyralid	54	103	1 (0.05)	0	0	-	2	0	0.06
Azoxystrobin	Azoxystrobin	129	290		25	1	0.11	7	0	0.03
	CyPM	129	290		123	32	1.00	69	13	**0.52**
Bentazone	Bentazone	118	219	3 (0.01;-;-)	39	0	0.06	14	0	0.02
	6-hydroxy-bentazone	10	53	2(-)	0	0	-	0	0	-
	8-hydroxy-bentazone	10	53	2(-)	0	0	-	0	0	-
	N-methyl-bentazone	10	53	2(-)	0	0	-	0	0	-
Bromoxynil	Bromoxynil	24	70		0	0	-	0	0	-
Clomazone	Clomazone	45	118	1 (-)	0	0	-	0	0	-
	FMC 65317	45	118	1 (-)	0	0	-	0	0	-
Diflufenican	Diflufenican	52	100		6	0	0.02	0	0	-
	AE-05422291	52	100		0	0	-	0	0	-
	AE-B107137	50	109		4	0	0.03	2	0	0.03
Fluazifop-P-buthyl	*TFMP*	39	124		0	0	-	0	0	-
Fludioxonil	*CGA 192155*	88	366	4 (-)	0	0	-	1	0	0.05
	CGA 339833	88	355	4 (-)	0	0	-	1	1	**0.37**
Flupyrsulfuron-methyl	**Flupyrsulfuron-methyl**	58	345	2 (-)	0	0	-	0	0	-
	IN-JV460	58	345	2 (-)	0	0	-	0	0	-
	IN-KC576	58	345	2 (-)	0	0	-	0	0	-
	IN-KY374	58	345	2 (-)	4	3	0.45	0	0	-
Foramsulfuron	**Foramsulfuron**	70	174		23	2	0.32	4	0	0.04
	AE-F092944	70	174		1	0	0.01	0	0	-
	AE-F130619	70	174		9	0	0.02	7	0	0.03
Glyphosat	Glyphosate	134	273		48	5	0.32	21	1	**0.13**
	AMPA	134	273		114	10	0.21	16	0	0.06
Ioxynil	Ioxynil	24	70		0	0	-	0	0	-
Mancozeb	*EBIS*	30	152	2 (-)	0	0	-	0	0	-
Mesotrione	Mesotrione	89	267	1 (-)	34	13	3.30	3	1	**0.13**
	AMBA	89	267	1 (-)	4	0	0.04	0	0	-
	MNBA	89	265	1 (-)	13	1	0.46	1	0	0.02
Metalaxyl-M	Metalaxyl-M	44	152	2 (-)	0	0	-	30	1	**0.11**
	CGA 108906	43	152	2 (0.029;-)	21	2	0.20	98	9	**0.34**
	CGA 62826	43	152	2 (0.071;-)	8	0	0.03	44	1	**0.15**
Metrafenone	Metrafenone	43	84		0	0	-	0	0	-
Propyzamid	Propyzamide	15	54		0	0	-	0	0	-
	RH-24580	15	54		0	0	-	0	0	-
	RH-24644	15	54		0	0	-	0	0	-
	RH-24655	15	54		0	0	-	0	0	-
Prosulfocarb	Prosulfocarb	27	65	1 (-)	0	0	-	0	0	-
Tebuconazole 2014 Epoxiconazole 2015 Prothioconazole 2015	*1,2,4-triazole*	195	590	4 (-)	130	78	0.45	278	38	**0.26**
Fluroxypyr	***Fluroxypyr-methoxypyridine***	1	16		0	0	-	0	0	-
	Fluroxypyr-pyridinol	1	16		0	0	-	0	0	-
Triasulfuron	*Triazinamin*	3	16		0	0	-	0	0	-
Sub total	43-45 (15-17 Pesticides; 28 *Degradation products*)	2434	7449	38	**606**	**147**		**598**	**65**	
Percent		25%	75%	0.4%	**25%**	**6%**		**8%**	**1%**	
Total			**9921**							

The results of the PLAP-monitoring in the period May 1999–June 2016 have contributed to the regulatory work in different manners, some of which are summarized in the following examples:

- **Clayey till soils are more vulnerable to leaching compared to sandy soils**
  Both the number of detections at 1 m depth (water from suction cups and drainage) and in groundwater reveal that more pesticides and/or their degradation products leach through the clayey till than through the sandy soils, which makes them

generally more vulnerable to leaching. Long-term leaching of degradation products in high concentrations is detected at the sandy fields, whereas both pesticides and their degradation products are found to leach more dynamicly/momentarily through the clayey till fields due to the presence of biopores and fractures. The aim of including the new clayey till field overlaying chalk (Lund) in PLAP is to contribute to an improved understanding of the vulnerability of clayey tills and hereby improve the early warning in relation to leaching through these.

- **Degradation products can leach in concentrations exceeding 0.1 µg L^{-1} in up to five years after application**
  PLAP results indicate that the pesticide metribuzin applied to potatoes is retarded in the plough layer and then very slowly released and degraded to diketo-metribuzin. This compound leaches over a long period to the groundwater, and is detected in concentrations exceeding 0.1 µg L^{-1} for up to five years after application. This type of long-term leaching is not possible to capture with the current description of sorption incorporated in models, but the conservative Danish approach to modelling assures that compounds with a high leaching risk are banned. New guidance on how to more accurately describe this type of sorption will soon be available.

- **Pesticide degradates like TFMP, often more soluble than the pesticide, have a relatively high leaching potential especially associated with heavy precipitation events shortly after application**
  After four applications of fluazifop-P-butyl, where the dose for the two latter was reduced by regulation, the weather within the first week after application was imperative for the numbers of detections of TFMP. To be able to assess the risk of leaching it is therefore important to make use of updated and relevant climate data in regulatory models. Denmark is working to improve this in the EU. Today data from the period 1961-1990 is applied as standard climatic conditions for EU including Denmark.

- **The very toxic degradation product nitrofen can be formed in soil after application of bifenox**
  Detections of nitrofen in water from drainage resulted in the Danish EPA announcing bifenox to be banned in Denmark. The manufacturer immediately removed bifenox from the Danish market before the ban was finally issued in Denmark.

- **The degradation potential in the plough layer is crucial for the leaching risk of pesticides and their degradation products**
  An example of this is MCPA, which does not leach to the groundwater because of significant microbiological degradation in the plough layer. MCPA was only detected once; in a groundwater sample collected shortly after a significant rain event.

Results covering the period May 1999–June 2015 have been reported previously (Kjær *et al.*, 2002, Kjær *et al.*, 2003, Kjær *et al.*, 2004, Kjær *et al.*, 2005c, Kjær *et al.*, 2007, Kjær *et al.*, 2008, Kjær *et al.*, 2009, Rosenbom *et al.*, 2010b, Kjær *et al.*, 2011, and Brüsch *et al.*, 2013a, Brüsch *et al.*, 2013b, Brüsch *et al.*, 2014, Brüsch *et al.*, 2015, Brüsch *et al.*, 2016, Rosenbom *et al.*, 2016). 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 July 2014-June 2016. All reports and associated peer-reviewed articles can be found at: www.pesticidvarsling.dk.

1 Introduction

In Denmark, untreated groundwater is used as drinking water. As Denmark is intensively cultivated, there is a public concern about pesticides and their degradation products being increasingly detected in groundwater during the past decades. Since 1989 this has initiated monitoring programmes reporting on the quality of the Danish groundwater (the Danish National Groundwater Monitoring Programme; GRUMO; Thorling *et al.*, 2015) and the effect of agricultural practices (Pesticide Leaching Assessment Programme, PLAP). The reported results have and are still continuesly adressed in the regulation of pesticides. GRUMO results seem to indicate that this combined effort has reduced the detection frequence of pesticides and/or their degradation products in the groundwater collected from depth of up to 20 m.

The detection of pesticides in groundwater over the past three decades has fuelled the need for 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 clayey till 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 present in Denmark (Kördel, 1997; Jacobsen and 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, Annexe VI (Council Directive 97/57/EC of 22 September 1997) enables field leaching study results to be included in the risk assessments.

1.1 Objective

In 1998, the Danish Government initiated the Pesticide Leaching Assessment Programme (PLAP), an intensive monitoring programme with the purpose of evaluating the leaching risk of pesticides under field conditions. The PLAP is intended to serve as an early warning system providing decision-makers with advance warning if otherwise approved pesticides leach in unacceptable concentrations. The programme focuses on pesticides used in arable farming and PLAP monitors leaching at five agricultural test fields representative of Danish conditions. To increase this representability a new clayey till field will be included in PLAP from 2017.

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 to the groundwater at levels exceeding the maximum allowable concentration of 0.1 µg L^{-1}.

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 64 degradation products have been included in the PLAP. All the compounds analysed since 1999 are listed in Appendix 1.

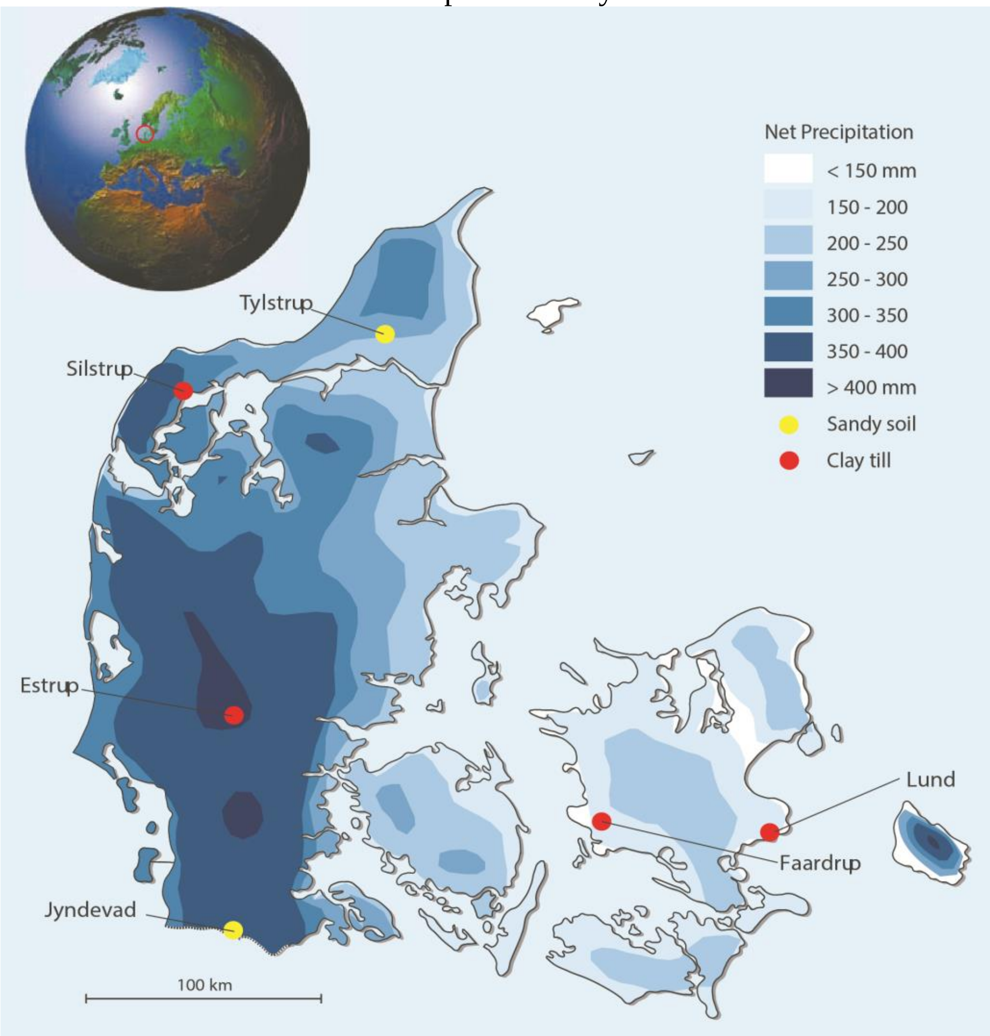

Figure 1.1. Annual net precipitation across Denmark (http://www2.mst.dk/Udgiv/publikationer/1992/87-503-9581-5/pdf/87-503-9581-5.pdf in Danish) and the geographical location of the five PLAP fields: **Tylstrup** (sandy), **Jyndevad** (sandy), **Silstrup** (clayey till), **Estrup** (clayey till) and **Faardrup** (clayey till) included in the monitoring programme of 1999-2016 and the new PLAP field **Lund** (clayey till) to be included in PLAP from July 2017. It can be seen that the span in net precipitation observed in Denmark is well represented by the PLAP fields.

Soil type and climatic conditions are considered to be some of the most important parameters controlling pesticide leaching. Today, the PLAP encompasses five fields that are representative of the dominant soil types and the climatic conditions in Denmark (Figure 1.1). 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 done in accordance with conventional agricultural practice in the area. The pesticides are applied at maximum permitted doses and in the manner specified in the regulations. Thus, any pesticides or degradation products appearing in the groundwater downstream of the fields can be related to the current approval conditions and use pertaining to the individual pesticides.

Results and data in the present report stem from the five test fields that 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). The sixth PLAP field at Lund has recently been established and monitoring initiated from July 2017 (not included in this report).

Table 1.1. Characteristics of the five PLAP fields included in the PLAP-monitoring for the period 1999-2016 (modified from Lindhardt *et al.*, 2001).

	Tylstrup	**Jyndevad**	**Silstrup**	**Estrup**	**Faardrup**
Location	Brønderslev	Tinglev	Thisted	Askov	Slagelse
Precipitation[1)] (mm y^{-1})	668	858	866	862	558
Pot. evapotransp.[1)] (mm y^{-1})	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)	1.2	2.4	1.7	1.3	2.3
Tile drain	No	No	Yes	Yes	Yes
Depths to tile drain (m)			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)	6	5–9	1.3	1–4[2)]	1.5
– Depth to the reduced matrix (m)	>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})	–	–	<1	11	4
– Ks in C horizon (m s^{-1})	$2.0 \cdot 10^{-5}$	$1.3 \cdot 10^{-4}$	$3.4 \cdot 10^{-6}$	$8.0 \cdot 10^{-8}$	$7.2 \cdot 10^{-6}$
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.

Field 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 2016, but the main focus of this report is on the leaching risk of pesticides applied during July 2014–June 2016. For a detailed description of the earlier part of the monitoring periods (May 1999–June 2015), 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 period 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 2016. The five field models have been calibrated for the monitoring period May 1999–June 2004 and validated for the monitoring period July 2004–June 2016.

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 Field 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 at Tylstrup 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.

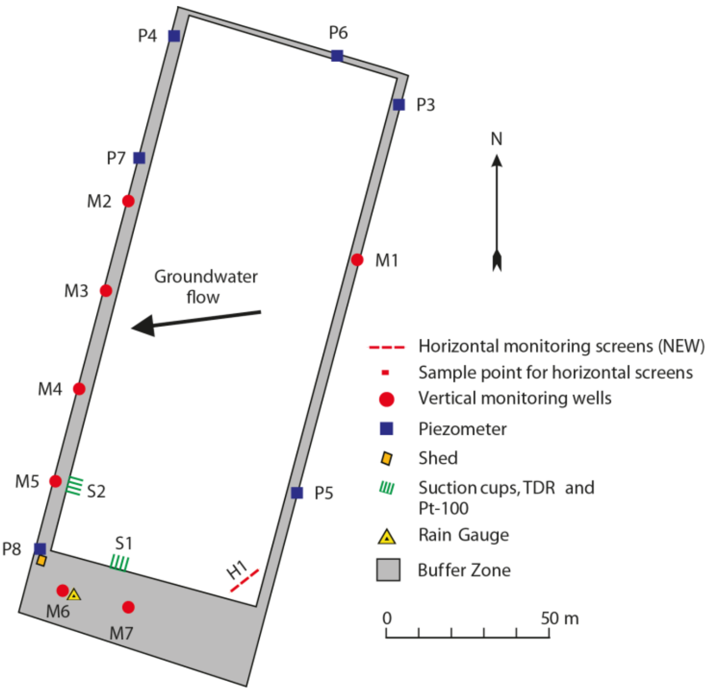

Figure 2.1. Overview of the **Tylstrup** field. The innermost white area indicates the cultivated land, while the grey area indicates the surrounding buffer zone. The positions of the various installations are indicated, as is the direction of groundwater flow (arrow). Pesticide monitoring is conducted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

2.1.2 Agricultural management

Management practice during the 2015-16 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/monitor_uk/index.html.

Liming of the field was done 15 September 2014 using 4 t ha^{-1} of lime. Having been disk harrowed and stubble cultivated the field was sown with winter wheat 22 September (cv. Mariboss). The wheat emerged 2 October 2014, and was sprayed with the herbicide flupyrsulfuron on 30 October 2014 and the fungicide tebuconazole on 14 November 2014. Spraying with flupyrsulfuron was repeated on 9 April 2015. Only the degradation product 1,2,4-triazole from tebuconazole was included in the monitoring. On 14 May 2015 fluroxypyr and florasulam were used against weeds and prothioconazole against fungi. These substances were not monitored as parent compounds, but prothioconazole may degrade to 1,2,4-triazole, which was already monitored. A last application of prothioconazole was done 12 June 2015.

The winter wheat was irrigated once applying 26 mm on 21 July 2015. A catch crop of oil seed rape (cv. Akiro) was broad sown simultaneously with an application of glyphosate (not monitored) against weeds on 20 August. The winter wheat was harvested 8 September yielding 74.0 hkg ha^{-1} of grain (85 % dry matter) and 46.4 hkg ha^{-1} of straw (100% dry mater) was removed on 10 September.

The field was ploughed on 22 March 2016. A crop of spring barley (cv. Evergreen) was sown 15 April 2016 and on 21 April 2016 a catch crop of clover grass mixture (AgrowGrass 350 MidiMaize). On 1 May, the spring barley emerged. The field was sprayed on 19 May 2016 with the herbicide bentazone. Bentazone and its three degradation products N-methyl bentazone, 8-hydroxy-bentazone and 6-hydroxy-bentazone were included in the monitoring. The field was irrigated 27 mm on 9 June 2016.

2.1.3 Model setup and calibration

The numerical model MACRO (version 5.2 Larsbo *et al.*, 2005) was applied to the Tylstrup field with a model domain 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 2016 and to establish an annual water balance.

Compared to Rosenbom *et al.* (2016), one additional year of “validation” was added to the MACRO-setup for the Tylstrup field. The setup was therefore calibrated for the monitoring period May 1999-June 2004 and “validated” for the monitoring period July 2004-June 2016.

Daily time series of 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 (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).

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 simulated successfully except for the summer period of 2014. Here the model was not able to capture the drop in soil water at all depths (Figure 2.2B-E). During the last eight hydraulic years, excluding spring 2013, the level of water saturation at 25 cm b.g.s. was overestimated and the initial decrease in water saturation observed during the summer periods at 25, 60 and 110 cm b.g.s. was less well captured.

The dynamics of the groundwater table were to some extent captured even though the groundwater table declined approx. 0.5 m in the summer period 2014 without it being captured by the model (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 2015–June 2016, precipitation and the actual evapotranspiration were in the high end of the range observed, since the monitoring began at the field and also compared to the normal value. This results in the groundwater recharge/percolation and level also being high compared to the other hydraulic years (Figure 2.2A-B). The monthly precipitation pattern for the hydraulic year 2015-2016 was medium to high compared to earlier years, though precipitation in October 2015 was very low compared to earlier years and normal values.

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).

Period	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	1073	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	1147	59	591	615
01.07.07–30.06.08	773	913	126	572	467
01.07.08–30.06.09	773	1269	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
01.07.14–30.06.15	773	1064	78	562	581
01.07.15-30.06.16	773	1093	53	502	644

[1)] Accumulated for a two-month period. [2)] Normal values based on time series for 1961–1990.

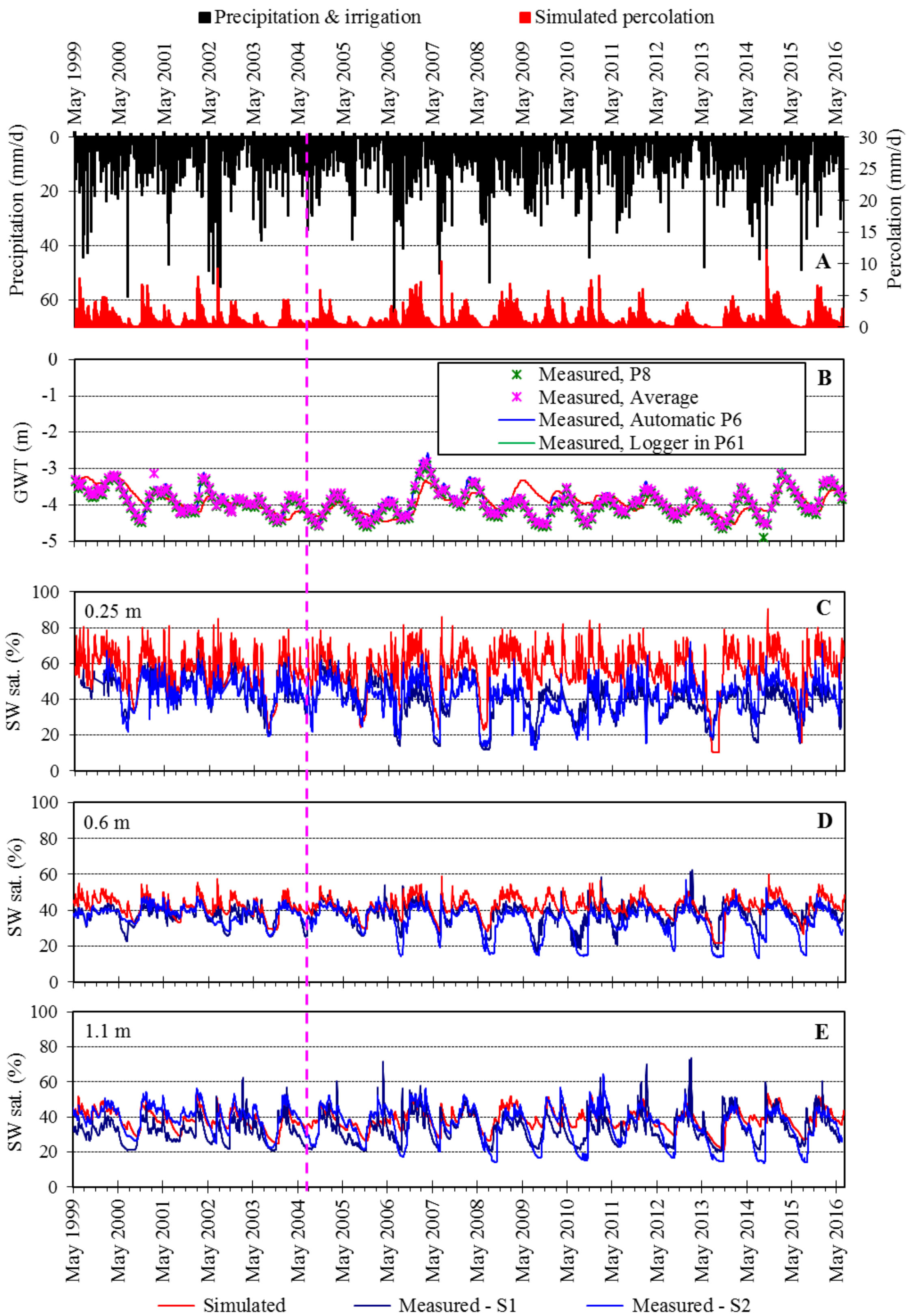

Figure 2.2. Soil water dynamics at **Tylstrup**: Measured precipitation, irrigation and simulated percolation 1 m b.g.s. (A), simulated and measured groundwater table GWT (B), and simulated and measured soil water saturation (SW sat.) at three different soil depths (C, D and E). The measured data in 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 2016).

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, M5 (Figure 2.4) and H1 (Figure 2.5). Bromide is detected at monitoring well M4 within the first year after application, whereas the bulk tracer arrives at M1, M3 and M5 after more than 2 years.

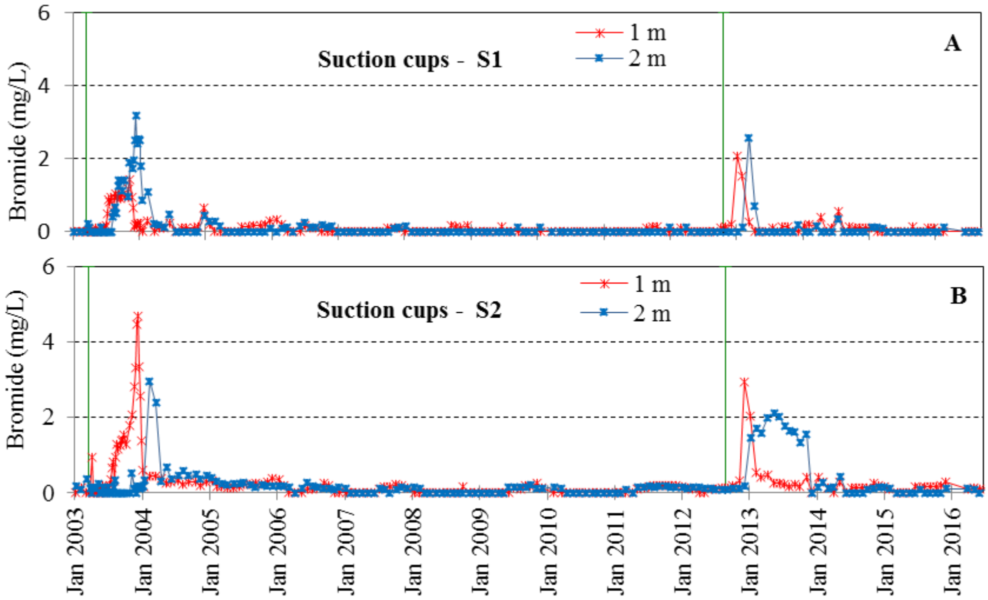

Figure 2.3. Measured bromide concentration in the variably-saturated zone at **Tylstrup**. The measured data derive from suction cups installed 1 m b.g.s. and 2 m b.g.s. at locations S1 (A) and S2 (B) indicated in Figure 2.1. The green vertical lines indicate the dates of bromide applications.

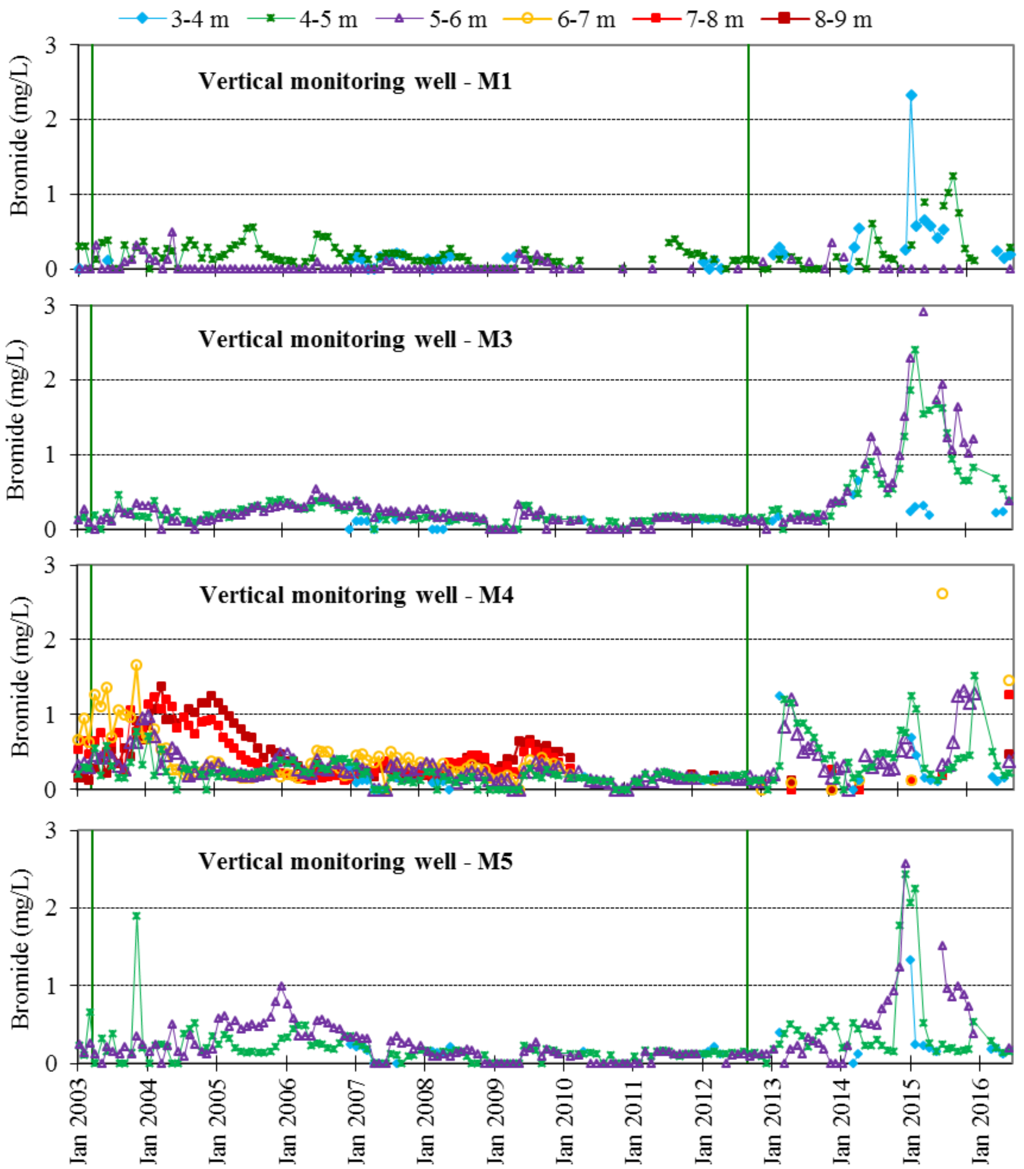

Figure 2.4. Bromide concentration in the groundwater at **Tylstrup.** The data derive from monitoring wells M1 and M3–M5. Screen depth is indicated in m b.g.s. The green vertical lines indicate the dates of bromide application.

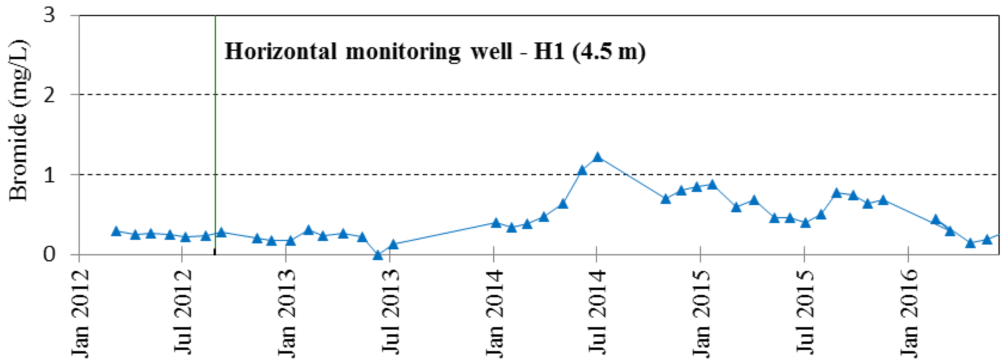

Figure 2.5. Bromide concentration in the groundwater at **Tylstrup.** Data derives from the horizontal monitoring well H1. The green vertical line indicate the date of bromide application.

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 2016 are not evaluated in this report and they are not included in Figure 2.6, but such compounds are nevertheless listed in Table 2.2.

The present report primarily focuses on the pesticides applied from 2014 and onwards, while the leaching risk of pesticides applied before 2014 has been evaluated in previous monitoring reports (see http://pesticidvarsling.dk/publ_result/index.html).

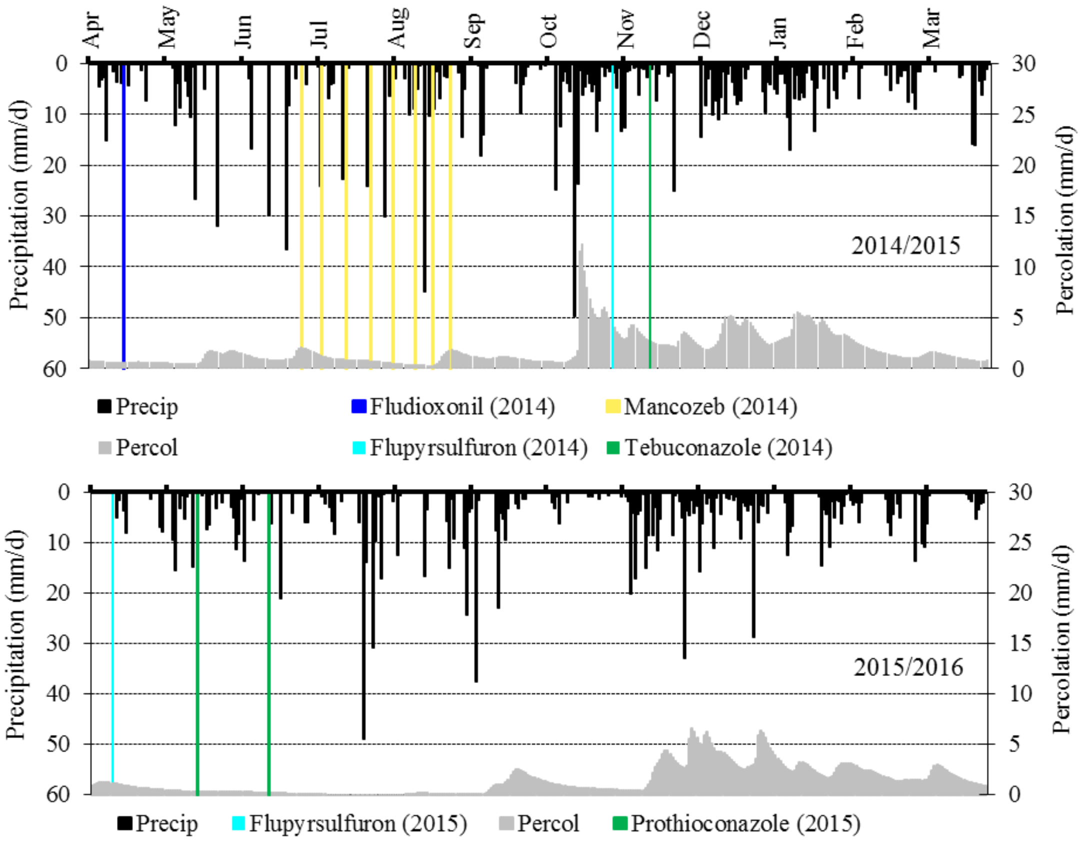

Figure 2.6. Application of pesticides included in the monitoring programme, precipitation and irrigation (primary axis) together with simulated percolation 1 m b.g.s. (secondary axis) at **Tylstrup** in 2014/2015 (upper) and 2015/2016 (lower).

Table 2.2. Pesticides analysed at **Tylstrup**. For each pesticide (P) and degradation product (M) the application date (appl. date) as well as end of monitoring period (End mon.) is listed. Precipitation and percolation 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 [µg L^{-1}] at 1 m b.g.s. the first year after application. See Appendix 2 for calculation method and Appendix 8 (Table A8.1) for previous applications of pesticides.

Crop	Applied product	Analysed pesticide	Appl. date	End mon.	Y 1st precip.	Y 1st percol.	M 1st precip.	M 1st percol.	C_{mean}
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	Mar 15	934	514	127	43	<0.01
		CGA 108906(M)	Jul 10	Mar 15	934	514	127	43	0.03-0.12**
		CGA 62826(M)	Jul 10	Mar 15	934	514	127	43	<0.01-0.02**
Spring barley 2011	Bell	Boscalid(P)	Jun 11	Dec 12	959	467	106	20	<0.01
Spring barley 2012	Fox 480 SC	Bifenox(P)	May 12	Dec 12	803	338	100	23	<0.02
		Bifenox acid(M)	May 12	Dec12	803	338	100	23	<0.05
		Nitrofen(M)	May 12	Dec12	803	338	100	23	<0.01
	Mustang forte	Aminopyralid(P)	May 12	Apr 15	852	335	121	22	<0.02
Winter rye 2012	Boxer	Prosulfocarb(P)	Oct 12	Mar 15	507	285	79	49	<0.01
Potatoes 2014	Maxim 100 FS Fludioxonil(P)	CGA 339833(M)	Apr 14	Mar 16	1178	699	86	17	<0.03
		CGA 192155(M)	Apr 14	Mar 16	1178	699	86	17	<0.01
	Dithane NT Mancozeb(P)	EBIS(M)	Jun 14	Mar 15	1134	654	93	34	<0.02
Winter wheat 2014	Orius 200 EW Tebuconazole(P)	1,2,4-triazole(M)	Nov 14	Jun 16*	1045	467	105	80	<0.01
	Proline EC 250 *Prothioconazole (P)*	1,2,4-triazole(M)	May 15	Jun 16*	1060	504	76	9	<0.01
Spring barley 2016	Fighter 480 Bentazone(P)	Bentazone(P)	May 16	Jun 16*	-	-	132	23	<0.01
		6-hydroxy-bentazone(M)	May 16	Jun 16*	-	-	132	23	<0.01
		8-hydroxy-bentazone(M)	May 16	Jun 16*	-	-	132	23	<0.01
		N-methyl-bentazone(M)	May 16	Jun 16*	-	-	132	23	<0.01

Systematic chemical nomenclature for the analysed pesticides is given in Appendix 1.
**Monitoring continues the following year.*
***If difference between S1 and S2.*

Aminopyralid was applied on spring barley in May 2012. In the previous monitoring period there were no detections in the variably-saturated zone, two detections (0.027 and 0.058 µg L^{-1}) in groundwater samples collected from the lowest upstream screen M1.4 and one detection in the water samples collected from the water used for irrigation. The three detections were obtained from water samples collected more than a year after the application of aminopyralid on the field. These detections clearly indicate no leaching of aminopyralid through the field, but a contribution from other fields via groundwater and irrigated water (0.05 µg L^{-1}). This monitoring ended in April 2015 (Table 2.2).

Prosulfocarb was applied on winter rye October 2012. During the last monitoring period the compound was not detected in any samples, and the monitoring was terminated in March 2015 (Table 2.2).

Fludioxonil was applied on potatoes in April 2014. The degradation products of fludioxonil CGA 339833 and CGA 192155 were not detected during the monitoring period and the monitoring of these compounds ended in March 2016.

Leaching of **metalaxyl-M** applied in potatoes in July 2010 and its two degradation products CGA 108906 and CGA 62826 was minor at Tylstrup compared to Jyndevad. With high background concentration of especially CGA 108906 detected in water samples collected from the vertical groundwater monitoring wells, it is 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 applications on the upstream neighbouring fields, where both metalaxyl and metalaxyl-M have been applied (Rosenbom *et al.*, 2016, Appendix 7).

Mancozeb was applied on potatoes in June 2014. The degradation product from mancozeb, EBIS, was not detected in any of the 91 samples collected during this monitoring period. Given no detections monitoring was terminated in March 2015.

Two fungicides were applied to winter wheat in 2014-2015. **Tebuconazole** was applied once on 11 November 2014 and **prothioconazole** was applied twice on 14 May 2015 and 12 June 2015. Prothioconazole was included in PLAP to confirm that this pesticide only degrades to 1,2,4-triazol in minor amounts as stated in the EFSA conclusion for this pesticide. In 2014 only the degradation product 1,2,4-triazole was included in the monitoring programme, since tebuconazole itself had been tested at Tylstrup before with only a few detections in the groundwater zone. Like for tebuconazole, 1,2,4-triazole was detected and often in samples collected from groundwater and only once in a sample from 1 m depth. Among the groundwater samples having detections of 1,2,4-triazole some were collected at the upstream well M1; hereamong two obtained before the tebuconazole application. This indicates a contribution from upstreams fields. Other samples were collected from the horizontal screens of H1, which is situated just below the fluctuating groundwater, indicated a contribution from the field. These findings made it difficult to interpret the 1,2,4-triazole contribution from the tebuconazole application at this PLAP-field to the groundwater underneath. A dual application of prothioconazole within a month in early summer 2015 was hence conducted. These applications resulted initially in an increase in concentration detected in samples from H1 and the downstream well M5 at 3-4 m depth. Detections in concentrations up to 0.04 µg L^{-1} was continuously obtained in samples from H1 one year after these applications. Yet, half a year after these applications 1,2,4-triazole was detected in the samples from S1 and S2 and in both 1 and 2 m depth in concentrations up to 0.06 µg L^{-1} (Figure 2.7B). This clearly indicates a contribution through the variably-saturated zone. The monitoring period from November 2014 – June 2016 does not reveal the cause for this late appearance of 1,2,4-triazole in samples collected from the variably saturated zone (13%; 7/53) nor the high proportion of groundwater samples having detections (39%; 61/156), whereamong 21% (13/61) of the groundwater samples with detections (max. 0.02 µg L^{-1}) were collected at the upstream well M1. Two of these detections from M1 were obtained before the tebuconazole application. This was also the case for one detection at M3.4 (0.02 µg L^{-1}) and M5.3 (0.03 µg L^{-1}) (Figure 2.7C).

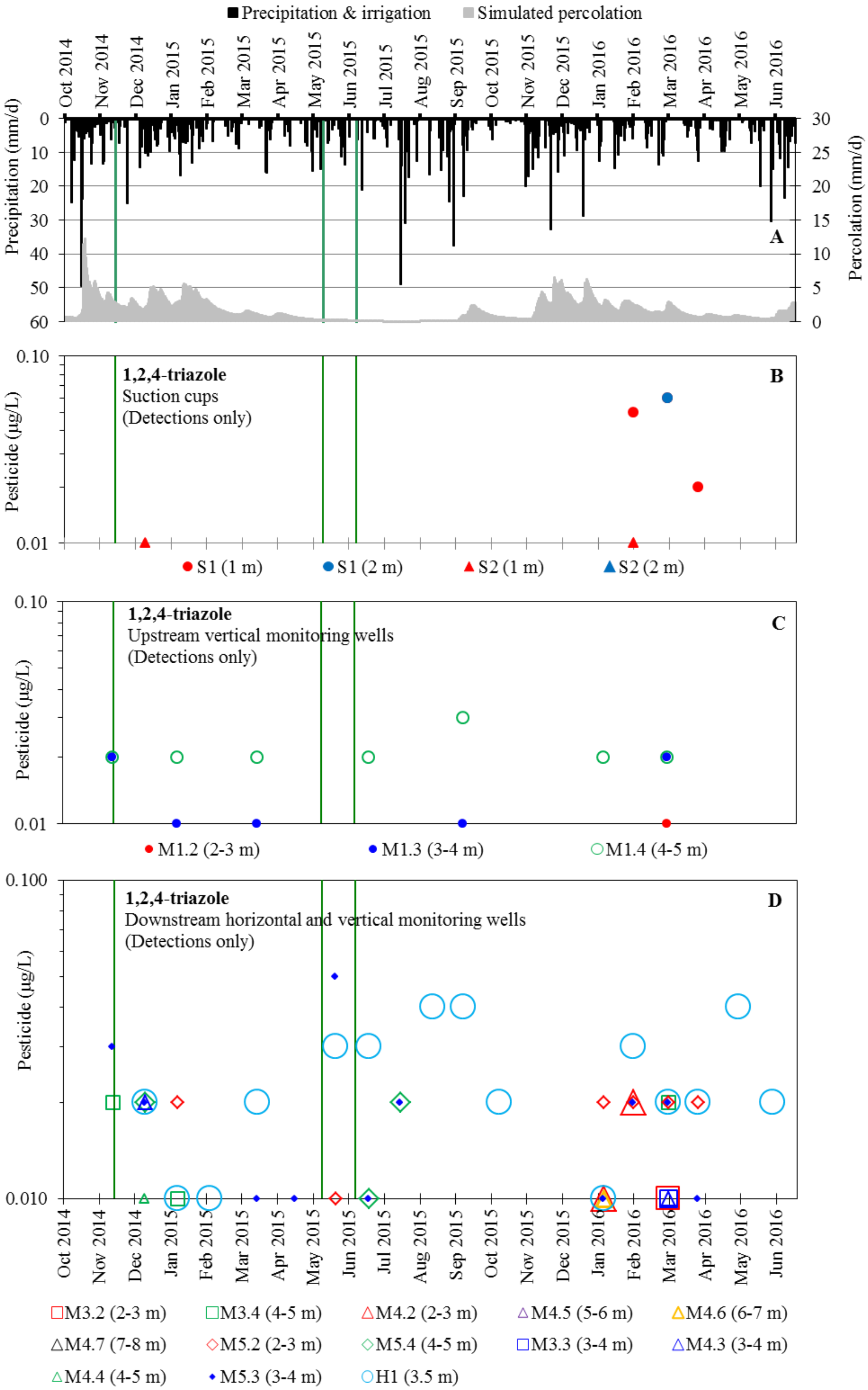

Figure 2.7. 1,2,4-triazole detections at **Tylstrup**: Precipitation, irrigation and simulated percolation 1 m b.g.s. (A) together with measured concentration of 1,2,4-triazole detections in the variably-saturated zone (B; water collected from suction cups at S1 and S2 in 1 and 2 m depth) and saturated zone (C-D; Water collected from upstream and downstream horizontal (H) and vertical screens (M)). The green vertical lines indicate the date of pesticide application.

3 Pesticide leaching at Jyndevad

3.1 Materials and methods

3.1.1 Field 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 2015-16 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.

Having been harrowed twice winter wheat (cv. Mariboss) was sown in the field 18 September 2014, emerging 26 September 2014. The herbicide flupyrsulfuron was applied on 22 October 2014 and 20 March 2015, and the fungicide tebuconazole on 11 November 2014. Flupyrsulfuron-methyl and three of its degradation products IN-KC576, IN-KY374 and IN-JV460 as well as 1,2,4-triazole from tebuconazole were included in the monitoring.

Fungicides were further applied on 8 May 2015, using a mixture of epoxiconazole and pyraclostrobin, and on 17 June 2015 using prothioconazole. None of these parent compunds were included in the monitoring programme. The degradation product of 1,2,4-triazole, a degradation product of azole-based compounds was included in the monitoring programme. The winter wheat was irrigated 27 mm ha^{-1} on 11 June 2015 as well as 30 mm ha^{-1} on 30 June 2015 and 13 June 2015. At harvest on 20 August 2015 the winter wheat yielded 79.7 hkg ha^{-1} of grain (85% dry matter). At the day of harvest 71.5 hkg ha^{-1} of shredded straw was incorporated with a rotor harrow.

Ploughing of the field was done 7 March 2016, and on 21 March 2016 a crop of spring barley (cv. KWS Irena) was sown. A catch crop of grass and clover (Foragemax 42) was sown 20 April 2016. The field was sprayed with the herbicide bentazone on 3 May 2016.

Bentazone and its three degradation products N-methyl bentazone, 8-hydroxy-bentazone and 6-hydroxy-bentazone were included in the monitoring. The fungicide propiconazole was used 2 June 2016 and the degradation product 1,2,4-triazole was already included in the montoring. Propiconazole was by mistake applied in only half the allowed dosage, i.e. 125 g ha^{-1} active ingredient instead of 250 g ha^{-1}. Irrigation of 30 mm was done on both 3 and 8 June 2016.

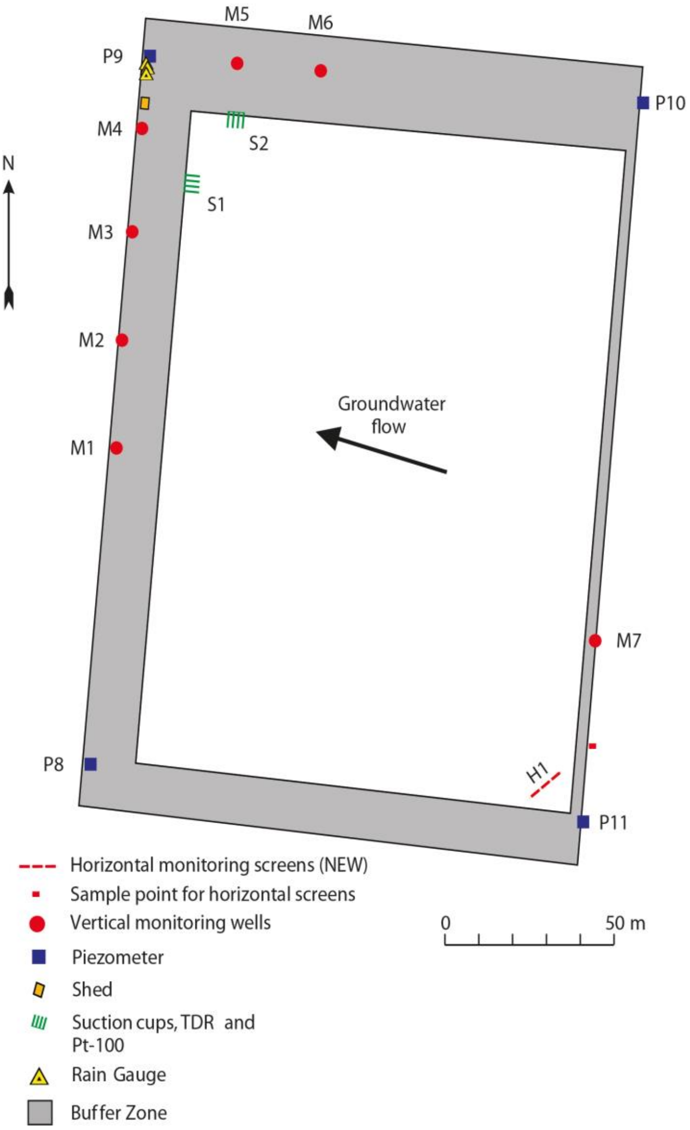

Figure 3.1. Overview of the **Jyndevad** field. The innermost white area indicates the cultivated field, while the grey area indicates the surrounding buffer zone. The positions of the various installations are indicated, as is the direction of groundwater flow (by an arrow). Pesticide monitoring is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

3.1.3 Model setup and calibration

The numerical model MACRO (version 5.2, Larsbo *et al.*, 2005) was applied to the Jyndevad 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 2016 and to establish an annual water balance.

Compared with the setup in Rosenbom *et al.* (2016), 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 2016. For this purpose, the following time series were used: 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 3.2), and the bromide concentration measured in the suction cups located 1 and 2 m b.g.s. (Figure 3.3). See Figure 3.1 for location of individual sample points. 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 at Jyndevad (Figure 3.2). The dynamics of the simulated groundwater table were well described with MACRO 5.2 (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 consequent delay of water flow through the soil profile 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 hydraulic year 2015-2016, was characterised by having very high precipitation, medium simulated actual evapotranspiration and irrigation, and a high groundwater recharge. Unlike at Tylstrup the precipitation values in the autumn of 2015 were closer to normal values. Continuous percolation 1 m b.g.s. was simulated for this hydraulic year.

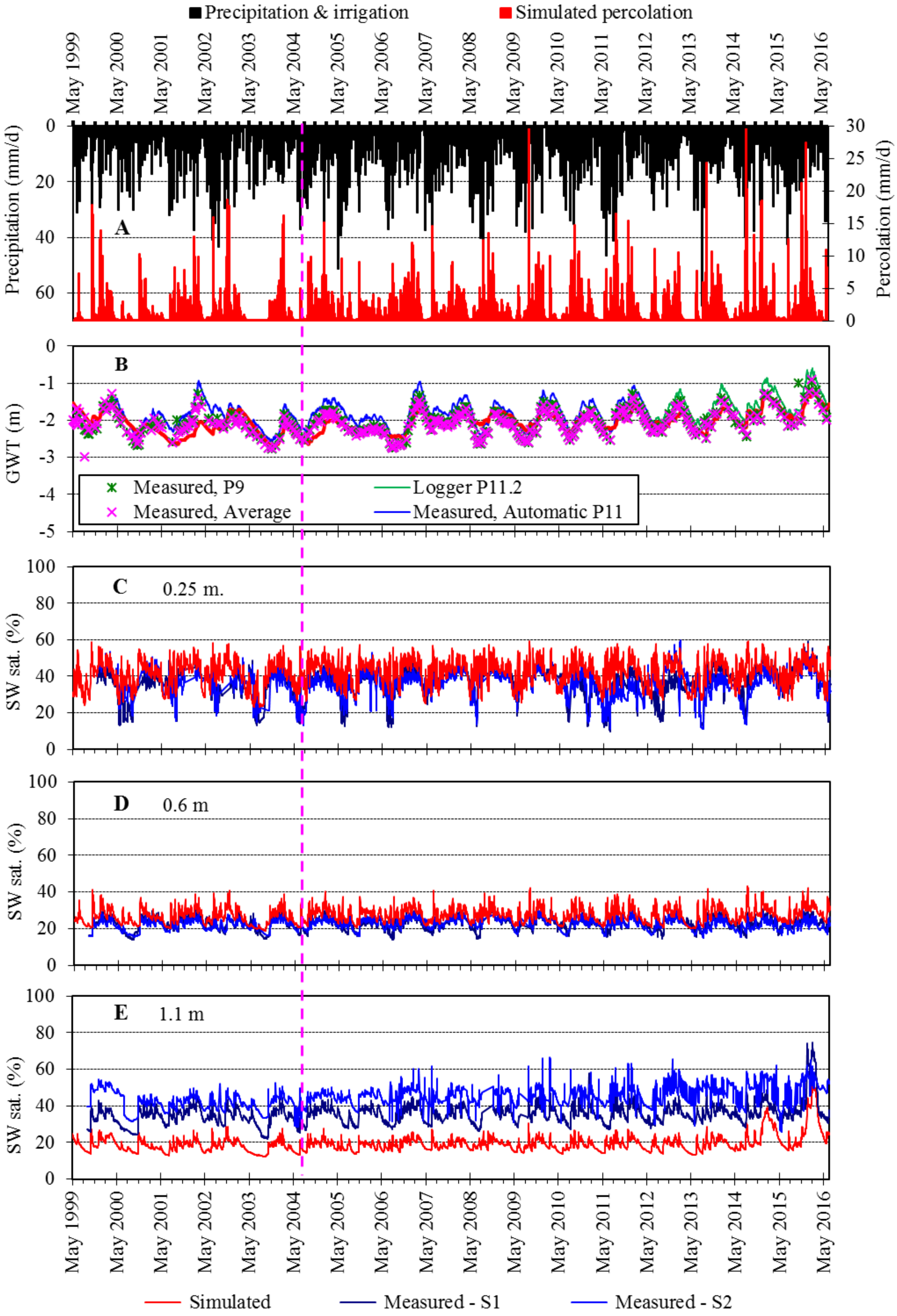

Figure 3.2. Soil water dynamics at **Jyndevad**: Measured precipitation, irrigation and simulated percolation 1 m b.g.s. (A), simulated and measured groundwater table, GWT (B), and simulated and measured soil water saturation (SW sat.) at three different soil depths (C, D and E). The measured data in 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 2016).

Table 3.1. Annual water balance for **Jyndevad** (mm yr^{-1}). Precipitation is corrected to the soil surface according to the method of Allerup and Madsen (1979).

	Normal precipitation[1)]	Precipitation	Irrigation	Actual evapotranspiration	Groundwater recharge[2)]
01.07.99–30.06.00	995	1073	29	500	602
01.07.00–30.06.01	995	810	0	461	349
01.07.01–30.06.02	995	1204	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	1218	87	578	727
01.07.05–30.06.06	995	857	117	490	484
01.07.06–30.06.07	995	1304	114	571	847
01.07.07–30.06.08	995	1023	196	613	605
01.07.08–30.06.09	995	1078	84	551	610
01.07.09–30.06.10	995	1059	80	530	610
01.07.10–30.06.11	995	1070	92	554	607
01.07.11–30.06.12	995	1159	30	490	699
01.07.12–30.06.13	995	991	60	478	572
01.07.13–30.06.14	995	1104	75	485	693
01.07.14–30.06.15	995	1267	102	569	800
01.07.15–30.06.16	995	1362	90	579	872

[1)]Normal values based on time series for 1961-1990.
[2)]Groundwater recharge is calculated as precipitation + irrigation - actual evapotranspiration.

3.2.2 Bromide leaching

Bromide has now been applied three times at Jyndevad. The bromide concentrations measured until April 2003 (Figure 3.3, Figure 3.4 and Figure 3.5) relate to the bromide applied in autumn 1999, as described further in Kjær *et al.* (2003). Leaching of the bromide applied in March 2003 is evaluated in Barlebo *et al.* (2007). The bromide applied in May 2012 showed the same response time in the variably-saturated zone as in April 2003 (Figure 3.3), but in the downstream wells M1, M2 and M4 the response time was quicker (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).

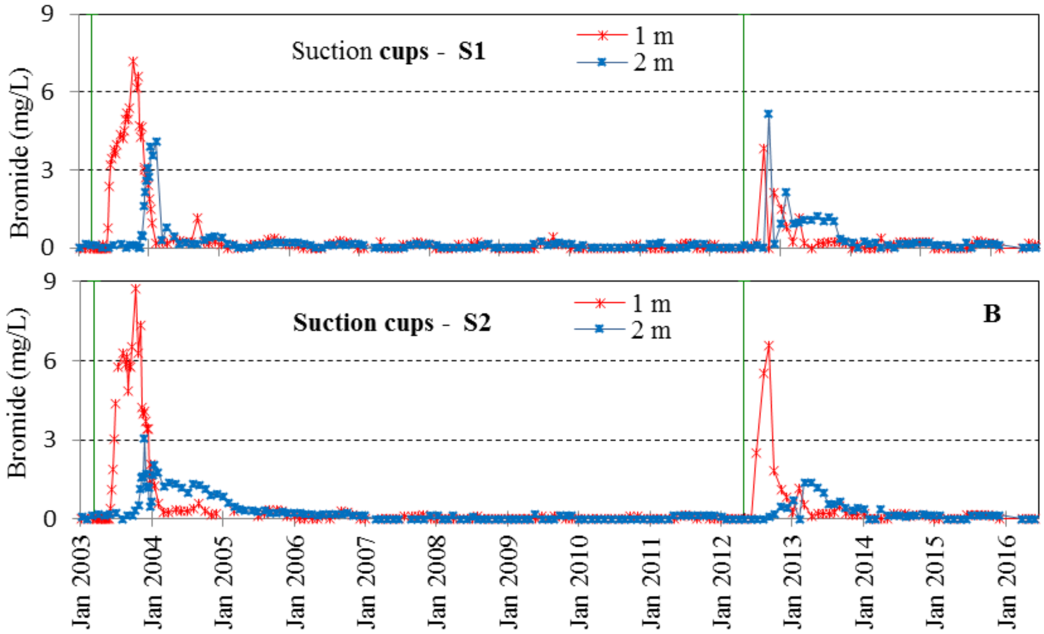

Figure 3.3. Bromide concentration in the variably-saturated zone at **Jyndevad**. The measured data derive from suction cups installed 1 m b.g.s. (A) and 2 m b.g.s. (B) at locations S1 and S2 (Figure 3.1). The green vertical lines indicate the dates of bromide applications.

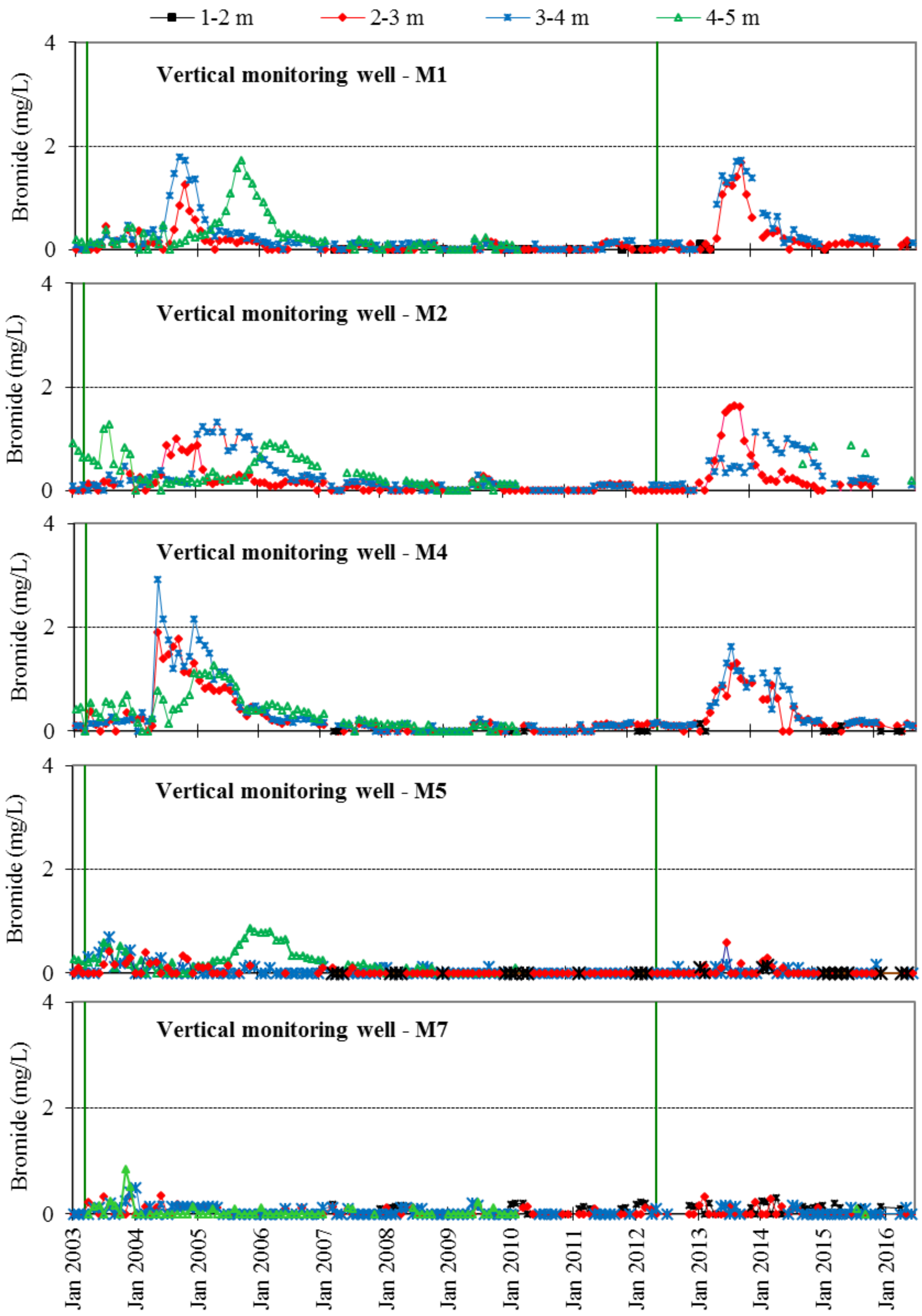

Figure 3.4. Bromide concentration in the groundwater at **Jyndevad**. The data derive from monitoring wells M1, M2, M4, M5 and M7. Screen depth is indicated in m b.g.s. The green vertical lines indicate the dates of bromide applications.

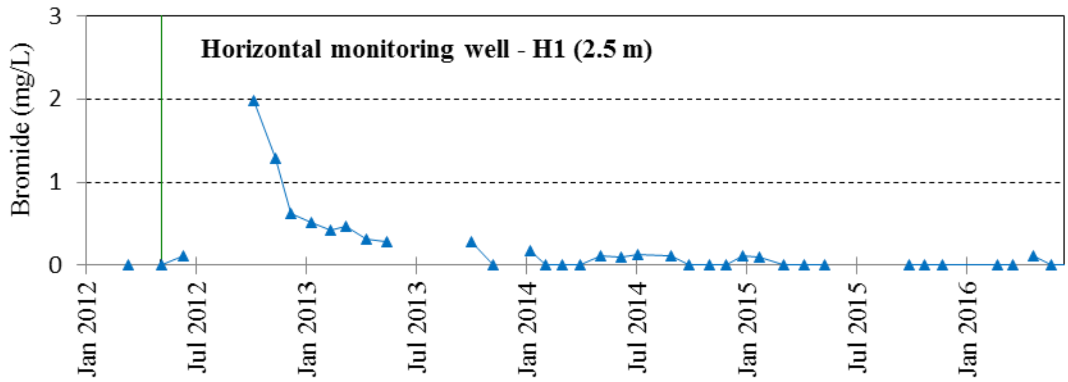

Figure 3.5. Bromide concentration in the groundwater at **Jyndevad.** The data derive from the horizontal monitoring well H1. The green vertical line indicates the date of bromide application.

3.2.3 Pesticide leaching

Monitoring at Jyndevad began in September 1999 and encompasses the pesticides and degradation products, as indicated in Appendix 7. Pesticide application during the most recent growing seasons is listed in Table 3.2 and shown together with precipitation and simulated precipitation in Figure 3.6. It should be noted that precipitation is corrected to the soil surface according to Allerup and Madsen (1979), whereas percolation (1 m b.g.s.) refers to accumulated percolation as simulated with the MACRO model (Table 3.2). Pesticides applied later than May 2016 are not evaluated in this report, but such compounds are nevertheless listed in Table 3.2.

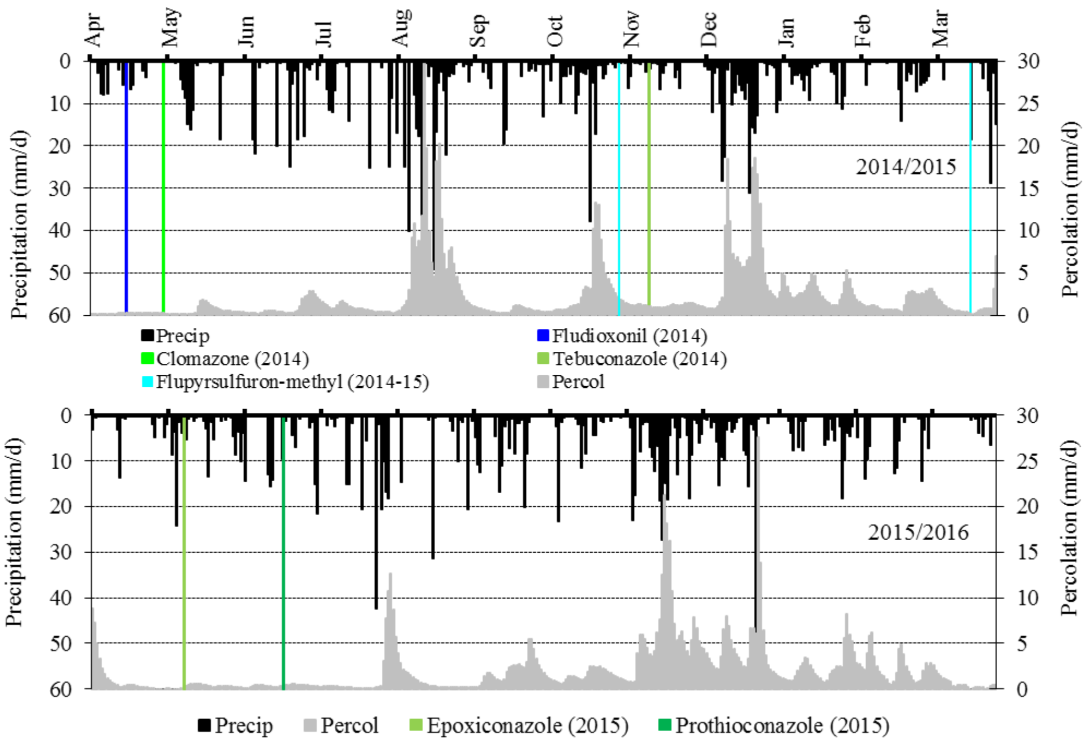

Figure 3.6. Application of pesticides included in the monitoring programme, precipitation and irrigation (primary axis) together with simulated percolation 1 m b.g.s. (secondary axis) at **Jyndevad** in 2014/2015 (upper) and 2015/2016 (lower).

The current report focuses primarily on the pesticides applied from 2014 and onwards, while leaching risk of pesticides applied before 2014 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 were not measured in S2 during the first months after applications.

Table 3.2. Pesticides analysed at **Jyndevad**. For each compound it is listed whether it is a pesticide (P) or degradation product (M), as well as the application date (Appl. date) and end of monitoring period (End. mon.). Precipitation (precip. in mm) and percolation (percol. in mm) 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 [μg L^{-1}] at 1 m b.g.s. the first year after application. See Appendix 2 for calculation method and Appendix 8 (Table A8.2) for previous applications of pesticides.

Crop	Applied product	Analysed pesticide	Appl. date	End mon.	Y 1st precip.	Y 1st percol.	M 1st precip.	M 1st percol.	C_{mean}
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
		PPU-desamino(M)	Jun 10	Jun 12	1160	592	137	13	<0.01
	Ridomil Gold	Metalaxyl-M(P)	Jul 10	Mar 15	1073	613	161	41	0.02
	MZ Pepite	CGA 108906(M)	Jul 10	Mar 15	1073	613	161	41	0.37-0.6**
		CGA 62826(M)	Jul 10	Mar 15	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	Mar 15	993	512	109	11	<0.01
	Callisto	AMBA(M)	Jun 12	Mar 15	993	512	109	11	<0.01
	Callisto	MNBA(M)	Jun 12	Mar 15	993	512	109	11	<0.01
	Fighter 480	Bentazone(P)	May 12	Mar 15	994	513	114	2	0.04-0.22**
Peas 2013	Fighter 480	Bentazone(P)1)	May 13	Mar 15	1175	703	84	0.2	0.02-0.16**
Potatoes 2014	Comand CS	Clomazone(P)	Apr 14	Mar 15	1393	855	87	18	<0.01
		FMC 65317(M)	Apr 14	Mar 15	1393	855	87	18	<0.02
	Maxim 100 FS Fludioxonil (P)	CGA 339833(M)	Apr 14	Apr 16	1404	856	83	10	<0.03
		CGA 192155(M)	Apr 14	Apr 16	1404	856	83	10	<0.01
	Dithane NT Mancozeb (P)	EBIS(M)	Jun 14	Mar 15	1407	844	138	37	<0.02
Winter wheat 2014	Lexus 50 WG	Flupyrsulfuron-methyl (P)	Oct 14 +Mar 15	Jun 16*	1221	670	45	76	<0.01
		IN-KC576(M)	Oct 14 +Mar 15	Jun 16*	1221	670	45	76	<0.01
		IN-KY374(M)	Oct 14 +Mar 15	Jun 16*	1221	670	45	76	<0.01
		IN-JV460(M)	Oct 14 +Mar 15	Jun 16*	1221	670	45	76	<0.01
	Orius 200 EW Tebuconazole (P)	1,2,4-triazole(M)	Nov 14	Jun 16*	1253	645	86	35	<0.01
	Opus Epoxiconazole(P)	1,2,4-triazole(M)	May 15	Jun 16*	1323	754	81	10	0.08
	Proline EC 250 Prothioconazole(P)	1,2,4-triazole(M)	Jun 15	Jun16*	1435	789	103	10	0.08
Spring barley 2016	Fighter 480	Bentazone(P)	May 16	Jun 16*	-	-	85	6	0.01
		6-hydroxy-bentazone(M)	May 16	Jun 16*	-	-	85	6	<0.01
		8-hydroxy-bentazone(M)	May 16	Jun 16*	-	-	85	6	<0.01
		N-methyl-bentazone(M)	May 16	Jun 16*	-	-	85	6	<0.01
	Bumper 25 EC Propiconazole(P)2	1,2,4-triazol(M)	Jun 16	Jun 16*	-	-	-	-	-

Systematic chemical nomenclature for the analysed pesticides is given in Appendix 1.
1) Bentazone applied on 7 May and 16 May 2013.
2) Propiconazole only applied in half of the maximum allowed dose.
**Monitoring continues the following year.*
***If difference between S1 and S2.*

The fungicide **metalaxyl-M** was applied on potatoes in July 2010 and the compound itself, as well as the two degradation products CGA 62826 and CGA 108909, could still be found in the groundwater 5 years after the application (Rosenbom *et al.*, 2016). Whereas metalaxyl-M, with a single exception, was found only in the vertical monitoring well M7 upstream the PLAP field, both of the degradation products were found in both suction cups 1.0 m b.g.s., the vertical wells up- and downstream the field, and the horizontal well beneath the field.

The **bentazone** that was applied in peas May 2013, was not detected in the groundwater. However, it was found frequently in the variably-saturated zone (Figure 3.7). The bentazone was present in low concentration in water from suction cups at 1 m depth, before the applications of May 2013, due to a previous application in May 2012. Having initially leached in concentrations up to 2.0 µg L^{-1} in July 2013, a concentration of 0.015 µg L^{-1} was found in March 2015. Bentazone is still present in minute concentrations in suction cup samples, but no traces are found in water samples collected from neither horizontal nor vertical well screens. Three degradation products of bentazone, **N-methyl bentazone**, **8 hydroxy-bentazone** and **6 hydroxy-bentazone** have been monitored since the application of bentazone in May 2015. However, none of these have been detected.

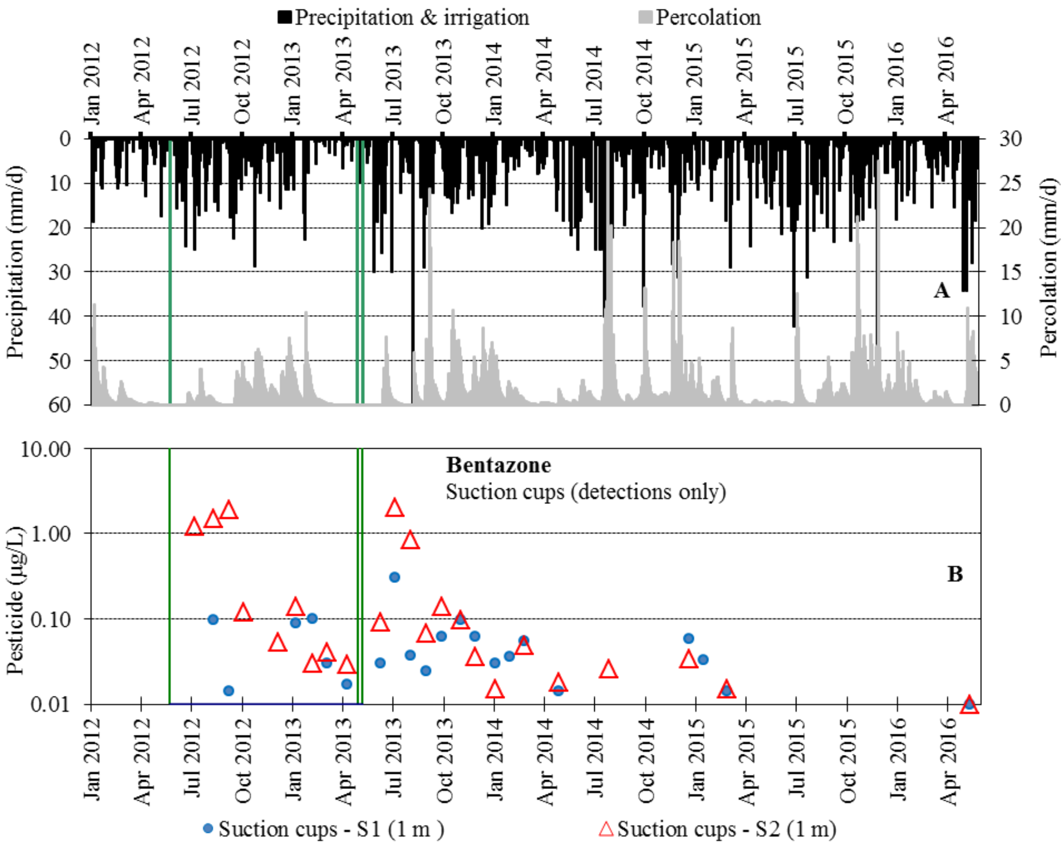

Figure 3.7. Precipitation, irrigation and simulated percolation 1 m b.g.s. (A) together with measured concentrations of **bentazone** in water samples collected from suction cups at 1 m depth at S1 and S2 in **Jyndevad**. The green vertical lines indicate the dates of bentazone application.

Tebuconazole, **epoxiconazole** and **prothioconazole** were applied to the winter wheat on 11 November 2014, 8 May 2015 and 17 June 2015, respectively. Their degradation product 1,2,4-triazole was monitored from the 13 November 2014. As there had not been taken a background sample prior to the application of tebuconazole it is difficult to evaluate, whether the detections shown in Figure 3.8 are due to this application. On two occasions 0.1 µg L^{-1} has been exceeded in the groundwater, being 0.15 µg L^{-1} in the uppermost screen (3.0-4.0 m depth) of the vertical monitoring well M2, two days after the tebuconazole application. Additionally, that day water from the uppermost screen of M7 (1.6-2.6 m depth) upstream contained 0.1 µg L^{-1}. Since these two initial detections, all detections of 1,2,4-triazole in groundwater have been less than 0.1 µg L^{-1}. Following each application, an increase in the concentration level is detected. A similar pictures has emerged in the variably-saturated zone at location S2, where 1,2,4-triazole was detected for the first time 5 February 2015 in a concentration of 0.06 µg L^{-1}. All but the most recently sampled water on 9 June 2016 have contained 1,2,4-triazole. 6 out of 14 samples have exceeded 0.1 µg L^{-1}. The highest concentrations detected in the variably-saturated zone was 0.16 µg L^{-1} on the 18 August 2015 as well as 9 February 2016. In 1 m depth at location S1, there were, however, no detections of 1,2,4-triazole until 9 February and 5 April 2016, when concentrations of 0.01 and 0.03 µg L^{-1} were detected, respectively. The concentrations in the variably-saturated zone at location S2 and the saturated zone do not vary much throughout the years. The detections following the application of epoxiconazole and prothioconazole do reveal an increase in concentration of 1,2,4-triazole, indicating a degradation of the applied pesticides and a 1,2,4-triazole leaching through the variably saturated zone to groundwater. In total 1,2,4-triazol has been detected in: 16 out of 30 water samples from suction cells, among these 5 exceeded 0.1 µg L^{-1}, 16 out of 24 water samples from H1 with no detections exceeding 0.1 µg L^{-1}, 46 out of 112 water samples from downgradient wells with one exceedance of 0.1 µg L^{-1}, 49 out of 60 water samples from the upstream well M7 with no exceedings of 0.1 µg L^{-1}. Whether the concentration level is caused by the three applications alone or in combination with other sources cannot be concluded from this monitoring. More detailed studies into the degradation processes in situ are therefore needed to decide, whether the agricultural uses of triazole pesticides may constitute a threat to the groundwater.

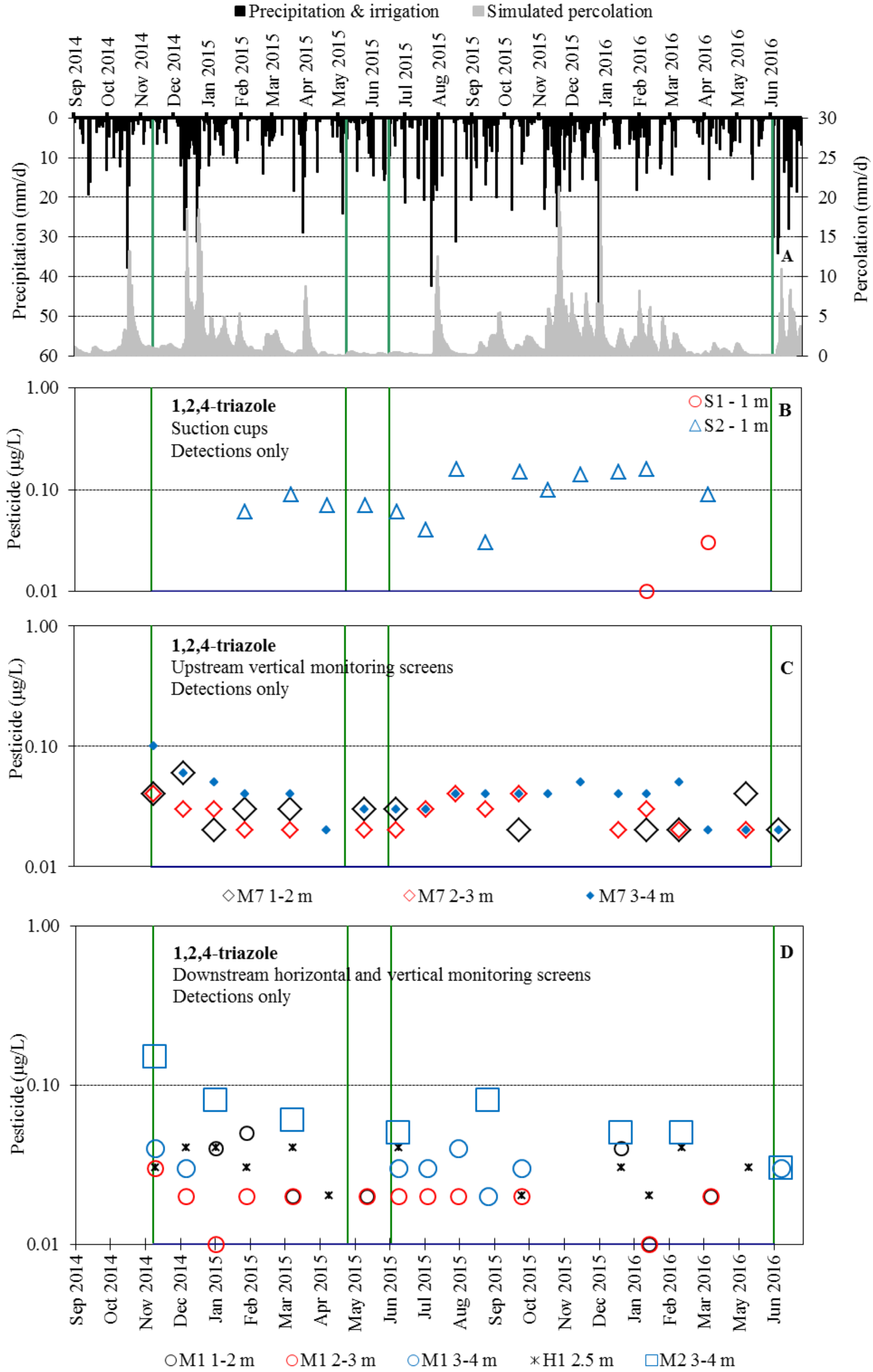

Figure 3.8. 1,2,4-triazole detections at **Jyndevad**: Precipitation, irrigation and simulated percolation 1 m b.g.s. (A) together with measured concentration of 1,2,4-triazole detections in the variably-saturated zone (B; water collected from suction cups at S1 and S2 in 1 and 2 m depth) and saturated zone (C-D; Water collected from upstream and downstream horizontal (H) and vertical screens (M)). The green vertical lines indicate the date of pesticide application.

Fludioxonil was sprayed onto the potato tubers at planting in April 2014. The leaching of its two degradation products CGA 339833 and CGA 192155 was monitored. Except for 0.048 µg L^{-1} of CGA 192155 found 15 October 2015, in the vertical monitoring well M1 (1.6 - 2.6 m depth), neither of the substances were detected.

Clomazone, applied in the field before the emergence of the potatoes in April 2014 did not leach, nor did its degradation product FMC 65317. Monitoring was ended 19 March 2015.

Flupyrsulfuron-methyl was applied twice, October 2014 and March 2015, to a crop of winter wheat. The compound itself as well as the three degradation products IN-KC576, IN-JV460 and IN-KY374 were monitored. The degradation product, IN-KY374 was detected in total four times in water samples from the variably-saturated zone sampled by suction cups five to eight months after the March 2015 application. The highest concentration was 0.45 µg L^{-1}, Figure 3.9B

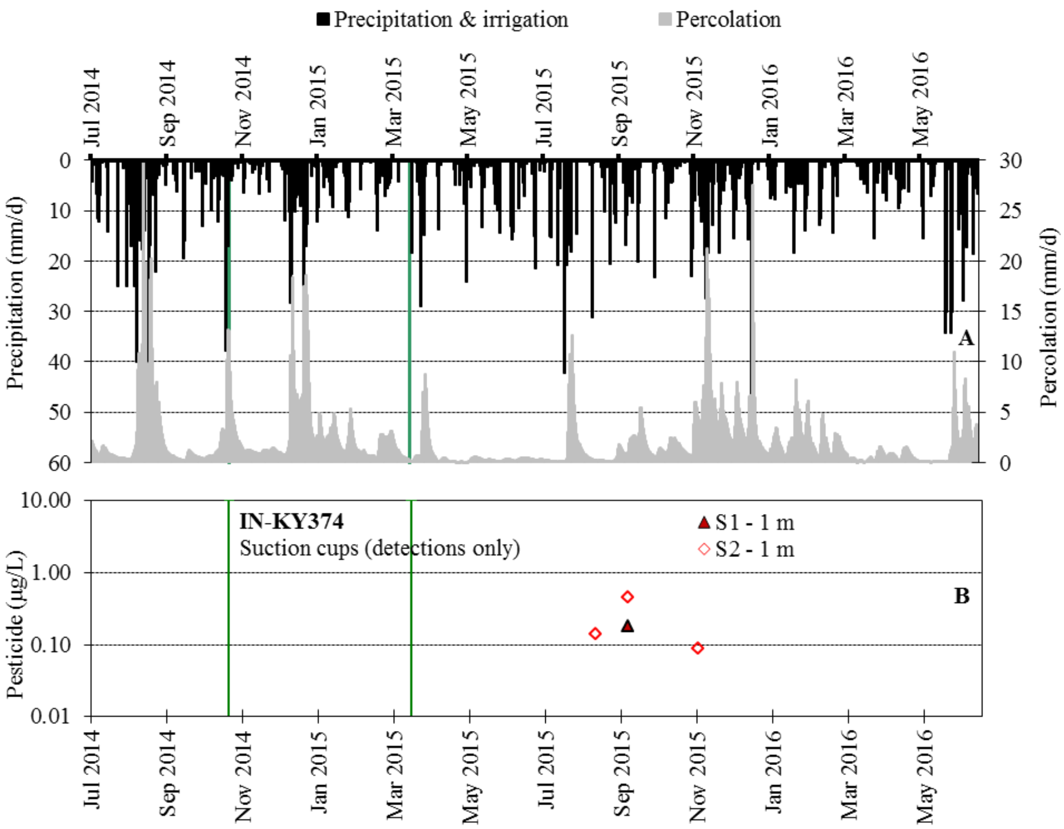

Figure 3.9. Precipitation, irrigation and simulated percolation at 1 m depth (A) together with measured concentrations of IN-KY374 in water samples from the variably-saturated zone at 1 m depth (suction cups S1 and S2) (B) at **Jyndevad**. The green vertical lines indicate the dates of application of the parent compound, flupyrsulfuron-methyl.

4 Pesticide leaching at Silstrup

4.1 Materials and methods

4.1.1 Field description and monitoring design

The test field at Silstrup is located south of the city Thisted in northwestern 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 clay content in the topsoil was 18% and 26%, and the organic carbon content was 3.4% and 2.8%, respectively (Table 1.1). The geological description showed a rather homogeneous clayey 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 is located just below a 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 at Silstrup during the 2015-16 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.

On 28 April 2015 acidified pig slurry was applied using a trail hose and subsequently ploughed in. Maize (cv. Ambition) was sown on 2 May 2015. Spraying of weeds was done on three occacions, using mesotrione and thifensulfuron-methyl on 27 May 2015, mesotrione, foramsulfuron and iodosulfuron on 9 June 2015 as well as foramsulfuron and iodosulfuron on 23 June 2015. Mesotrione and two of its degradation products, AMBA and MNBA, as well as foramsulfuron and two of its degradadation products, AE-F130619 and AEF092944, were included in the monitoring. The maize was harvested 31 October 2015 yielding 64.98 hkg ha^{-1} of silage (100% dry matter).

Stubble was crushed with a cutter 5 November 2015 and incorporated in the soil 28 April 2016. On 9 May 2016, 34 t ha^{-1} of pig slurry was trail hose applied. Ploughing took place the following day. A crop of maize (cv. Activate) was sown 13 May 2016. The herbicides mesotrione and thifensulfuron-methyl were applied on 6 June 2016, and on 22 June 2016 mesotrion, foramsulfuron and iodosulfuron were applied. The monitoring of mesotrione and its degradation products AMBA and MNBA continued, as did that of foramsulfuron and its degradation products AE-F130619 and AE-F092944. New to the monitoring was the degradation product triazinamine (IN-A4098), which can be formed from both thifensulfuron-methyl and iodosulfuron.

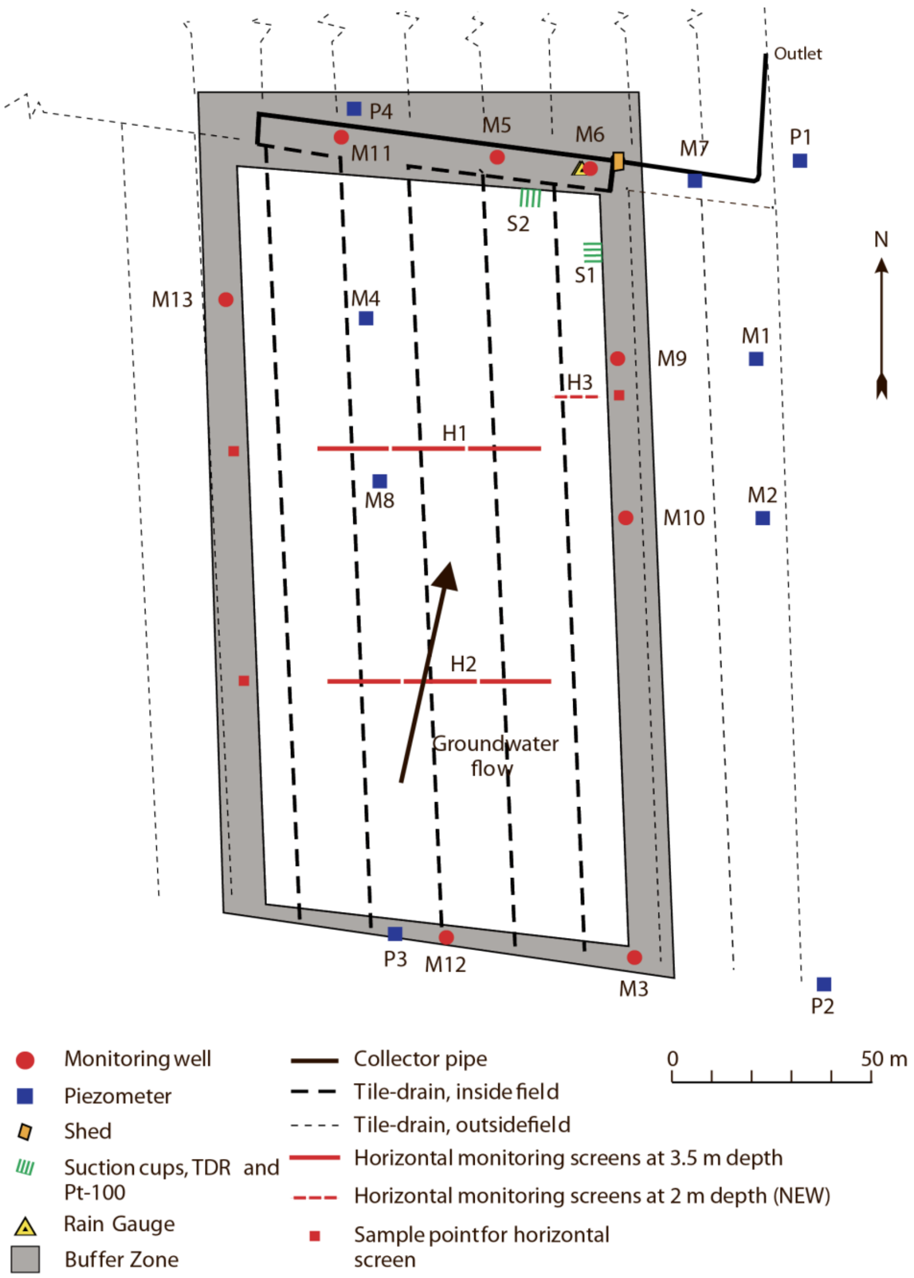

Figure 4.1. Overview of the **Silstrup** field. The innermost white area indicates the cultivated land, while the grey area indicates the surrounding buffer zone. The positions of the various installations are indicated, as is the direction of groundwater flow (by an arrow). Pesticide monitoring is conducted weekly from the drainage system (during periods 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 Rosenbom *et al.* (2016), 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 2016. 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 Brüsch *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 describes 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 inititation of the drainage periode in October 2013 compared to the measured.

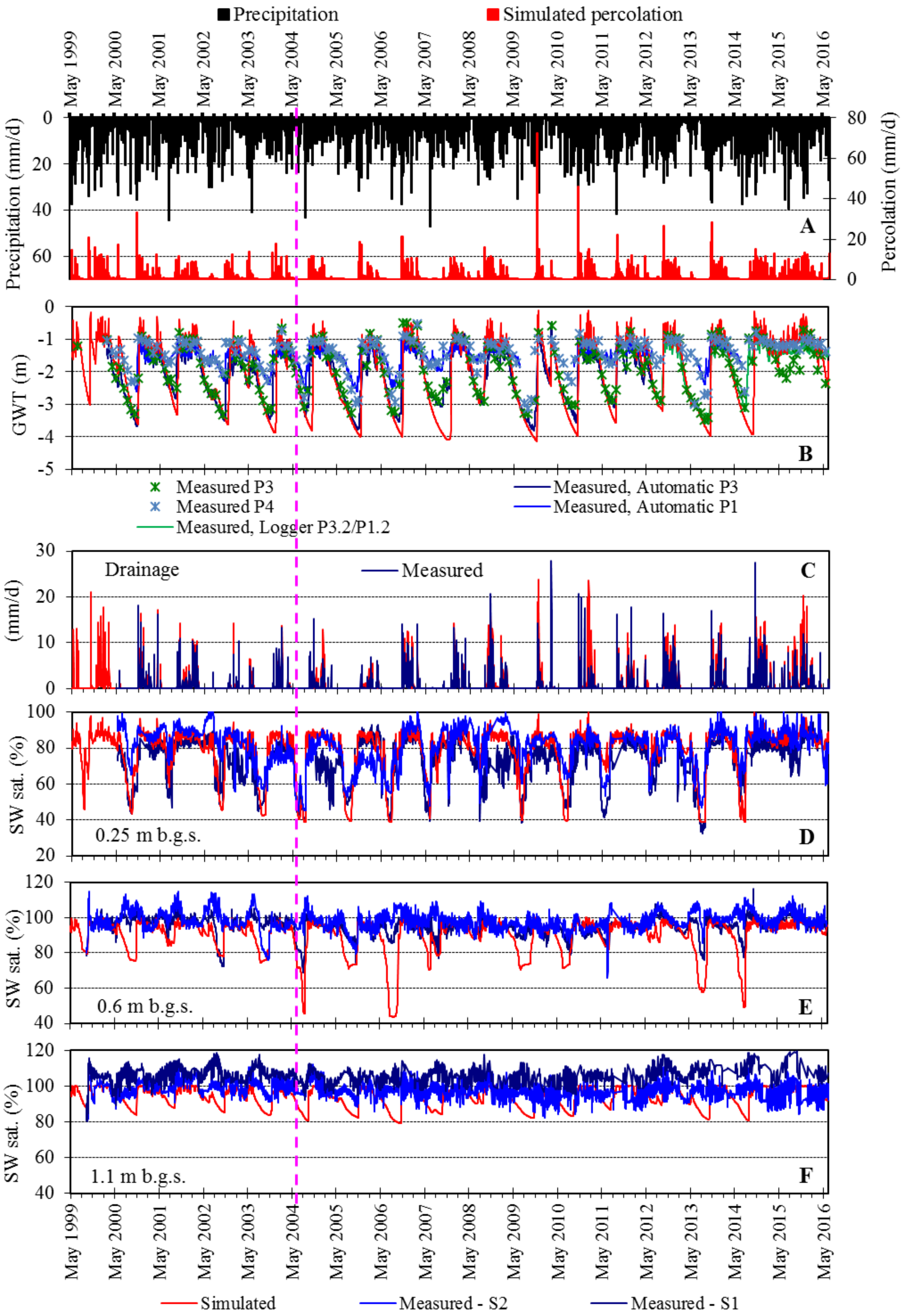

Figure 4.2. Soil water dynamics at **Silstrup**: Measured precipitation and simulated percolation 1 m b.g.s. (A), simulated and measured groundwater table, GWT (B), simulated and measured drainage (C), and simulated and measured soil water saturation (SW sat.) at three different soil depths (D, E and 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 2016).

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	1175	457	–	443	275[4)]
01.07.00–30.06.01	976	909	413	217	232	279
01.07.01–30.06.02	976	1034	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	1150	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	1063	399	172	569	492
01.07.11–30.06.12	976	1103	432	230	321	444
01.07.12–30.06.13	976	1020	469	249	333	302
01.07.13–30.06.14	976	1067	558	275	335	234
01.07.14–30.06.15	976	1314	461	329	412	524
01.07.15–30.06.16	976	1193	349	293	517	551

[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)] *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 16 years, the recent hydraulic year July 2015-June 2016 was characterised by having a high precipitation, low actual evapotranspiration, and low drainage. The second half of 2015 was in general rather wet with July 2015 being the wettest ever at Silstrup, and November and December 2015 having the second-highest precipitation measured at Silstrup (Appendix 4). Due to this precipitation pattern continuous downward percolation at 1 m depth was simulated during the entire 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 (Figure 4.2B and 4.2C). Compared to the hydrological year July 2014–June 2015, more water was entering the soil media than the drainage system, resulting in a higher groundwater recharge.

4.2.2 Bromide leaching

The bromide concentrations prior to April 2009, 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 30.5 kg ha^{-1} potassium bromide was applied to the field.

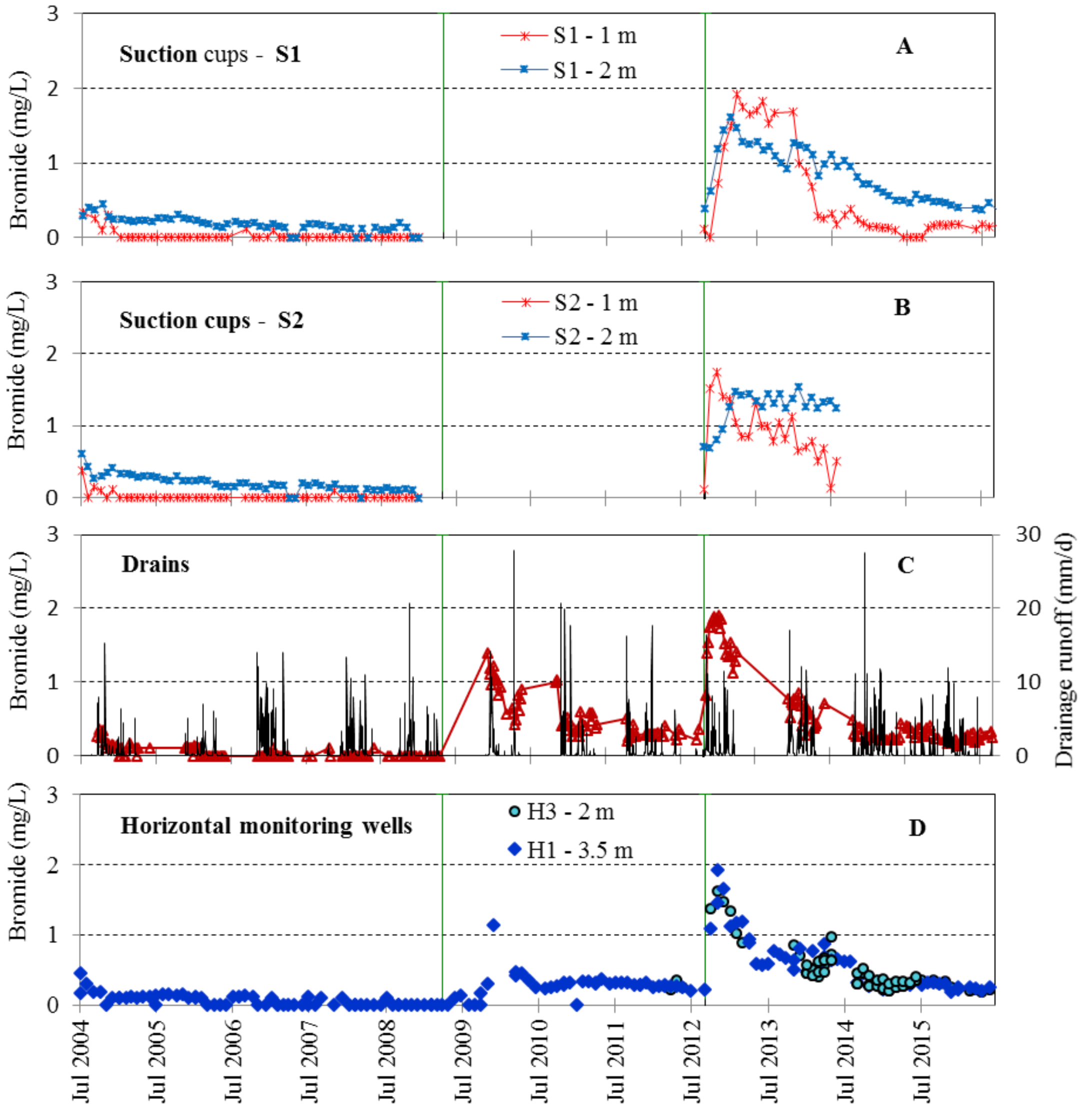

Figure 4.3. Bromide concentration at **Silstrup**. A and B refer to suction cups located at S1 and S2 (see Figure 4.1). The bromide concentration is also shown for drainage runoff (C) and the horizontal monitoring wells H1 and H3 (D). From January 2009 to September 2012, bromide measurements in the suction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

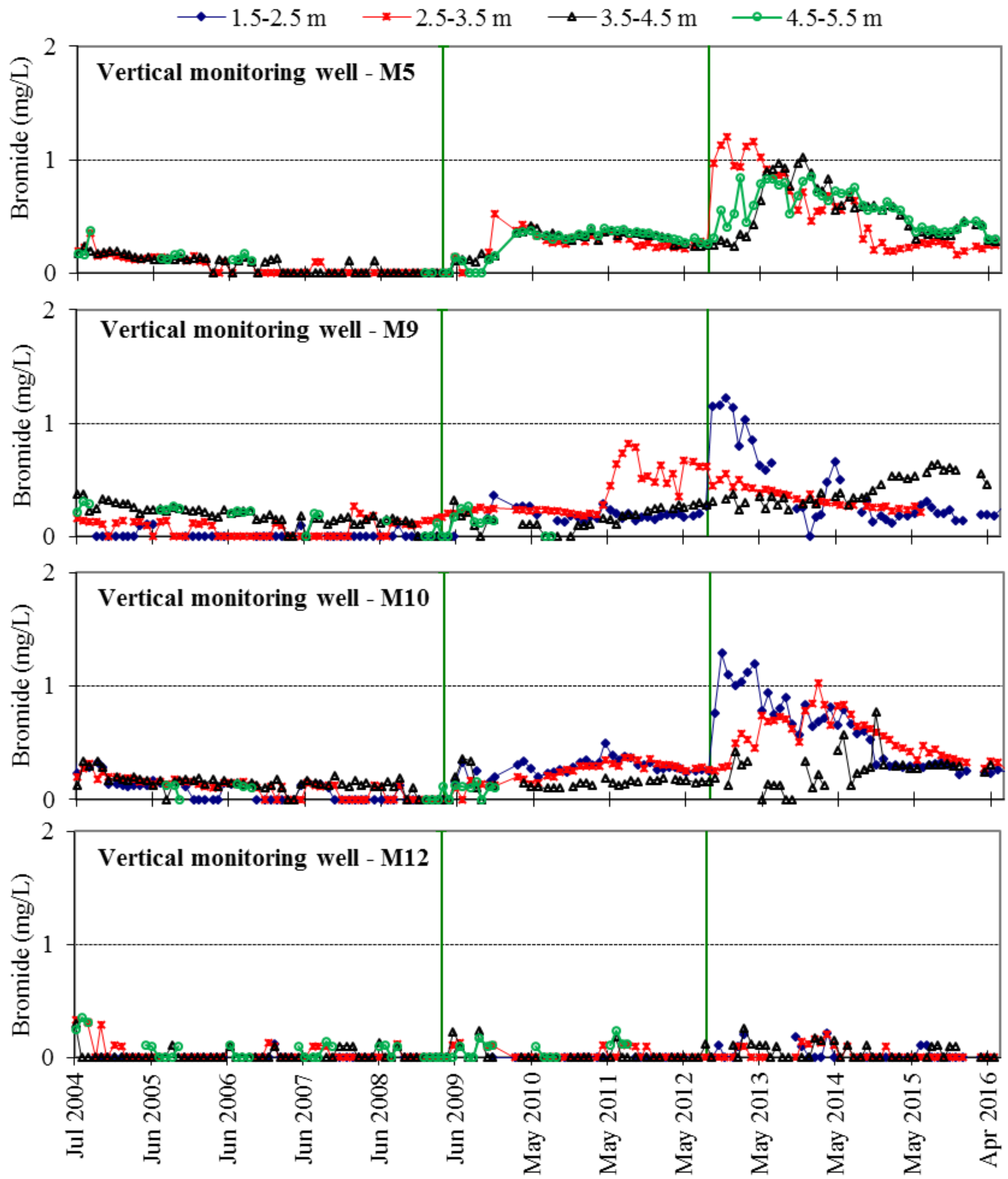

Figure 4.4. Bromide concentration at **Silstrup**. The data derive from the vertical monitoring wells (M5, M9, M10 and M12). In September 2008, monitoring wells M6 and M11 were suspended (Appendix 2). Screen depth is indicated in m b.g.s. The green vertical lines indicate the dates of bromide applications.

4.2.3 Pesticide leaching

Monitoring at Silstrup began in May 2000 and a list of the monitored pesticides and degradation products is given in Appendix 7. Pesticide application from 2009 to 2016 is summarized in Table 4.2 and shown together with precipitation and simulated percolation in Figure 4.5. It should be noted that the 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 May 2016 are not evaluated in this report and although they are included in Table 4.2.

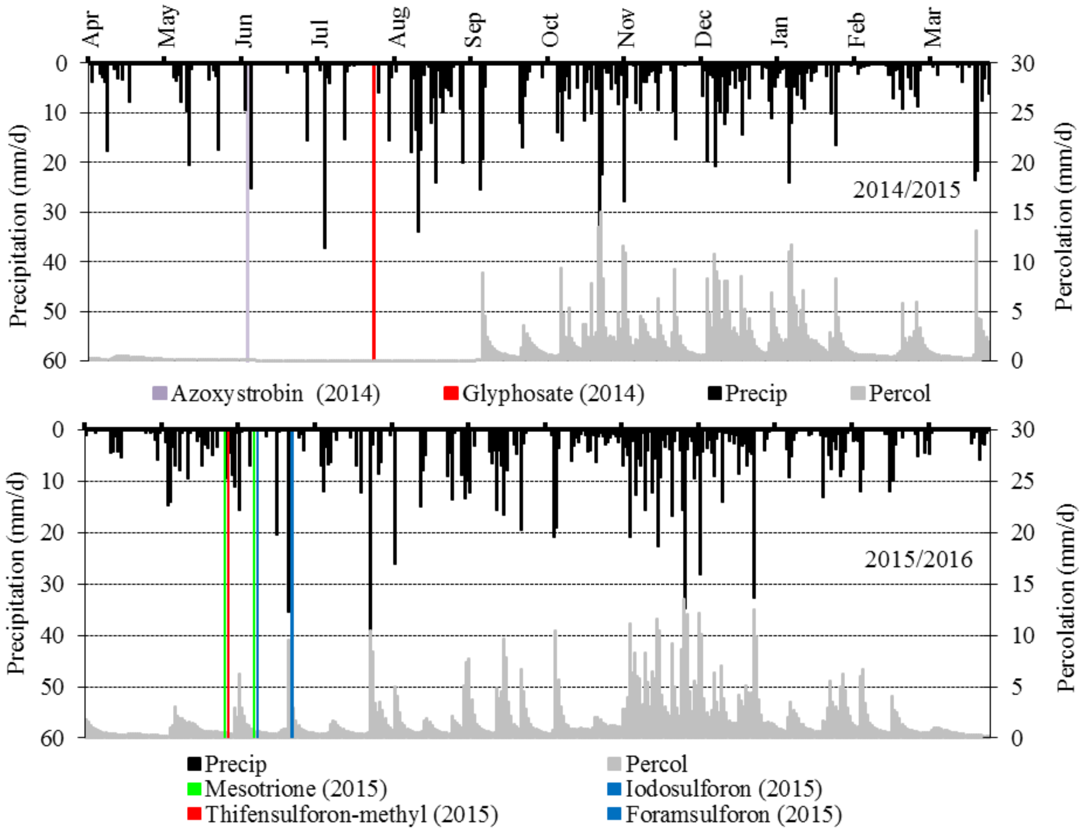

Figure 4.5. Application of pesticides included in the monitoring programme, precipitation and irrigation (primary axis) together with simulated percolation 1 m b.g.s. (secondary axis) at **Silstrup** in 2014/2015 (upper) and 2015/2016 (lower).

Table 4.2. Pesticides analysed at **Silstrup**. For each compound it is listed whether it is a pesticide (P) or degradation product (M), as well as the application date (Appl. date) and end of monitoring period (End. mon.). Precipitation (precip. in mm) and percolation (percol. in mm) 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 [µg L^{-1}] at 1 m depth the first year after application. See Appendix 2 for calculation method and Appendix 8 (Table A8.3) for previous applications of pesticides.

Crop	Applied product	Analysed pesticide	Appl. date	End mon.	Y 1st Precip.	Y 1st Percol	M 1st Precip	M 1st Percol	C_{mean}
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	Mar 15	1067	584	112	56	0.009
		AE-05422291(M)	Apr 12	Mar 15	1067	584	112	56	<0,01
		AE-B107137(M)	Apr 12	Mar 15	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	Mar 15	1073	581	127	64	0.074
	Glyfonova 450 Plus	Glyphosate(P)	Sep 12	Jun 15*	836	514	207	121	0.15
		AMPA(M)	Sep 12	Jun 15*	836	514	207	121	0.067
Winter wheat 2012	DFF	Diflufenican	Nov 12	Mar 15	463	270	68	69	0.006
		AE-05422291(M)	Nov 12	Mar 15	463	270	68	69	<0.01
		AE-B107137(M)	Nov 12	Mar 15	463	270	68	69	0.01
Spring barley 2013**	Duotril 400 EC	Ioxynil(P)	May 13	Mar 15	804	543	222	188	<0.01
	Duotril 400 EC	Bromoxynil (P)	May 13	Mar 15	804	543	222	188	<0.01
	Amistar	CyPM(M)	Jun 13	Jun 15*	1059	534	15	0	0.132
	Glyfonova 450 Plus	Glyphosate(P)	Aug 13	Jun 15*	1008	538	125	0	0,01
		AMPA(M)	Aug 13	Jun 15*	1008	538	125	0	0,01
Winter wheat 2013	Oxitril CM	Ioxynil(P)	Oct 13	Mar 15	804	542	222	189	<0.01
	Oxitril CM	Bromoxynil(P)	Oct 13	Mar 15	804	542	222	189	<0.01
	DFF	Diflufenican(P)	Oct 13	Mar 15	804	542	222	189	0.01
		AE-05422291(M)	Oct 13	Mar 15	804	542	222	189	<0.01
		AE-B107137(M)	Oct 13	Mar 15	804	542	222	189	<0.01
	Amistar	Azoxystrobin(P)	Jun 14	Jun 16	1288	630	46	0	0.013
		CyPM(M)	Jun 14	Jun 16	1288	630	46	0	0.13
	Glyfonova 450 Plus	Glyphosate(P)	Jul 14	Jun 16*	1309	691	187	0	<0.01
		AMPA(M)	Jul 14	Jun 16*	1309	691	187	0	<0.01
Maize 2015	Callisto	Mesotrione(P)	May 15***	Jun 16*	1219	783	117	52	0.05
		AMBA(M)	May 15***	Jun 16*	1219	783	117	52	<0.01
		MNBA(M)	May 15***	Jun 16*	1219	783	117	52	<0.01
	MaisTer	Foramsulfuron (P)	Jun 15****	Jun 16*	1257	791	100	37	<0.01
		AE-F130619(M)	Jun 15****	Jun 16*	1257	791	100	37	<0.01
		AE-F092944(M)	Jun 15****	Jun 16*	1257	791	100	37	<0.01
Maize 2016	Callisto	Mesotrione (P)	Jun 16*****	Jun 16*	-	-	79	29	-
		AMBA(M)	Jun 16*****	Jun 16*	-	-	79	29	-
		MNBA(M)	Jun 16*****	Jun 16*	-	-	79	29	-
	MaisTer Foramsulfuron	Foransulfuron (P)	Jun 16	Jun 16*	-	-	-	-	-
		AE-F130619(M)	Jun 16	Jun 16*	-	-	-	-	-
		AE-F092944(M)	Jun 16	Jun 16*	-	-	-	-	-
	Iodosulfuron	Triazinamine(M)	Jun 16	Jun 16*	-	-	-	-	-
	Harmony SX Thifensulfuron-methyl	Triazinamine(M)	Jun 16	Jun 16*	-	-	-	-	-

Systematic chemical nomenclature for the analysed pesticides is given in Appendix 1.
Monitoring continues the following year.
***3 May 2013: Sowing spring barley, replacing winter wheat injured by frost.*
**** Mesotrione was applied twice as Callisto on 27 May 2015 and 9 June 2015.*
***** Foramsulfuron was applied twice as MaisTer on 9 June 2015 and 23 June 2015.*
******Mesotrione was applied twice as Callisto on 6 June 2016 and 22 June 2016.*

The current report focuses on the pesticides applied from 2014 and onwards, while the leaching risk of pesticides applied in 2013 and before, has been evaluated in previous monitoring reports (see http://pesticidvarsling.dk/monitor_uk/index.html).

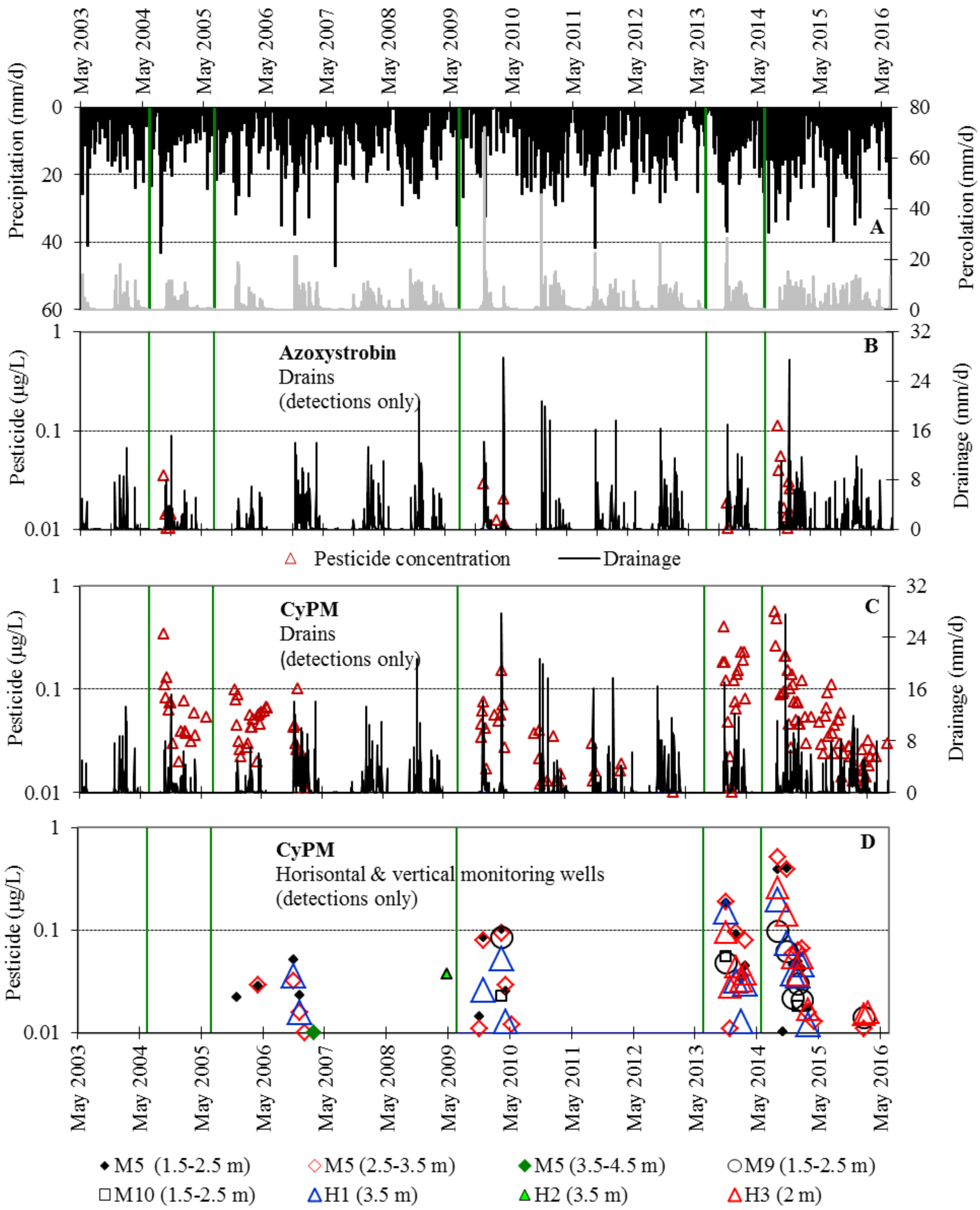

Figure 4.6. Azoxystrobin and **CyPM** detections at **Silstrup**: Precipitation and simulated percolation 1 m b.g.s. (A) together with the concentration of azoxystrobin (B) and CyPM (C) in the drainage runoff, and the concentration of CyPM (D) in water samples collected from the groundwater monitoring screens (including horizontal screens). The green vertical lines indicate the dates of azoxystrobin applications. Values below the detection limit of 0.01 µg L^{-1} are shown as 0.01 µg L^{-1} (all graphs).

In total, **azoxystrobin** has been applied at Silstrup five times between June 2004 and June 2014 (Figure 4.6), most recently on 4 June 2014. On 27 August 2014 the concentration of azoxystrobin was 0.11 µg L^{-1} in drainage (Figur 4.6B), which is the highest concentration ever at Silstrup. Throughout the period 2004-2016 azoxystrobin has been detected in only eight of 546 groundwater samples, and always below 0.1 µg L^{-1}. Seven of the detections have, however, been obtained since the June 2014 application (data not shown). In drainage, azoxystrobin has been detected in 23 of 162 samples, with 0.11 µg L^{-1} on 27 August 2014 as the sole above 0.1 µg L^{-1}. In a total of 208 drainage samples just 56 did not contain CyPM, a degradation product of azoxystrobin, whereas 26 contained more than 0.1 µg L^{-1}. Highest concentrations followed the 2013 and in particular the 2014 application (Figure 4.6C). The maximal concentration of CyPM in drainage was 0.56 µg L^{-1} found in a sample obtained on 27 August 2014. Out of 738 groundwater samples taken over the years at Silstrup, 100 samples contained CyPM, whereof 14 exceeded 0.1 µg L^{-1}. 10 of the 14 highest concentrations was found after the application in 2014, with a maximal concentration of 0.39 and 0.52 µg L^{-1} in the two uppermost screens of the vertical monitoring well M5 (Figure 4.6D). Since July 2014, CyPM has not been detected in the eight samples collected from the upgradient well M10, whereas it has been detected in: 57 out of 63 water samples from drainage (90 %) with 10 exceeding 0.1 µg L^{-1}, 22 water samples out of 101 (22%) collected from the downgradient wells with four detections exceeding 0.1 µg L^{-1}, 8 out of 30 water samples (27%) collected from H1 (3.5 m depth) with one detection exceeding 0.1 µg L^{-1}, 20 out of 42 water samples (48%) collected at H3 (2 m depth) with 4 exceeding 0.1 µg L^{-1}. This reveals that the distance from the surface reduce the number of detections and that the source is coming from the surface and not upgradient fields. Monitoring is ongoing.

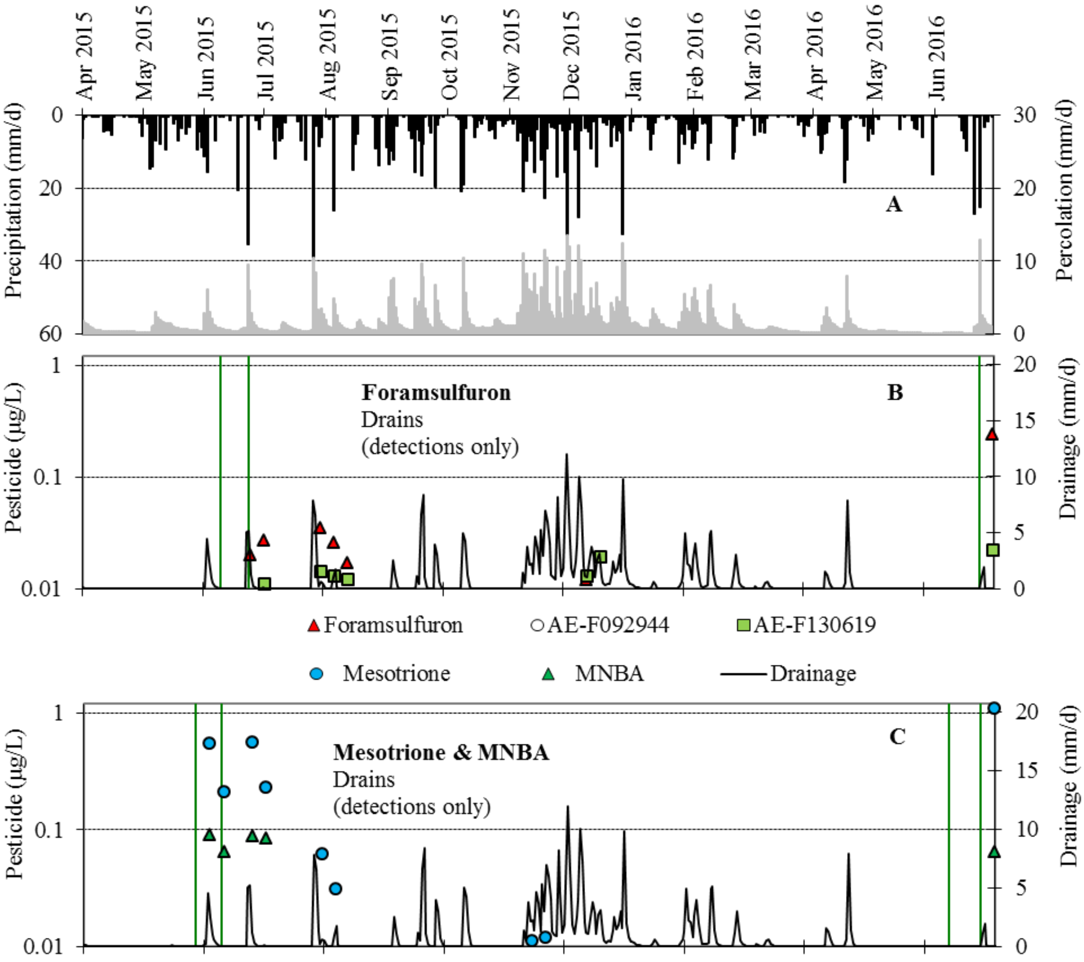

Figure 4.7. Foramsulfuron, AE-F092944, AE-F120619, and **Mesotrione** and **MNBA** detections in samples of drainage at **Silstrup**: Precipitation and simulated percolation 1 m b.g.s. (A) together with the concentration of mesotrione and MNBA (B); and foramsulfuron (C) in the drainage runoff. The green vertical lines indicate the dates of pesticide application. Values below the detection limit of 0.01 µg L^{-1} are shown as 0.01 µg L^{-1} (all graphs).

Foramsulfuron and two of its degradation products were included in PLAP in May 2015. Foramsulfuron has been applied on three occassions, twice in June 2015 and once in June 2016 (Figure 4.7B). In samples of drainage, foramsulfuron and the degradation product AE-F130619 were found in concentrations up to 0.035 µg L^{-1} and 0.014 µg L^{-1}, respectively in the months following the 2015 application. After the 2016 application the concentration of foramsulfuron in the drainage water was 0.24 µg L^{-1} and 0.022 µg L^{-1} of AE-F130619 (Figure 4.7B). The degradation product AE-F092944 was not found in drainage at all (Figure 4.7B). AE-F092944 was also never found in groundwater samples, whereas both foramsulfuron and AE-F130619 were detected in 4 and 7 samples, respectively. In none of 102 groundwater samples did the concentrations exceed 0.1 µg L^{-1}.

Mesotrione was applied to a crop of maize in late May and early June 2015, and again in twice in June 2016 (Figure 4.7C). Without any detected background concentration before application, a very high concentration (0.55 µg L^{-1}) was detected in the first drainage sample collected less than a week after the first application. The two next drainage samples collected in June 2015 also contained the compound in concentrations above 0.1 µg L^{-1} (Figure 4.7C). No detections of mesotrione was obtained from the groundwater samples in June 2015. The same detection pattern was found for its degradation product MNBA, with concentrations detected in drainage ranging between 0.065 µg L^{-1} and 0.09 µg L^{-1}. Another degradation product of mesotrione, AMBA, was not detected. After the two applications in June 2016, mesotrione was found in a very high concentration - 1.1 µg L^{-1} in samples of drainage. MNBA in drainage reached a concentration of 0.064 µg L^{-1}. These concentrations were obtained just one week after the second application of mesotrione. Results are preliminary and monitoring is ongoing.

Glyphosate was sprayed in July 2014, 23 days before the harvest of winter wheat. At the first sampling of drainage on 27 August 2014 (32 days after application), the concentration of glyphosate and AMPA (a degradation product of glyphosate) was 0.27 µg L^{-1} and 0.089 µg L^{-1}, respectively (Figure 4.8). Out of the 66 drainage samples, 22 (33%) contained glyphosate and 54 (82%) contained AMPA in concentrations up to 0.27 µg L^{-1} and 0.14 µg L^{-1}, respectively (Figure 4.8). Glyphosate and AMPA were detected in 15 and 16 groundwater samples out of 171, respectively, in concentrations not exceeding 0.1 µg L^{-1} (Figure 4.8D-E).

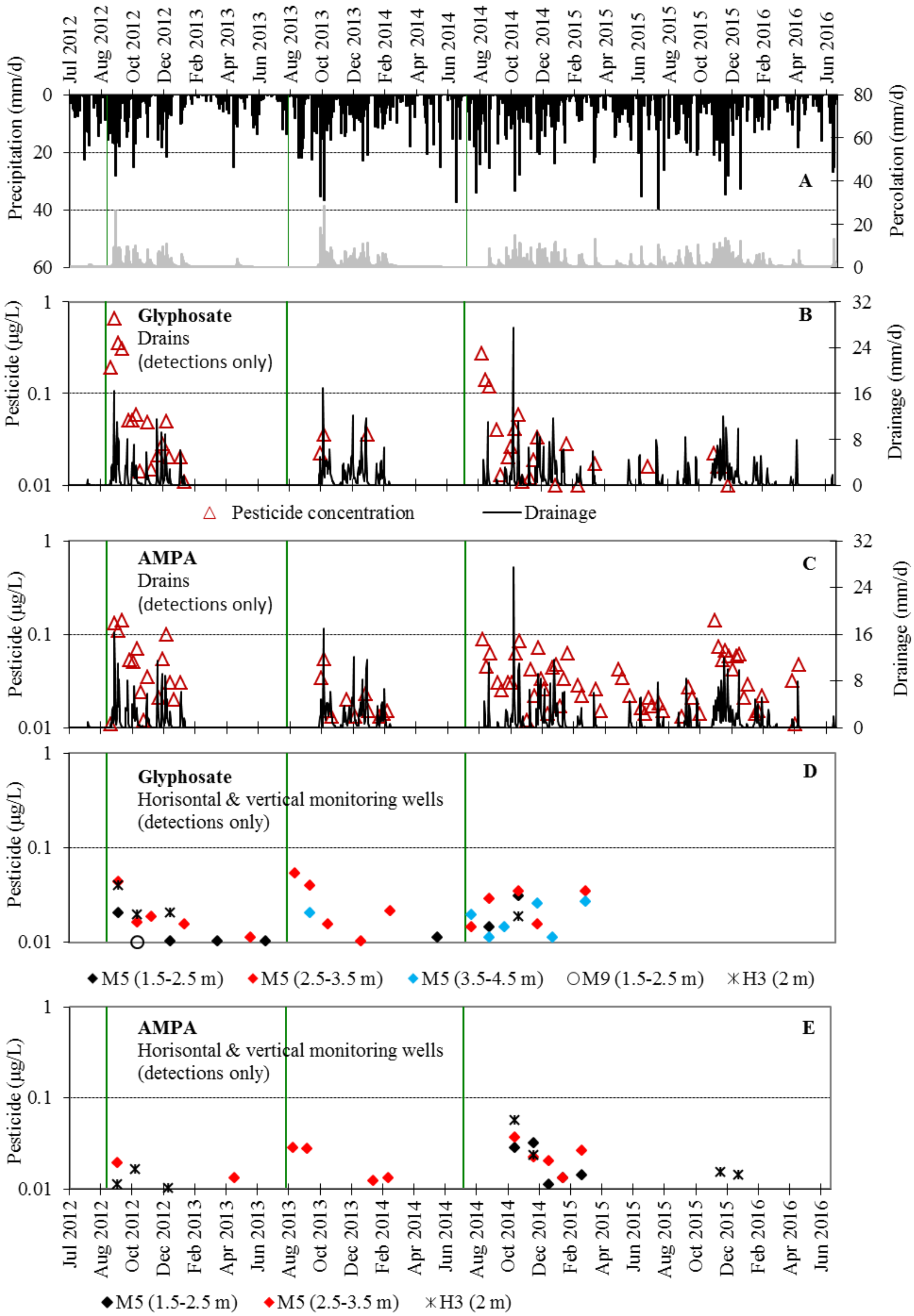

Figure 4.8. Glyphosate and AMPA detections at **Silstrup**: Precipitation and simulated percolation 1 m b.g.s. (A) together with the concentration of glyphosate (B) and AMPA (C) in water samples collected from the drainage and the concentration of glyphosate (D) and AMPA (E) in water samples collected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

5 Pesticide leaching at Estrup

5.1 Materials and methods

5.1.1 Field 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 nearly flat (Figure 5.1). The field is highly heterogeneous with considerable variation in both topsoil and aquifer characteristics (Lindhardt *et al.*, 2001), which is quite common for this geological formation. 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^{-1}, which is about two orders of magnitude lower than at the other clayey till fields (Table 1.1). The geological structure is complex comprising clayey 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 at 3.5 m b.g.s. to be installed in 2000. 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 at Estrup during the 2015-16 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/monitor_uk/index.html.

On 29 April 2015 the field was fertilized with acidified pig slurry and subsequently ploughed. On 11 May 2015 maize (cv. Ambition) was sown. Spraying of weeds was done on three occasions using mesotrione and thifensulfuron-methyl on 27 May 2015; mesotrione, foramsulfuron and iodosulfuron on 6 June 2015; and foramsulfuron, iodosulfuron and fluroxypyr on 30 June 2015. Mesotrione and two of its degradation products, AMBA and MNBA, as well as foramsulfuron and two of its degradation products, AE-F130619 and AE-F092944, were included in the monitoring. On 23 October 2015 the maize was harvested as silage yielding 105.98 hkg ha^{-1} (100 % dry matter).

Pig slurry was applied to the field 4 May 2016. On 5 May 2016 the field was ploughed. The field was sown with maize (cv. Ambition) 6 May 2016. Spraying of weeds was done three times: On 1 June 2016 mesotrione and thifensulfuron-methyl were used; on 11 June 2016 mesotrione, foramsulfuron and iodosulfuron, and on 16 June 2016 foramsulfuron and iodosulfuron. The monitoring program of 2015 was continued and complemented with triazinamine (IN-A4098), a degradation product of both thifensulfuron-methyl and iodosulfuron.

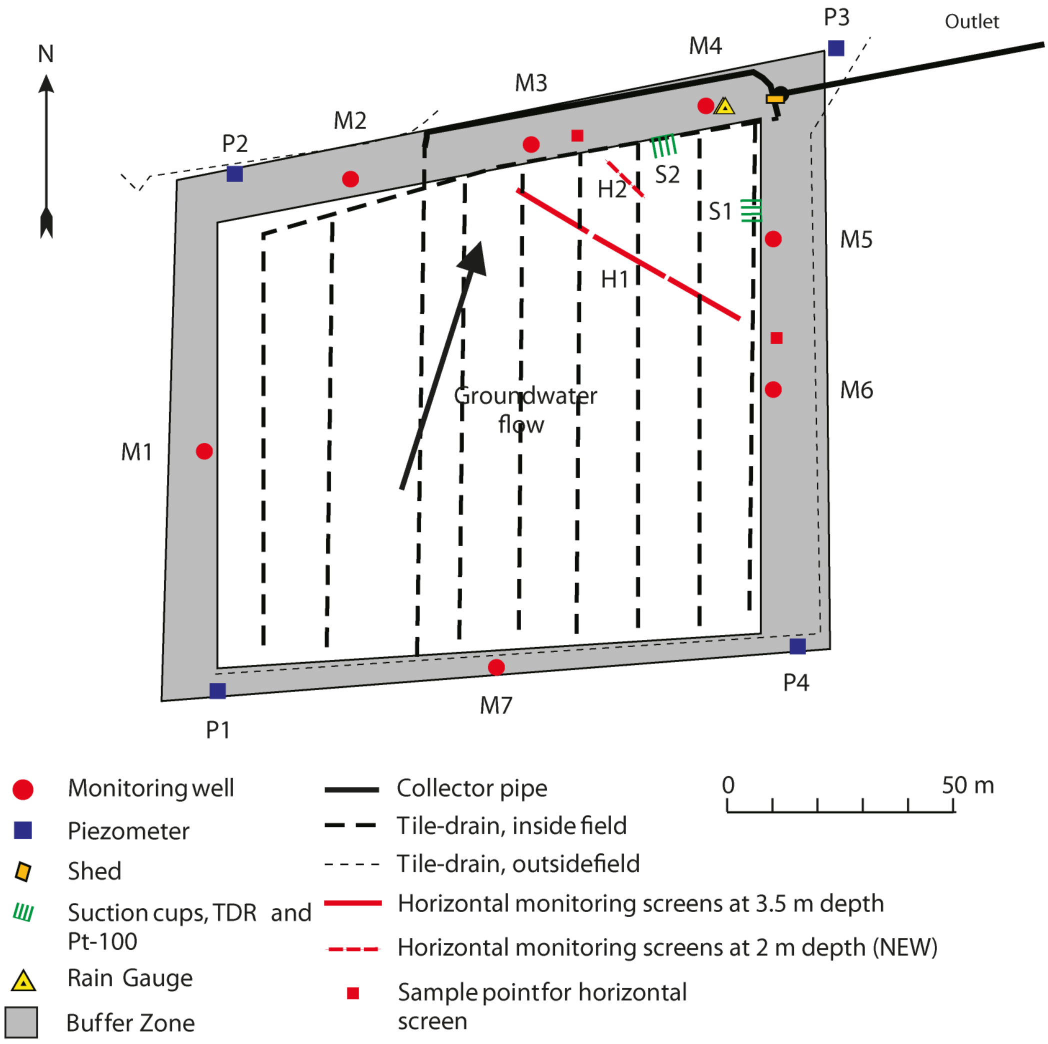

Figure 5.1. Overview of the **Estrup** field. The innermost white area indicates the cultivated area, while the grey area indicates the surrounding buffer zone. The positions of the various installations are indicated, as is the direction of groundwater flow. Pesticide monitoring is conducted weekly 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.

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 2016 and to establish an annual water balance.

Compared to the setup in Rosenbom *et al.* (2016), 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 2016. 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 except for the drop in level during summer 2015 and 2016 (Figure 5.2B). This drop normally captured by the model during the other summers, is coherent with a drop in water saturation at 0.25 m depth (Figure 5.2D), which is also not captured by the model. Since the subsoil TDR data are limited, a more detailed study of soil water dynamics in these layers is difficult. Sometimes TDR probes do not have a good contact to the surrounding soil, which could be the case at 25 cm depth where the TDR are reinstalled after ploughing. The high drainage values in the autumn of 2015 are not captured very well, since the model underpredicts these values, while also overpredicting the soil water content at 0.25 m b.g.s. (Figure 5.2C and 5.2D). As in previous years (Rosenbom *et al.*, 2016), the simulated groundwater table often fluctuates slightly above the drain depth resulting in long periods of measured drainage.

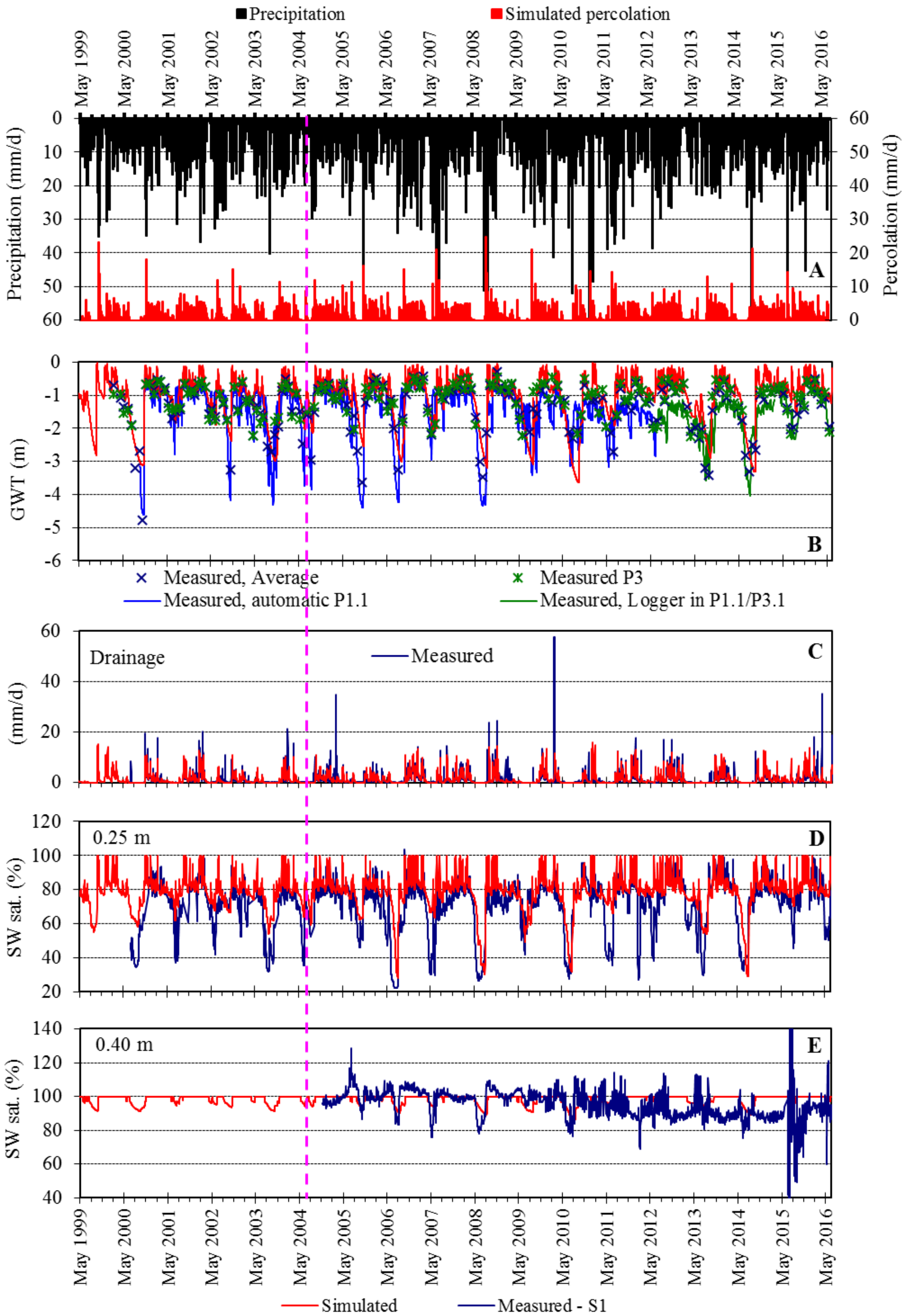

Figure 5.2. Soil water dynamics at **Estrup**: Measured precipitation and simulated percolation 0.6 m b.g.s. (A), simulated and measured groundwater table, GWT (B), simulated and measured drainage (C), and simulated and measured soil saturation (SW sat.) at two different soil depths (D and E). The measured 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 2016).

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	1173	466	–	553	154[4)]
01.07.00–30.06.01	968	887	420	356	340	111
01.07.01–30.06.02	968	1290	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	1087	476	525	468	86
01.07.05–30.06.06	968	897	441	258	341	199
01.07.06–30.06.07	968	1365	515	547	618	303
01.07.07–30.06.08	968	1045	478	521	556	46
01.07.08–30.06.09	968	1065	480	523	362	62
01.07.09–30.06.10	968	1190	533	499	523	158
01.07.10–30.06.11	968	1158	486	210	341	462
01.07.11–30.06.12	968	1222	404	479	577	339
01.07.12–30.06.13	968	1093	386	503	564	204
01.07.13–30.06.14	968	1015	513	404	449	97
01.07.14–30.06.15	968	1190	419	379	532	392
01.07.15–30.06.16	968	1208	386	491	618	330

[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 - actual evapotranspiration - 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 significant initiation of the continuous drainage period in fall 2014. Drainage measured in connection with snowmelt seemed more or less well captured this hydrological year. 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 16 years, the recent hydrological year July 2014-June 2016 was characterized by the third highest precipitation since monitoring started, an intermediate simulated actual evapotranspiration, high simulated drainage and intermediate-high measured drainage. Precipitation in the months of this year was characterized by January and May having the second highest precipitation since the PLAP-monitoring started and July and November being dry (Appendix 4).

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 at 3.5 m depth reflecting a slow transport due to the low hydraulic conductivity.

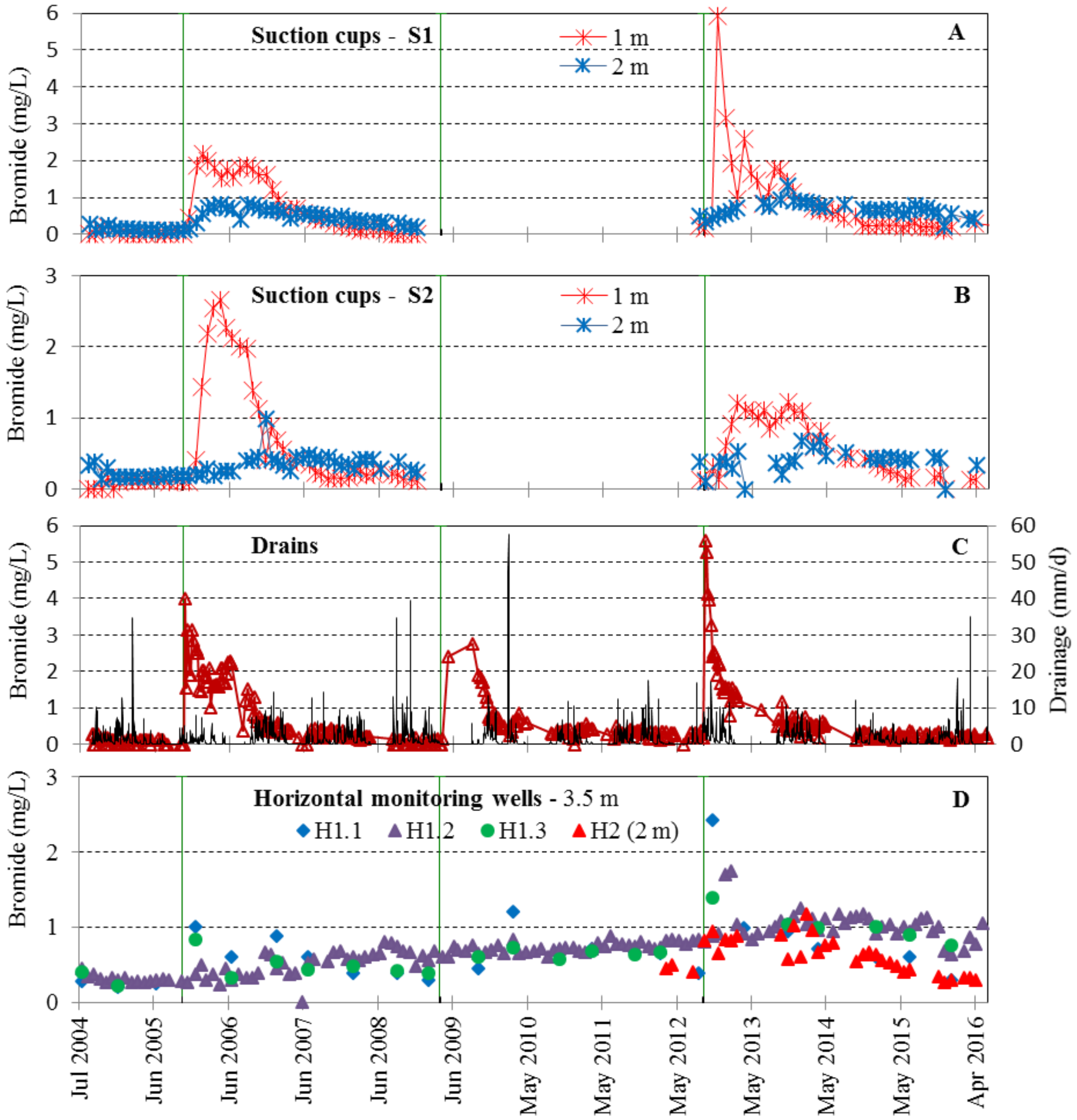

Figure 5.3. Bromide concentration at **Estrup**. A and B refer to suction cups located at S1 and S2, respectively. The bromide concentration is also shown for drainage runoff (C) and the horizontal monitoring well H1 and H3 (D). From September 2008 to August 2012, bromide measurements in the suction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

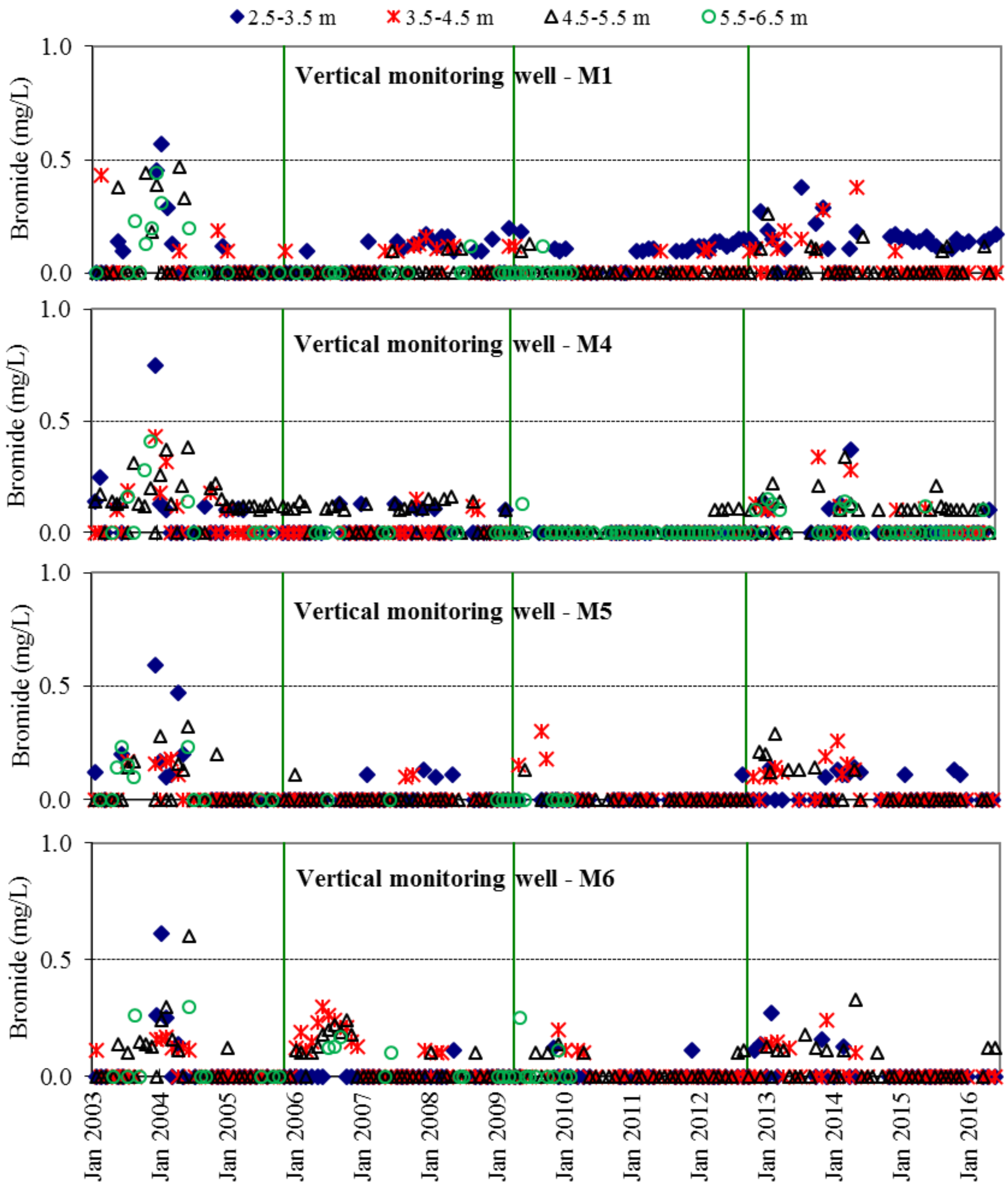

Figure 5.4. Bromide concentration at **Estrup**. The data derive from the vertical monitoring wells (M1, M4, M5 and M6). Screen depth is indicated in m b.g.s. In September 2008, monitoring wells M3 and M7 were suspended. The green vertical lines indicate the dates of the three most recent bromide applications.

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 (2008-2016) and Table A7.4 in Appendix 7 (2000-2007). Pesticide application during the most recent growing season (2014-2016) is shown together with precipitation and simulated percolation 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 June 2016 are not evaluated in this report and are although included in Table 5.2.

The current report focuses on pesticides applied from 2014 and onwards, while leaching risk of pesticides applied in 2013 and before has been evaluated in previous monitoring reports (see http://pesticidvarsling.dk/monitor_uk/index.html).

Table 5.2. Pesticides analysed at **Estrup**. For each compound it is listed, whether it is a pesticide (P) or degradation product (M), as well as the application date (Appl. date) and end of monitoring period (End. mon.). Precipitation (precip. in mm) and percolation (percol. in mm) 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 [µg L^{-1}] at 1 m depth the first year after application. See Appendix 2 for calculation method and Appendix 8 (Table A8.4) for previous applications of pesticides.

Crop	Applied product	Analysed Pesticide	Appl. date	End mon.	Y 1st precip	Y 1st percol	M 1st precip	M 1st percol	C_{mean}
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)	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 (M)	Apr 11	Dec 12	1217	276	45	2	<0.01
	Flexity	Metrafenone(P)	May 11	Apr 15	1219	283	114	6	0.02
	Roundup Max	Glyphosate(P)	Oct 11	Jun 15	1150	295	94	26	0.88
		AMPA(M)	Oct 11	Jun 15	1150	295	94	26	0.26
Spring barley 2012	Amistar	Azoxystrobin(P)	Jun 12	Jun 15*	1083	281	151	29	0.04
		CyPM(M)	Jun 12	Jun 15*	1083	281	151	29	0.24
	Fox 480 SC	Bifenox(P)	May 12	Dec 12	1090	281	39	13	< 0.02
		Bifenox acid(M)	May 12	Dec 12	1090	281	39	13	0.011
		Nitrofen(M)	May 12	Dec 12	1090	281	39	13	< 0.02
	Mustang forte	Aminopyralid(P)	May 12	Jun 13	1098	285	50	14	< 0.01
Pea 2013	Fighter 480	Bentazone(P)**	May 13	Jun 16*	1071	248	35	10	0.059
	Command CS	Clomazone(P)	Apr 13	Apr 15	1094	243	61	17	<0.01
		FMC-65317(M)	Apr 13	Apr 15	1094	243	61	17	<0.02
	Glyfonova 450 Plus	Glyphosate(P)	Aug 13	Jun 16*	928	237	131	13	0.10
		AMPA(M)	Aug 13	Jun 16*	928	237	131	13	0.07
Winter wheat 2013	DFF	Diflufenican(P)	Nov 13	Apr 15	582	165	86	30	0.19
		AE-05422291(M)	Nov 13	Apr 15	582	165	86	30	<0.01
		AE-B107137(M)	Nov 13	Apr 15	582	165	86	30	0.03
	Folicur EC 250 Tebuconazole (P)	1,2,4-triazole(M)	May 14	Jun 16*	1152	249	51	0.4	0.01
	Amistar	Azoxystrobin(P)	Jun 14	Jun 16*	1176	257	49	0	0.02
		CyPM(M)	Jun 14	Jun 16*	1176	257	49	0	0.38
	Glyfonova 450 Plus	Glyphosate(P)	Jul 14	May 16	1219	305	117	0	0.06
		AMPA(M)	Jul 14	May 16	1219	305	117	0	0.1
Maize 2015	Callisto***	Mesotrione(P)	May 15	Jun 16*	1196	299	91	23	0.11
		AMBA(M)	May 15	Jun 16*	1196	299	91	23	<0.01
		MNBA(M)	May 15	Jun 16*	1196	299	91	23	<0.01
	MaisTer****	Foramsulfuron(P)	May 15	Jun 16*	1196	299	91	23	<0.01
		AE-F130619(M)	May 15	Jun 16*	1196	299	91	23	<0.01
		AE-F092944(M)	May 15	Jun 16*	1196	299	91	23	<0.01
Maize 2016	Callisto	Mesotrione(P)	Jun 16	Jun 16*	-	-	110	0	<0.01
		AMBA(M)	Jun 16	Jun 16*	-	-	110	0	<0.01
		MNBA(M)	Jun 16	Jun 16*	-	-	110	0	<0.01
	Harmony SX Thifensulfuron-methyl (P)	Triazinamine(M)	Jun 16	Jun 16*	-	-	-	-	-
	MaisTer	Foramsulfuron(P)	Jun 16	Jun 16*	-	-	-	-	-
		AE-F130619(M)	Jun 16	Jun 16*	-	-	-	-	-
		AE-F092944(M)	Jun 16	Jun 16*	-	-	-	-	-

Systematic chemical nomenclature for the analysed pesticides is given in Appendix 1.
Monitoring continues the following year.
**Bentazone applied on 16 May 2013, and Command CS, clomazone, on 25 April 2013.*
***Mesotrione was applied twice as Callisto on 27 May 2015 and 6 June 2015.*
****Foramsulfuron was applied twice as MaisTer on 6 June 2015 and 30 June 2015.*

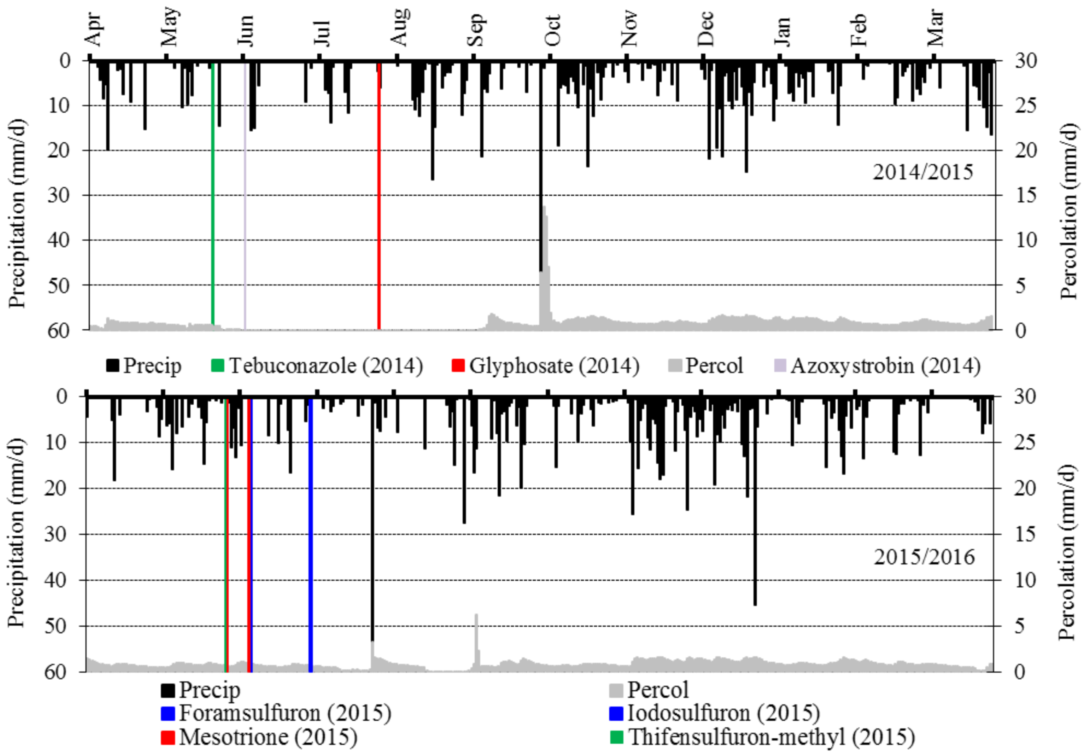

Figure 5.5. Application of pesticides included in the monitoring programme and precipitation (primary axis) together with simulated percolation 1 m b.g.s. (secondary axis) at **Estrup** in 2014/2015 (upper) and 2015/2016 (lower).

Azoxystrobin has now been applied six times at Estrup: 22 June 2004, 29 June 2006, 13 June 2008, 4 June 2009, 13 June 2012 and 2 June 2014 (Figure 5.6). Before that, azoxystrobin was applied in June 1998 (Lindhardt *et al.*, 2001). All six applications caused leaching of azoxystrobin and its degradation product CyPM to the drainage, when drainage flow commenced. Concentrations in drainage of the two compounds are shown in Figure 5.6B and 5.6C. The maximum concentrations detected in drainage was 1.4 µg $L^{-1}$of azoxystrobin on 24 August 2006, and 2.1 µg L^{-1} of CyPM on 11 September 2008. A total of 395 drainage samples were taken from August 2004 to April 2016. Azoxystrobin was detected in 141 of the samples and above 0.1 µg L^{-1} in 16 samples. In only 38 of the 395 drainage samples CyPM was absent, and 151 held a concentration above 0.1 µg L^{-1}. During the same period 726 groundwater samples were collected and only two had detections of azoxystrobin, highest reading being 0.04 µg L^{-1}. In the 726 groundwater samples CyPM was detected in 38, of which five were above the limit. The first one above being 0.13 µg L^{-1} in a sample from the horizontal well H2 collected October 2012. The remaining four samples exceeding the limit were also from H2, and the highest concentration found was 0.46 µg L^{-1} in November 2014 (Figure 5.6D). The leaching pattern of azoxystrobin and CyPM is further described in Jørgensen *et al.*, 2012a and Jørgensen *et al.*, 2013. Monitoring continues.

The herbicide **glyphosate** has been applied seven times at Estrup, of which 6 can be seen in Figure 5.7. Following all applications, both glyphosate and AMPA were detected in the drainage. Out of 578 drainage water samples analysed for glyphosate and AMPA during the period from 31 October 2000 to 20 April 2016, the concentrations of glyphosate and AMPA exceeded 0.1 µg L^{-1} in 113 and 125 samples, respectively (Figure 5.7B-C).

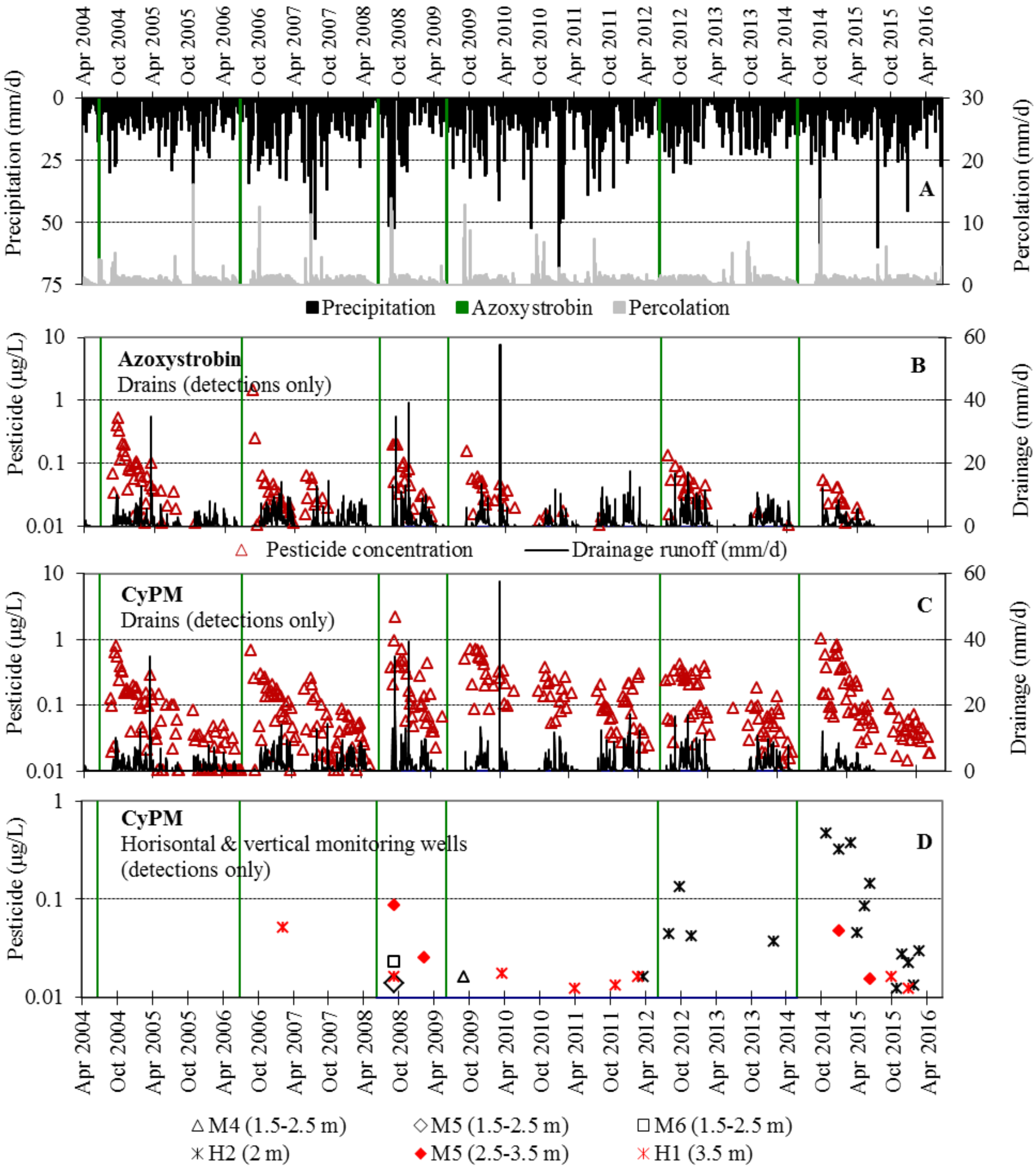

Figure 5.6. Azoxystrobin and CyPM detections at **Estrup**: Precipitation and simulated percolation 0.6 m b.g.s. (A) together with concentration of azoxystrobin (B) and CyPM (C) in water samples from drainage (DR on the secondary axis)**.** Detections of CyPM in water samples collected from groundwater monitoring screens are indicated in D. Azoxystrobin was only detected twice in groundwater collected from the horizontal and vertical monitoring screens (see text). The green vertical lines indicate the dates of applications. Values below the detection limit of 0.01 µg L^{-1} are shown as 0.01 µg L^{-1} (all graphs).

During that period AMPA never exceeded 0.1 µg L^{-1} in groundwater (Figure 5.7E and Table A5.4 in Appendix 5), whereas glyphosate did so in five of 1017 groundwater samples (Figure 5.7D). The highest concentrations of 0.59 µg L^{-1} and 0.67 µg L^{-1} were found in samples collected from two vertical wells on 7 July 2005. In the horizontal wells, the highest concentration of 0.21 µg L^{-1} was found in a sample collected on 6 October 2011 (Figure 5.7D and Table A5.4 in Appendix 5). Like in the beginning of 2013, snowmelt seems to cause detection of glyphosate exceeding 0.1 µg L^{-1} in the groundwater in March 2016, more than two years after application. Also a heavy rain event in August-September 2015 triggered a detection in the groundwater of 0.09 µg L^{-1}. Monitoring continues.

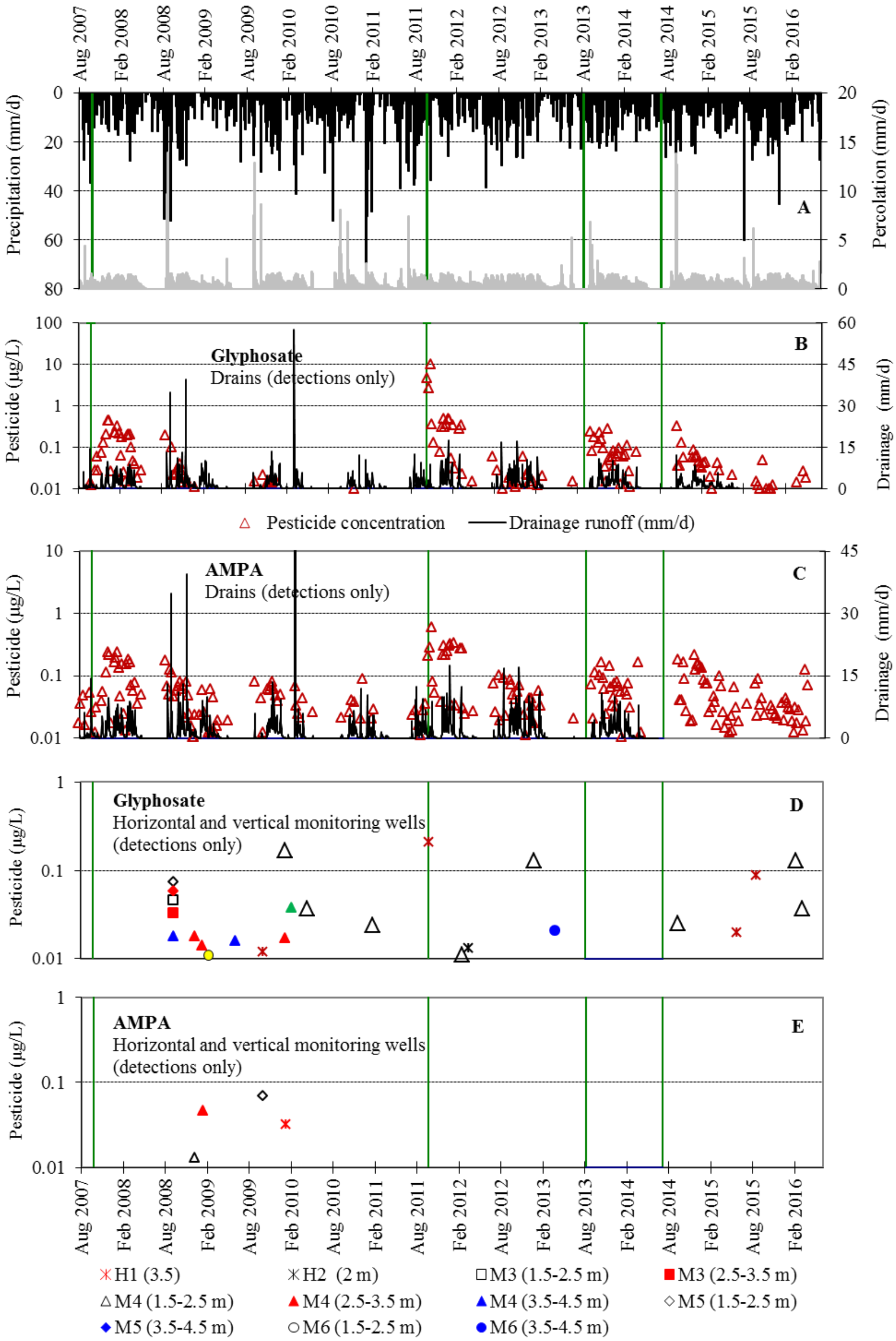

Figure 5.7. Glyphosate and **AMPA** detections at **Estrup**: Precipitation and simulated percolation 0.6 m b.g.s. (A) together with the concentration of glyphosate (B) and AMPA (C) in water samples from drainage (Drainage Runoff, DR, on the secondary axis). Data represent an eight-year period including four applications of glyphosate as indicated by the green vertical lines. Detection of glyphosate and AMPA in water samples from 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).

Bentazone has been used 3 times at Estrup since May 2001, and most recently on peas in May 2013. Out of a 432 samples of drainage water 222 contained bentazone, 15 thereof above 0.1 µg L^{-1}, the highest concentration being 20 µg L^{-1} in samples taken 8 July 2005. Related to the use of bentazone in 2013, the compound was found in 65 of 99 drainage water samples and in 28 of 167 groundwater samples. The highest concentration related to the 2013 application was 2.8 µg L^{-1} found in a drainage sample on 3 July 2013 (Figure 5.8B). Three drainage samples and no groundwater samples showed concentrations above 0.1 µg L^{-1} (Figure 5.8C). Monitoring was terminated 27 April 2016.

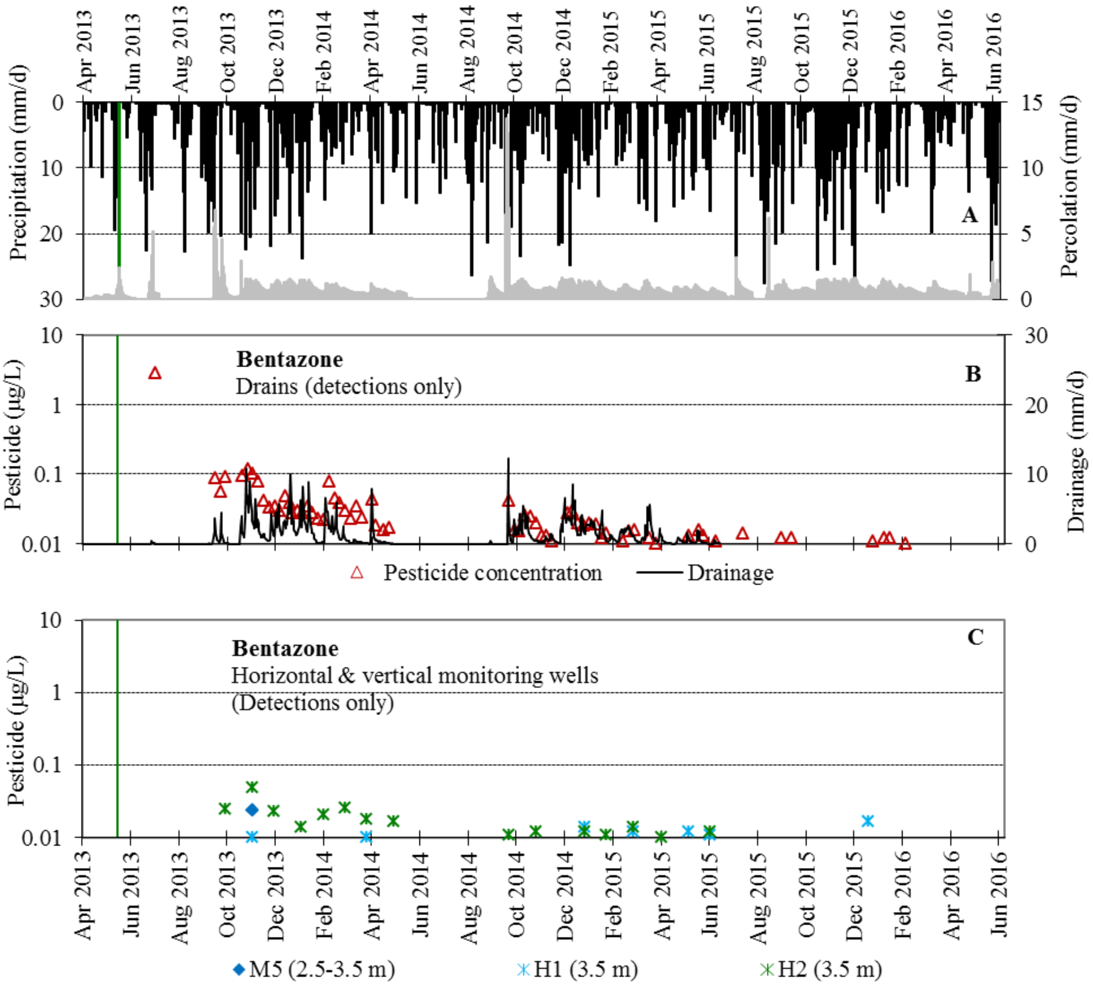

Figure 5.8. Bentazone detections at **Estrup**: Precipitation and simulated percolation 1 m b.g.s. (A) together with the concentration of bentazone (B) in water samples collected from drainage and in groundwater. The green vertical line indicates the date of bentazone application.

The herbicides **foramsulfuron** and iodosulfuron were applied in maize on 6 and 30 June 2015, and again on 11 and 16 June 2016. Foramsulfuron and its two degradation products AE-F130619 and AE-F092944, were included in the monitoring. The first detection of foramsulfuron was in a drainage sample 24 June 2015 at 0.025 µg L^{-1}. Out of 35 drainage water samples taken, 16 contained foramsulfuron, one being above 0.1 µg L^{-1}: 0.32 µg L^{-1} on 29 July 2015. In 67 groundwater samples there were no traces of foramsulfuron. The two degradation products were not found in groundwater samples. However one drainage water sample had a concentration of 0.012 µg L^{-1} of AE-F092944 and two held 0.011 µg L^{-1} and 0.023 µg L^{-1} of AE-F130619. Monitoring ended on 29 June 2016.

The herbicide **mesotrione** was used in maize in May and June 2015 and twice in June 2016. Mesotrione and two of its degradation products, AMBA and MNBA, are included in the monitoring (as also the case at Silstrup). The same detection pattern as in Silstrup is revealed. None of the three compounds were detected in the background samples collected before application (Figure 5.9). Mesotrione, AMBA and MNBA were detected in 25, 8 and 4 samples out of a total of 39 drainage samples, respectively. Shortly after application, the concentration of mesotrione in drainage samples was found to be 3.3 µg L^{-1}, and since the application in 2015 25 out of 39 drainage samples have contained mesotrion, 9 in concentrations higher than 0.1 µg L^{-1}. AMBA was detected 4 times in drainage always below 0.1 µg L^{-1}. The MNBA was found in 8 of 31 drainage samples, 2 were above 0.1 µg L^{-1} highest being 0.46 µg L^{-1} shortly after application. From the first application of mesotrione in May 2015 to last in June 2016, the horizontal and vertical monitoring wells were sampled at a total of 13 different dates. Only at the very first sampling, following the application, mesotrione and the degradation products MNBA could be detected in the samples. Mesotrione was detected in three groundwater samples, highest concentration being 0.13 µg L^{-1} in water from a horizontal well at 2 m depth. MNBA was only detected once in the groundwater from M5.2 (0.017 µg L^{-1}) together with mesotrione in a concentration of 0.047 µg L^{-1}. The AMBA was not detected in any of the groundwater samples. Monitoring is ongoing.

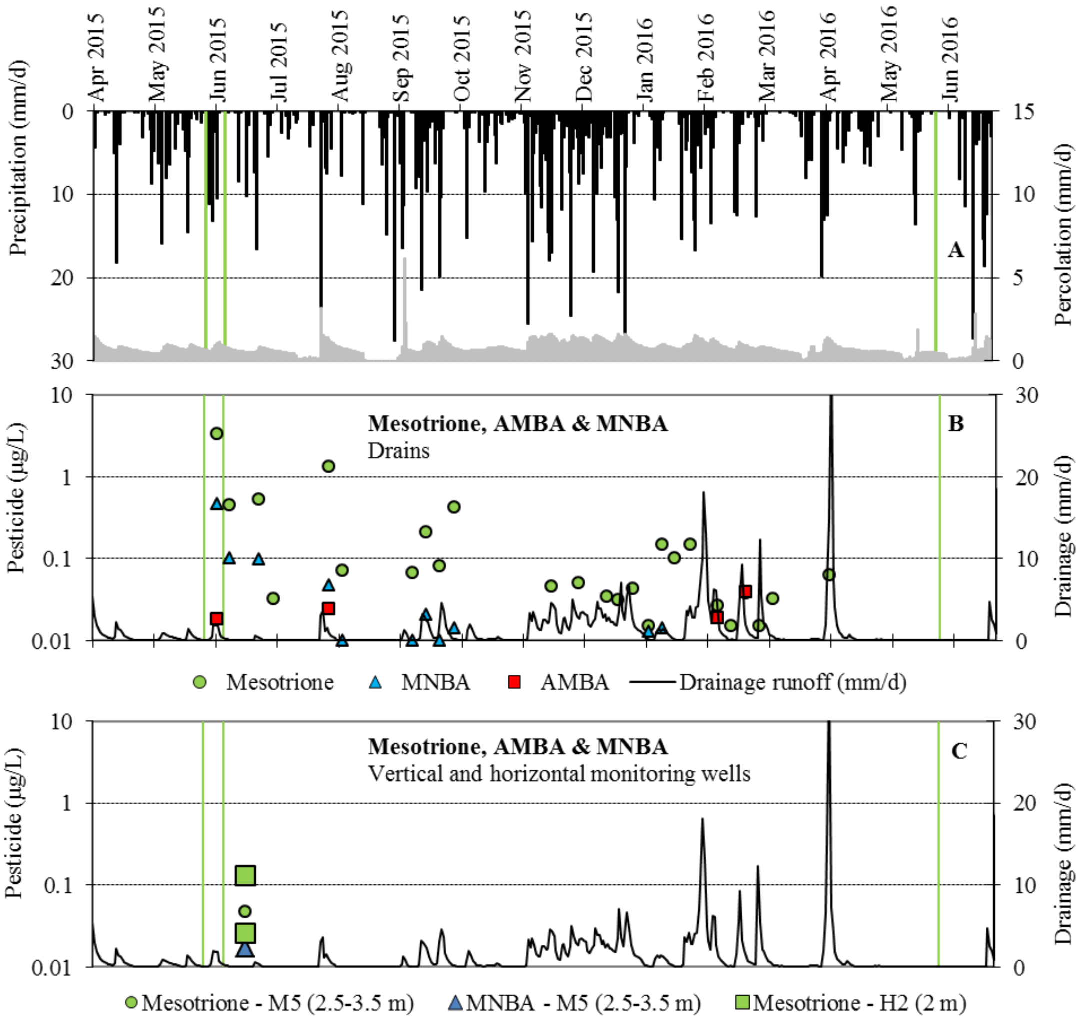

Figure 5.9. Mesotrione, AMBA and MNBA detections at **Estrup**: Precipitation and simulated percolation 1 m b.g.s. (A) together with the concentration of Mesotrione, AMBA and MNBA in water samples collected from drainage (B) and groundwater samples (C). The green vertical line indicates the date of mesotrione application.

The fungicide **tebuconazole** was sprayed on the winter wheat on 20 May 2014, and the leaching of its degradation product 1,2,4-triazole was monitored (Figure 5.10). As seen from Figure 5.10B, drainage did not start until 1 October 2014, at which time a concentration of 0.26 µg L^{-1} 1,2,4-triazole was detected. It was hence not possible to obtain background samples of the drainage before application. All 76 drainage samples collected between 1 October 2014 and 4 May 2015 contained 1,2,4-triazole and only two of these contained less than 0.1 µg L^{-1}. The highest concentration found was 0.45 µg L^{-1} on 29 July 2015. Figure 5.10C shows that 1,2,4-triazole was present in the groundwater before tebuconazole was applied and even in a concentration above 0.1 µg L^{-1} as detected in a groundwater sample collected from the uppermost screen of M4 (1.5-2.5 m depth). It is worth noticing that the concentration of 1,2,4-triazole is almost constant over time for most sampling points, and that the concentration levels seem to decline with sampling depth (no detections at 3.5-5.5 m depth). This could indicate that the source is from above. Nevertheless, the high background concentration in groundwater clearly indicates that other 1,2,4-triazole sources than the most recent application of tebuconazole must exist. Propiconazole, epoxiconazole and tebuconazole have all been applied on the PLAP-field before and perhaps there is also a 1,2,4-triazole contribution from upstream neighboring fields to the upper groundwater zone of the PLAP-field, as 1,2,4-triazole is also detected in the upstream well M1. The processes involving the formations and sources of 1,2,4-triazole needs to be resolved in detailed studies. Monitoring is ongoing.

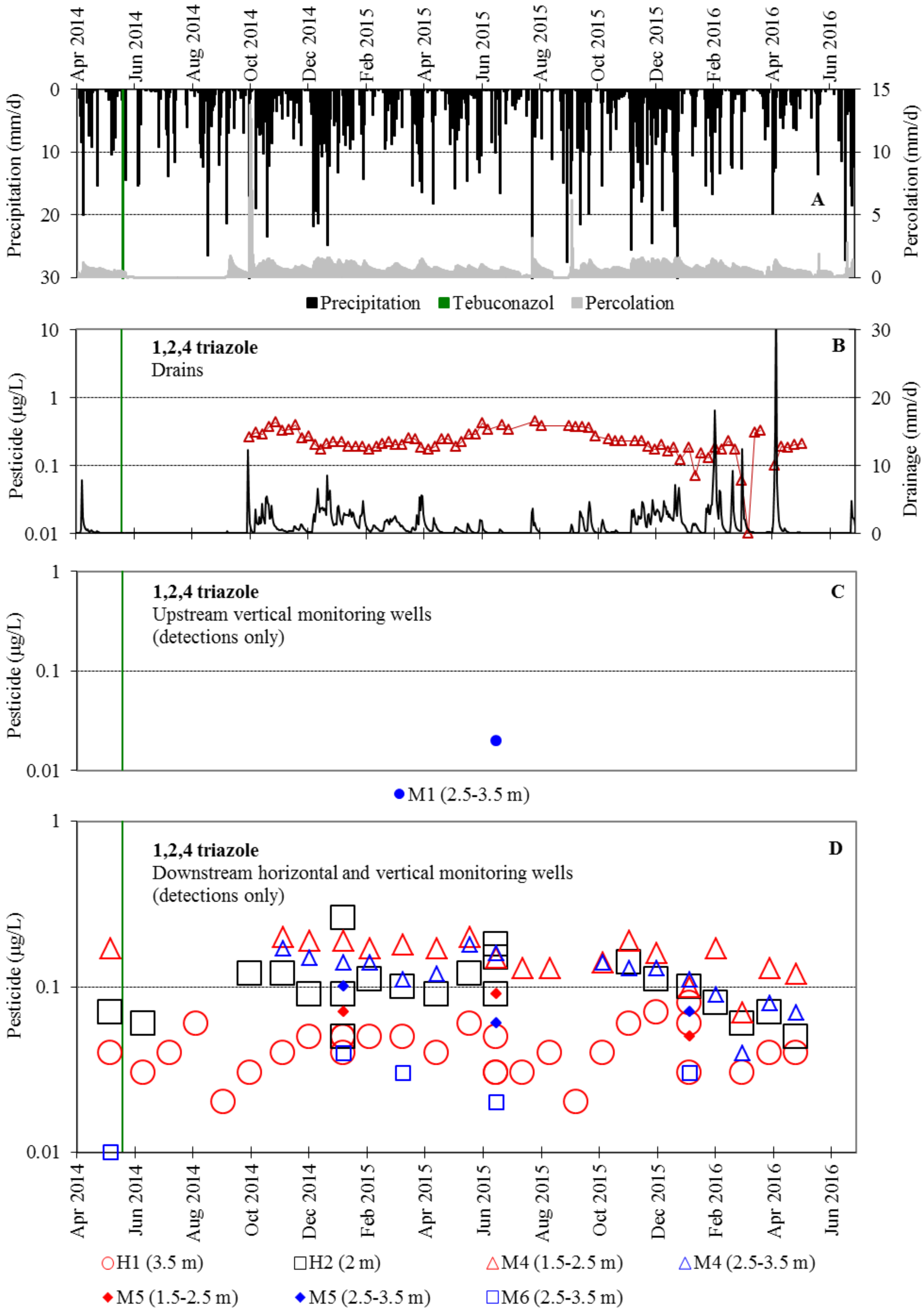

Figure 5.10. 1,2,4-triazole detections at **Estrup**: Precipitation, irrigation and simulated percolation 1 m b.g.s. (A) together with measured concentration of 1,2,4-triazole detections in drainage water and groundwater (C-D; Water collected from upstream and downstream horizontal (H) and vertical screens (M)). The green vertical lines indicate the date of pesticide application.

6 Pesticide leaching at Faardrup

6.1 Materials and methods

6.1.1 Field description and monitoring design

Faardrup is located in Southern Zealand (Figure 6.1) and the test field covers a cultivated area of 2.3 ha (150 x 160 m, Figure 6.1). The terrain slopes gently to the West by 1–3°. Based on three soil profiles excavated 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 dug nearby the field, 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 as compared to concentrations detected in water from the other vertical monitoring wells. This indicates 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 area 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.

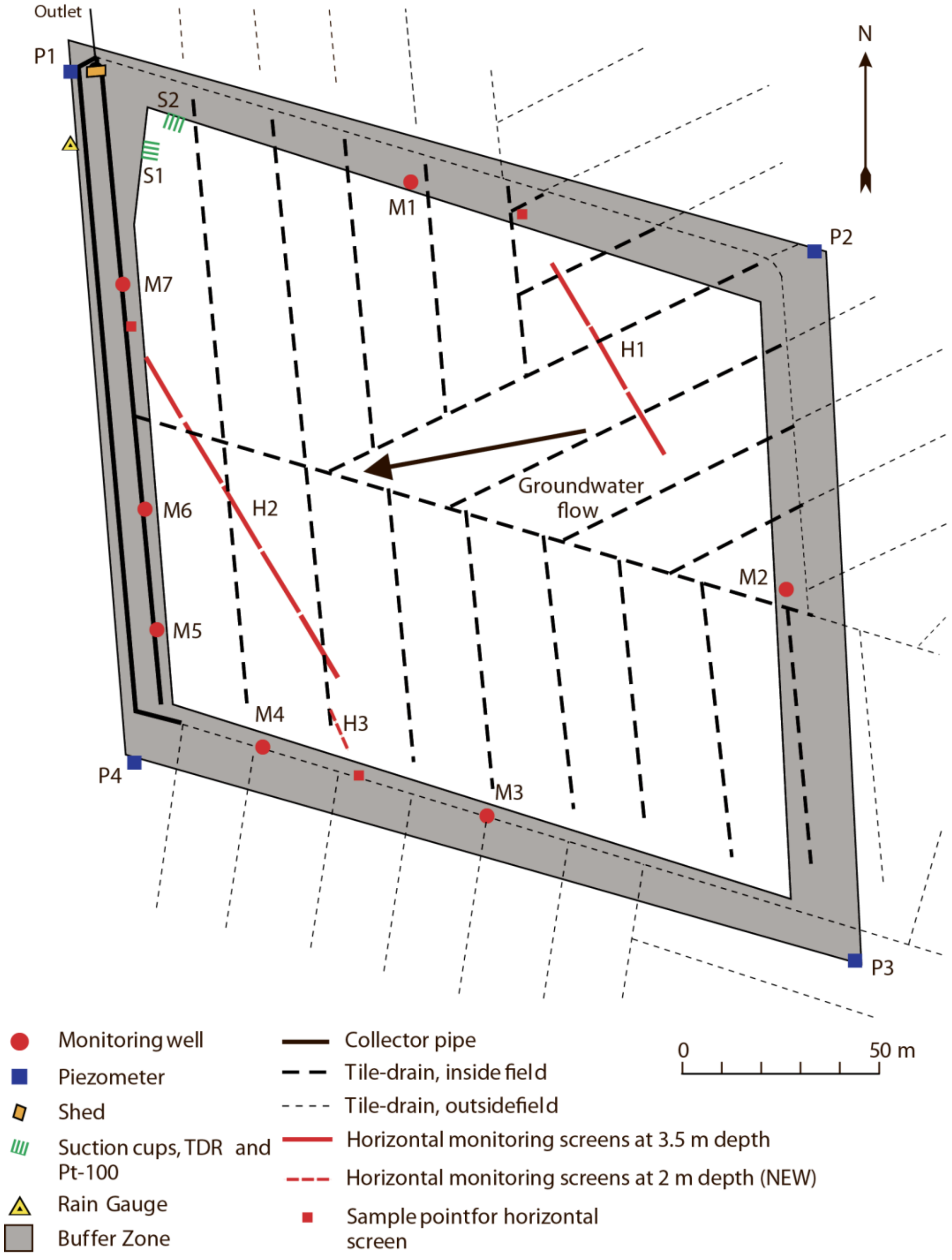

Figure 6.1. Overview of the **Faardrup** field. The innermost white area indicates the cultivated land, while the grey area indicates the surrounding buffer zone. The positions of the various installations are indicated, as is the direction of groundwater flow (arrow). Pesticide monitoring is conducted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

6.1.2 Agricultural management

Management practice at Faardrup during the 2015-16 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/monitor_uk/index.html.

Winter wheat (cv. Mariboss) was sown 23 September 2014. Spraying with the fungicide tebuconazole took place on 20 November 2014 and its degradation product 1,2,4-triazole was included in the monitoring programme. Weeds were sprayed on 30 November 2014, using flupyrsulfuron-methyl and prosulfocarb and on 22 April 2015 using flupyrsulfuron-methyl. Following the first application, flupyrsulfuron-methyl and its three degradation products IN-KC576, IN-KY374 and IN-JV460 were included in the monitoring programme. On 12 May 2015, the herbicides fluroxypyr and florasulam were used, but not included in the monitoring. A final spraying of fungi in the winter wheat was done on 12 May 2015 using prothioconazole, and its metabolite 1,2,4-triazole is included in the monitoring. Harvest of the winter wheat was done 2 September 2015. Grain yield of the wheat was 79.7 hkg ha^{-1} (85% dry matter). At the day of harvest 71.5 hkg ha^{-1} (100 % dry matter) of straw was shredded. On 11 April 2016 a mixture of spring barley varieties was sown. Weeds were sprayed with fluroxypyr, bromoxynil and ioxynil 27 May. Two degradation products of fluroxypyr - fluroxypyr pyridinol and fluroxypyr methoxypyridine - were included in the monitoring. On 16 June 2016 the fungicide propiconazole was applied and the monitoring of the degradation product 1,2,4-triazole continued. Propiconazole was by mistake applied in only half the allowed dosage, i.e. 125 g ha^{-1} active ingredient instead of 250 g ha^{-1}.

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 2016 and to establish an annual water balance.

Compared to the setup in Rosenbom *et al.* (2016), a year of "validation" was added to the MACRO setup for the Faardrup field. The setup was calibrated accordingly for the monitoring period May 1999-June 2004 and "validated" for the monitoring period July 2004-June 2016. 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-February 2005, January-February 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
01.07.14–30.06.15	626	819	456	123	196	239
01.07.15–30.06.16	626	799	403	124	167	273

[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 - actual evapotranspiration - measured drainage.*

6.2 Results and discussion

6.2.1 Soil water dynamics and water balance

The level and dynamics of the soil water saturation in all three horizons in the hydraulic year July 2015-June 2016 were generally well described by the model (Figure 6.2D, 6.2E and 6.2F). In contrast to earlier years the model captured the level of the measured water saturation at both 0.25 m b.g.s. (Figure 6.2D) during both summer and winter. As was the case with the previous hydraulic year, the magnitude of the decrease in water saturation at 1.1 m b.g.s. observed during the summer period is not well captured in regard to S1 measurements, whereas S2 meaurements resembles quit well the model outcome. This could be a result of the conceptual macropore model-setting, where the impact of macropores on the drying of the matrix is not well represented for the sediment profile representing S1 (also, the modelled drainage value for the period is much higher than measured (Fig 6.2C and Tabel 6.1)).

The resulting water balance of all monitoring periods is shown in Table 6.1. Compared with the previous 15 years, the latest hydraulic year (July 2015-June 2016) was characterised by high precipitation, an intermediate actual evapotranspiration, an intermediate measured drainage, and medium-high simulated drainage. This resulted in the highest groundwater recharge estimated for this field within the whole PLAP-period.

Precipitation during this year was characterised by normal values during the late summer 2015 and spring of 2016. November and December 2015 received very high amounts of precipitation (Appendix 4), November being the wettest ever at Faardrup. This probably also explains the very high amounts of simulated drainage in December 2015 as mentioned earlier.

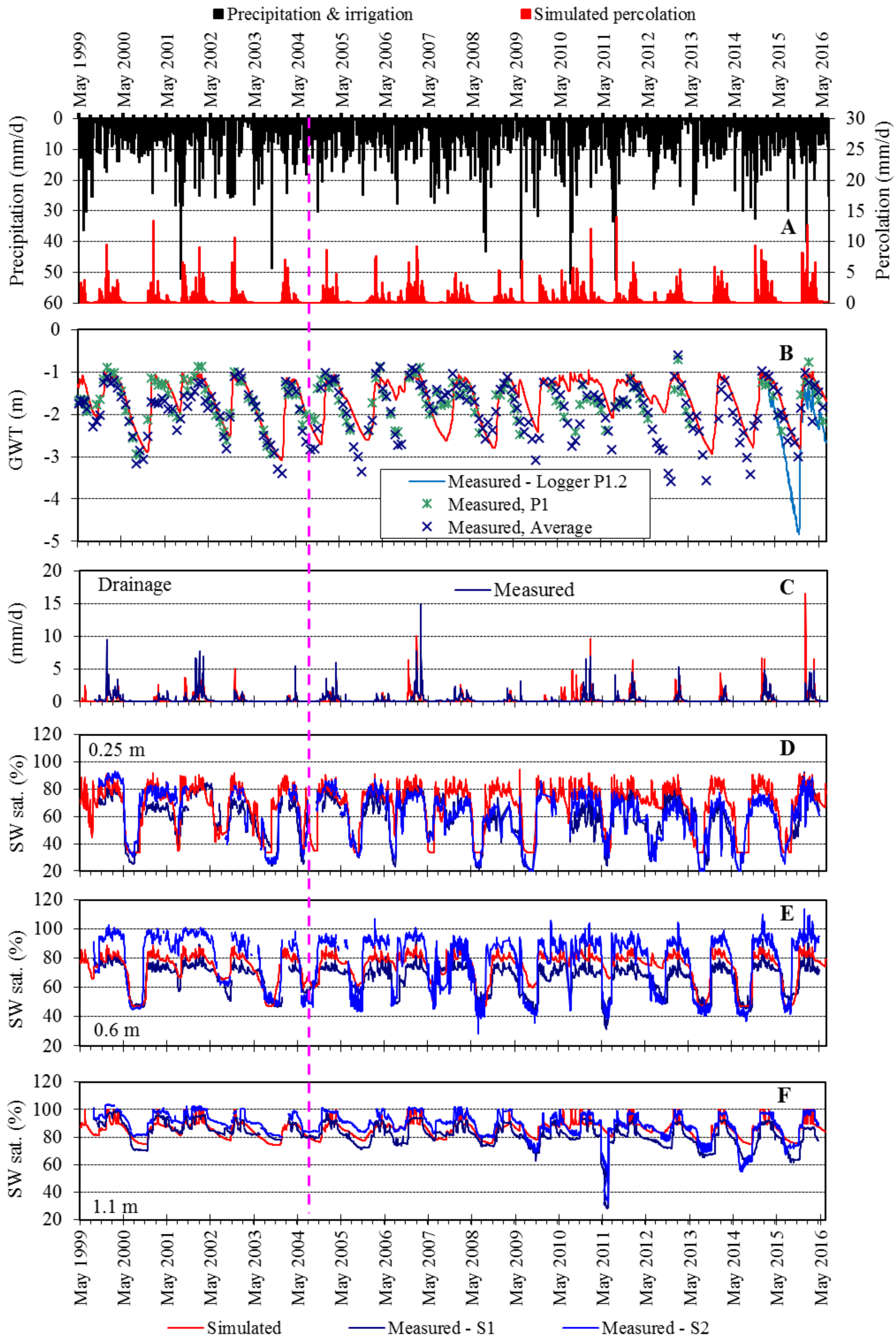

Figure 6.2. Soil water dynamics at **Faardrup.** Measured precipitation and simulated percolation 1 m b.g.s. (A), simulated and measured groundwater table, GWT (B), simulated and measured drainage (C), and simulated and measured soil water saturation (SW sat.) at three different soil depths (D, E and 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 2016).

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 the depth of the tile drains and 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 2015/2016. 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 may give a very local and uncertain picture of the overall bromide leaching.

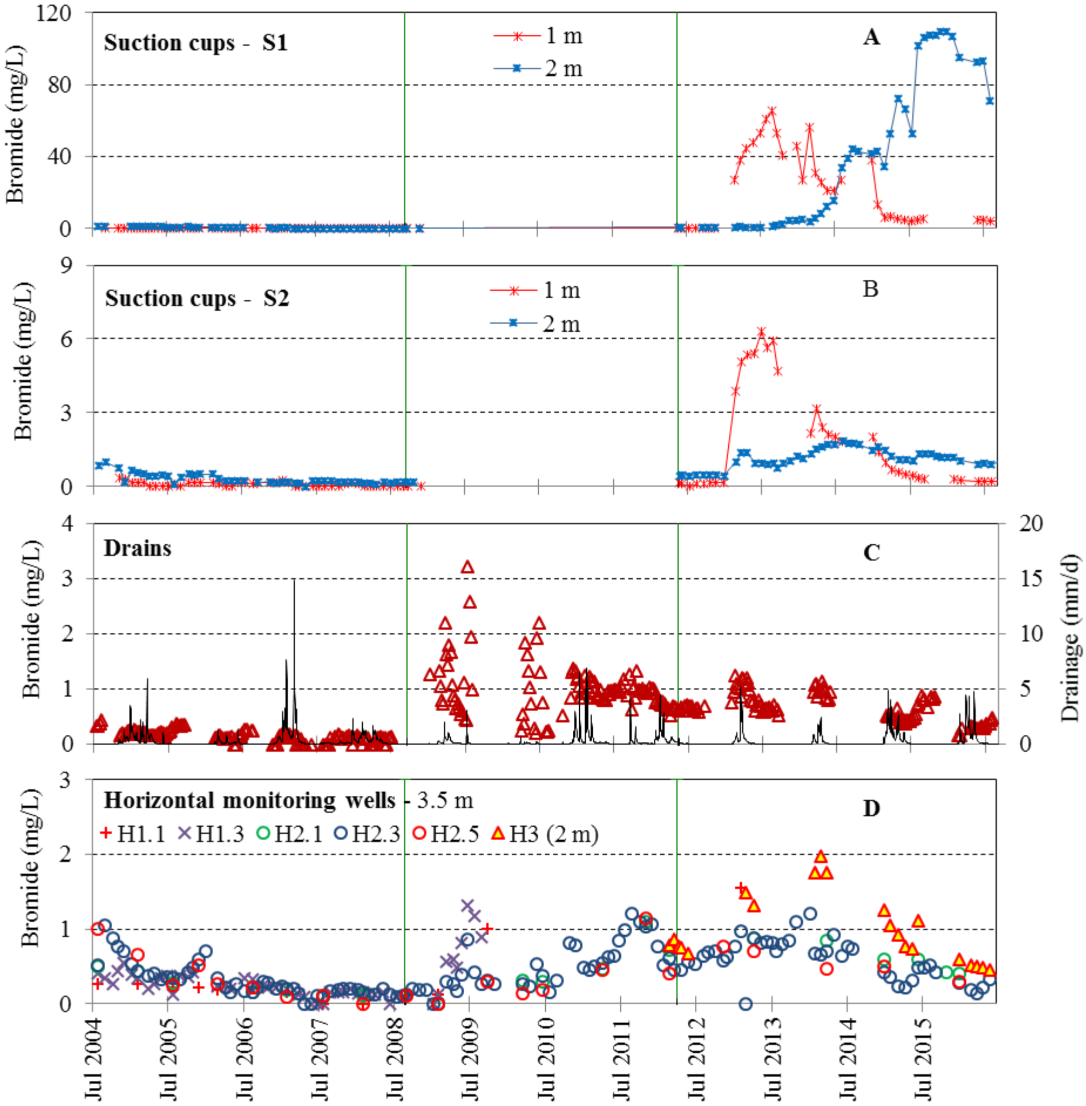

Figure 6.3. Bromide concentrations at **Faardrup** in the period July 2004–June 2016. A and B refer to suction cups located at S1 and S2. The bromide concentration is also shown for drainage runoff (C) and the horizontal monitoring wells. The horizontal wells H1 and H2 are situated 3.5 m b.g.s., and 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 the two most recent bromide applications.

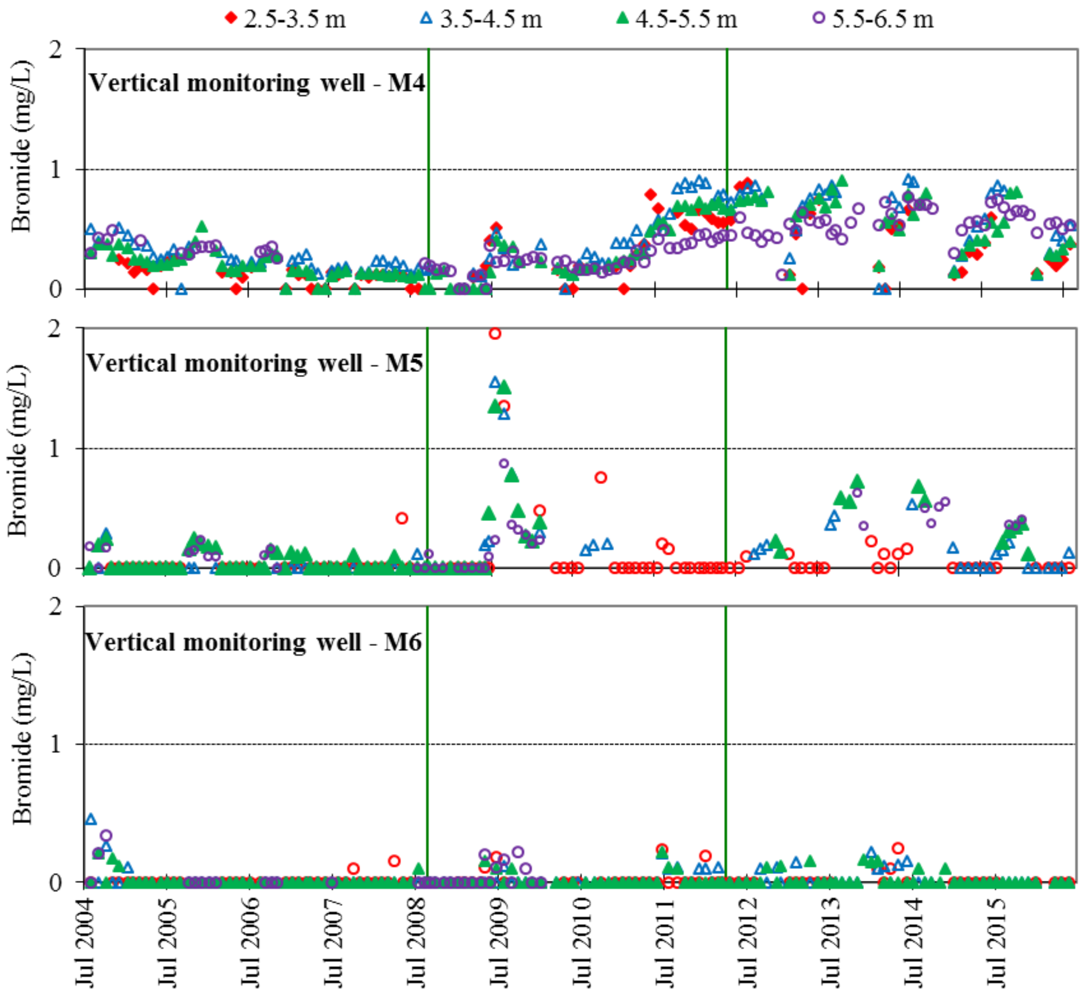

Figure 6.4. Bromide concentrations at **Faardrup** in the period July 2004–June 2016. The data derive from the vertical monitoring wells (M4, M5 and M6). Screen depth is indicated in m b.g.s. The green vertical lines indicate the dates of the two most recent bromide applications.

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.

The current report focuses on the pesticides applied from 2014 and onwards, while the leaching risk of pesticides applied before 2014 has been evaluated in previous monitoring reports (see http://pesticidvarsling.dk/publ_result/index.html). Bentazone, metrafenone, TFMP (degradation product of fluazifop-P-butyl) and propyzamide together with its three degradation products RH-24580, RH-24644 and RH-24655 were included in the monitoring programme until April-June 2015. Therefore, the results are included in this report. Except for bentazon, none of these compounds have been detected in water samples from Faardrup during the monitoring period July 2013–June 2015 and monitoring of these compounds were finalised in April-June 2015 (Table 6.2).

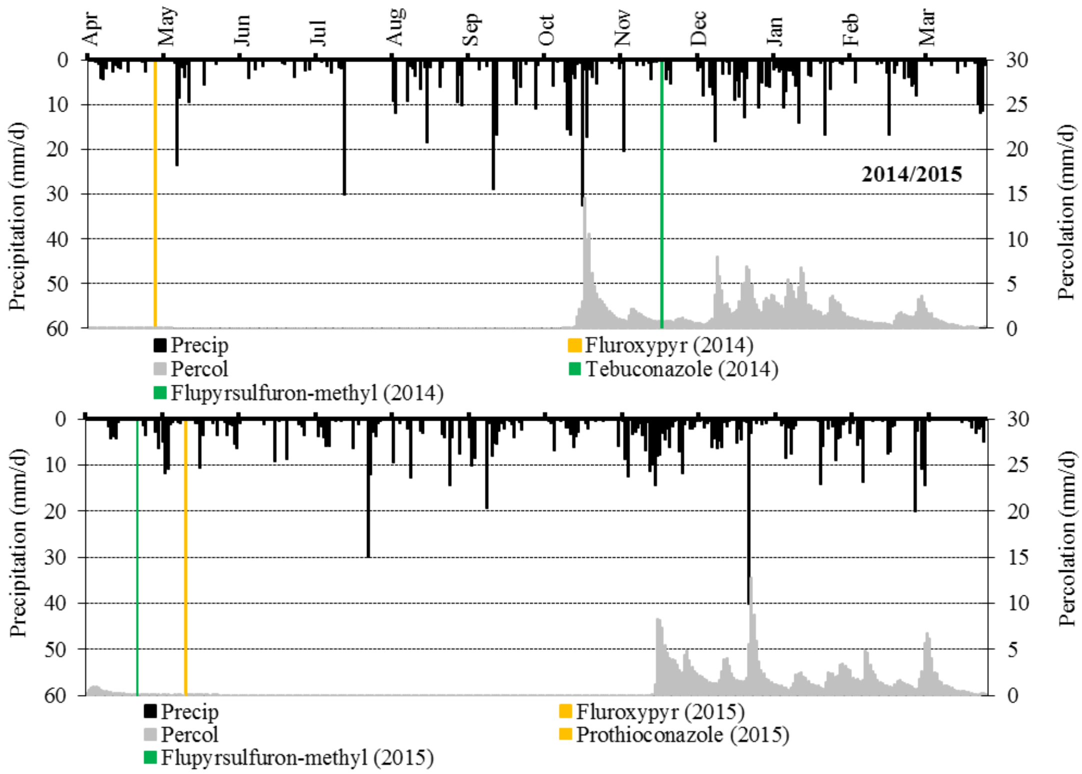

Figure 6.5. Application of pesticides included in the monitoring programme and precipitation (primary axis) together with simulated percolation (secondary axis) at **Faardrup** in 2014/2015 (upper) and in 2015/2016 (lower).

Besides flupyrsulfuron-methyl applied in November 2014 and April 2015 the following degradation products were included in the monitoring programme: 1,2,4-triazole (of tebuconazole and prothioconazole) and IN-JV460, IN-KC576 and IN-KY374 (of flupyrsulfuron-methyl). The monitoring of 1,2,4-triazole was ended on the 9 September 2015 caused by too high expenses on analysis. Given the economic constraints, new compounds could not be added to the monitoring programme of Faardrup until May 2016, where two degradation products of fluroxypyr, fluroxypyr pyridinol and fluroxypyr methoxypyridine, were included. As fluroxypyr had also been applied the year before, April 2014 and May 2015 (Figure 6.5), some background concentrations of the two degration products might be present. On 16 June 2016 the fungicide propiconazole was applied and the degradation product 1,2,4-triazole was once again included in the monitoring (not shown in Figure 6.5).

Only two compounds bentazone and 1,2,4-triazole out of 14 compounds (10 degradation products and four pesticides) have been detected at Faardrup during the monitoring period July 2014 – June 2016, and only the monitoring of flupyrsulfuron-methyl and its three degradation products (now 187 samples per each compound), 1,2,4-triazole (157 samples) and the two degradation products of fluroxypyr (17 samples) will continue after June 2016 (Table 6.2).

Table 6.2. Pesticides analysed at **Faardrup**. For each compound it is listed whether it is a pesticide (P) or degradation product (M), as well as the application date (Appl. date) and end of monitoring period (End. mon.). Precipitation (precip. in mm) and percolation (percol. in mm) 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 [µg L^{-1}] at 1 m depth the first year after application. See Appendix 2 for calculation method and Appendix 8 (Table A8.5) for previous applications of pesticides.

Crop	Applied Product	Analysed pesticide	Appl. date	End mon.	Y 1st Precip.	Y 1st Percol.	M 1st Precip.	M 1st Percol	C_{mean}
Spring barley and	Fighter 480	Bentazone(P)	Jun 10	Jun 15*	693	327	49	29	<0.01
Red fescue 2010	Fox 480 SC	Bifenox(P)	Oct 10	Jun 12	351	190	75	72	0.02
		Bifenox acid(M)	Oct 10	Jun 12	351	190	75	72	2.54
		Nitrofen(M)	Oct 10	Jun 12	351	190	75	72	0.01
Red fescue 2011	Fusilade Max	Fluazifop-P(M)	May 11	Mar 12	730	0	59	0	<0.01
		TFMP(M)	May 11	Apr 15	730	0	59	0	<0.01
Spring barley and	Glyphogan	Glyphosate(P)	Oct 11	Aug 12	425	17	56	17	<0.01
White clover 2012		AMPA(M)	Oct 11	Aug 12	425	17	56	17	<0.01
	Fighter 480	Bentazone(P)	May 12	Jun 15*	527	220	29	4	<0.01
	Flexity	Metrafenone(P)	Jun 12	Apr 15	580	215	96	14	<0.01
White clover 2013	Fighter 480	Bentazone(P)	May 13	Jun 15*	711	213	82	0	0.02
	Kerb 400 SC	Propyzamid(P)	Jan 13	Apr 15	640	213	64	51	<0.01
		RH-24560(M)	Jan 13	Apr 15	640	213	64	51	<0.01
		RH-24644(M)	Jan 13	Apr 15	640	213	64	51	<0.01
		RH-24655(M)	Jan 13	Apr 15	640	213	64	51	<0.01
Winter wheat 2014	Folicur EC250 Tebuconazole (P)	1,2,4-triazole (M)**	Nov 14	Sept 15	796	241	73	51	0.03
	Lexus 50 WG	Flupyrsulfuron-methyl(P)	Nov 14 +Apr 15	Jun 16*	796	241	94	81	<0.01
		IN-JV460(M)	Nov 14 +Apr 15	Jun 16*	796	241	94	81	<0.01
		IN-KY374(M)	Nov 14 +Apr 15	Jun 16*	796	241	94	81	<0.01
		IN-KC576(M)	Nov 14 +Apr 15	Jun 16*	796	241	94	81	<0.01
Spring Barley 2016	Starane 180S Fluroxypyr(P)	Fluroxypyr methoxy-pyridine(M)	May 15	Jun 16*	785	286	46	0	<0.01
		Fluroxypyr pyrdinol(M)	May 15	Jun 16*	785	286	46	0	<0.01
	Proline 250 EC Prothioconazole(P)1	1,2,4-triazole(M)	May 15	Jun 16*	785	286	46	0	-
	Bumper 25 EC Propiconazole(P)1)	1,2,4-triazole(M)	June 16	Jun 16*	-	-	-	-	-

Systematic chemical nomenclature for the analysed pesticides is given in Appendix 1.
1) Propiconazole only applied in half of the maximum allowed dose.
**Monitoring continues the following year.*
***Monitoring started in May 2014.*

In the hydrological year 2012/2013 **bentazone** was applied to test its leaching potential in a cereal (spring barley) undersown with white clover and in 2013/2014 on white clover in pure stand. The application onto spring barley and the undersown white clover on 18 May 2012 was followed by a dry period lasting until the end of June (Appendix 5). The application did not result in any detections of bentazone during the remaining part of 2012. At the end of January 2013 one detection (0.02 µg L^{-1}) 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 6.6) as also reflected by the bromide leaching (section 6.2.2). From then and onwords until May 2013, where bentazone was applied a second time on the pure stand of white clover, bentazone was not detected. The leaching scenario of bentazone following this second application was comparable to the scenario following the first application except for bentazone being detected seven times in the drainage at 1.2 m depth in 2014 (max. 0.029 µg L^{-1}) and in water from the horizontal well H3 situated at 2 m depth (at approx. 0.02 µg L^{-1}) twice in 2014 and six times in 2015 (max. 0.012 µg L^{-1}). All of these seemed to relate to the snowmelt (Figure 6.6). Monitoring has stopped September 2015.

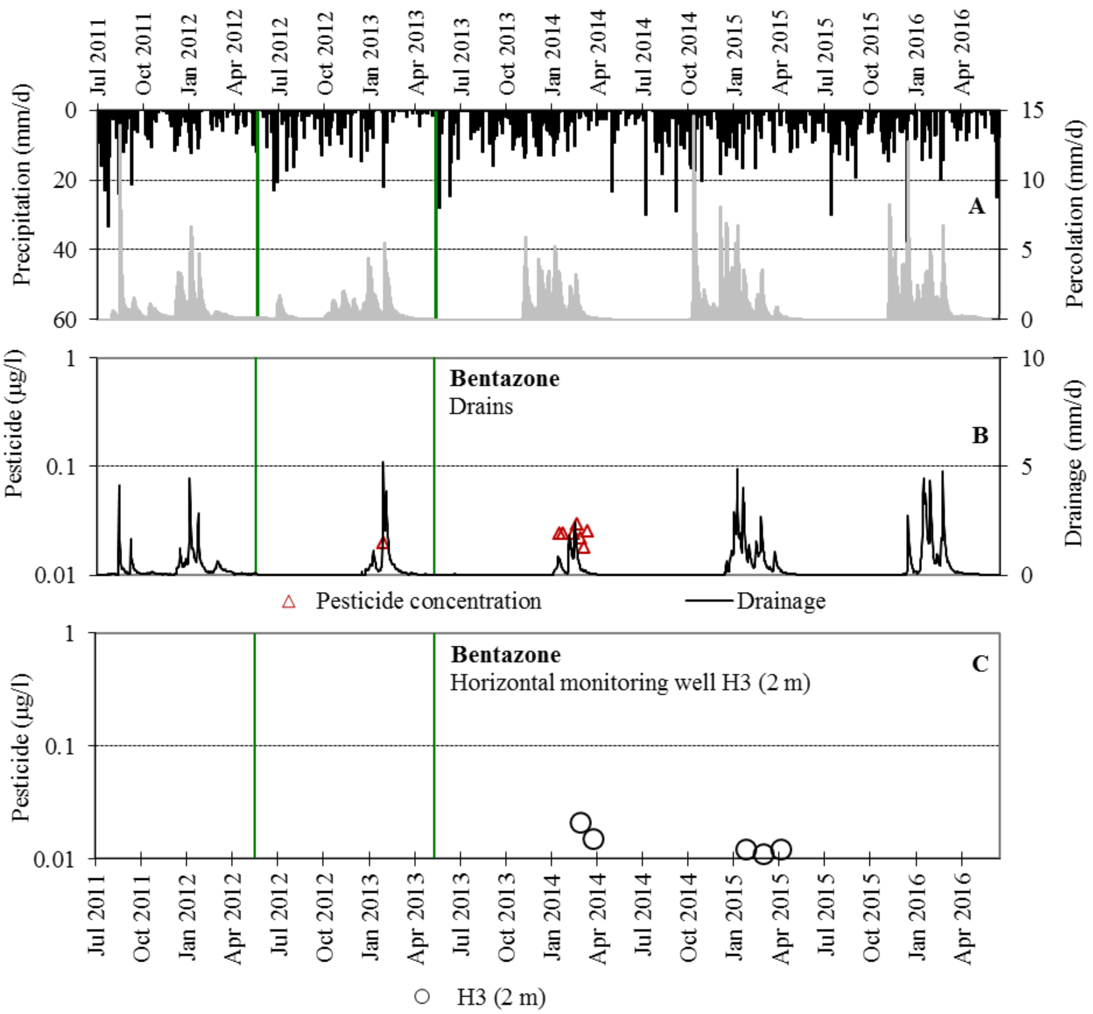

Figure 6.6. **Bentazone** detection at **Faardrup**: Precipitation and simulated percolation 1 m b.g.s. (A) together with the concentration of bentazone detections in water samples collected from drainage (B) and groundwater (C). The green vertical lines indicate the dates of bentazone applications.

In the hydrological years 2014/2015, **tebuconazole** was applied on winter wheat in November 2014 to test the leaching potential of its degradation product 1,2,4-triazole. It should be noted that it was not possible to obtain background samples of the drainage before this application. Background concentrations from water collected in the wells were obstained and 1,2,4-triazol was not detected. As illustrated in Figure 6.7, 1,2,4-triazole was detected more or less continously in the drainage until April 2015, but only twice (at 0.02 µg L^{-1}) in the groundwater. One detection in water from the horizontal wells at 2 m depth, and one detections in water from the vertical monitoring well M4 at 3-4 m depth. In May 2015, another fungicide **prothioconazole** was applied to spring barley to verify that it will not degrade to 1,2,4-triazol as specified in the EFSA conclusion. Following this application an increase in concentration of 1,2,4-triazole was detected in the water samples collected from drainage. Note that no samples were obtained from drainage between August 2015 and May 2016 given the economic constraints. The fact that 1,2,4-triazole is detected in water from drainage during the summer of 2016 at the same concentrations as in the months following application of the parent pesticide 1-2 years prior, indicates (i) a surface-near source, (ii) that 1,2,4-triazole is very persistent at detectable concentrations at 1 m depth and (iii) the very upper groundwater is temporarily exposed to it in low concentrations.

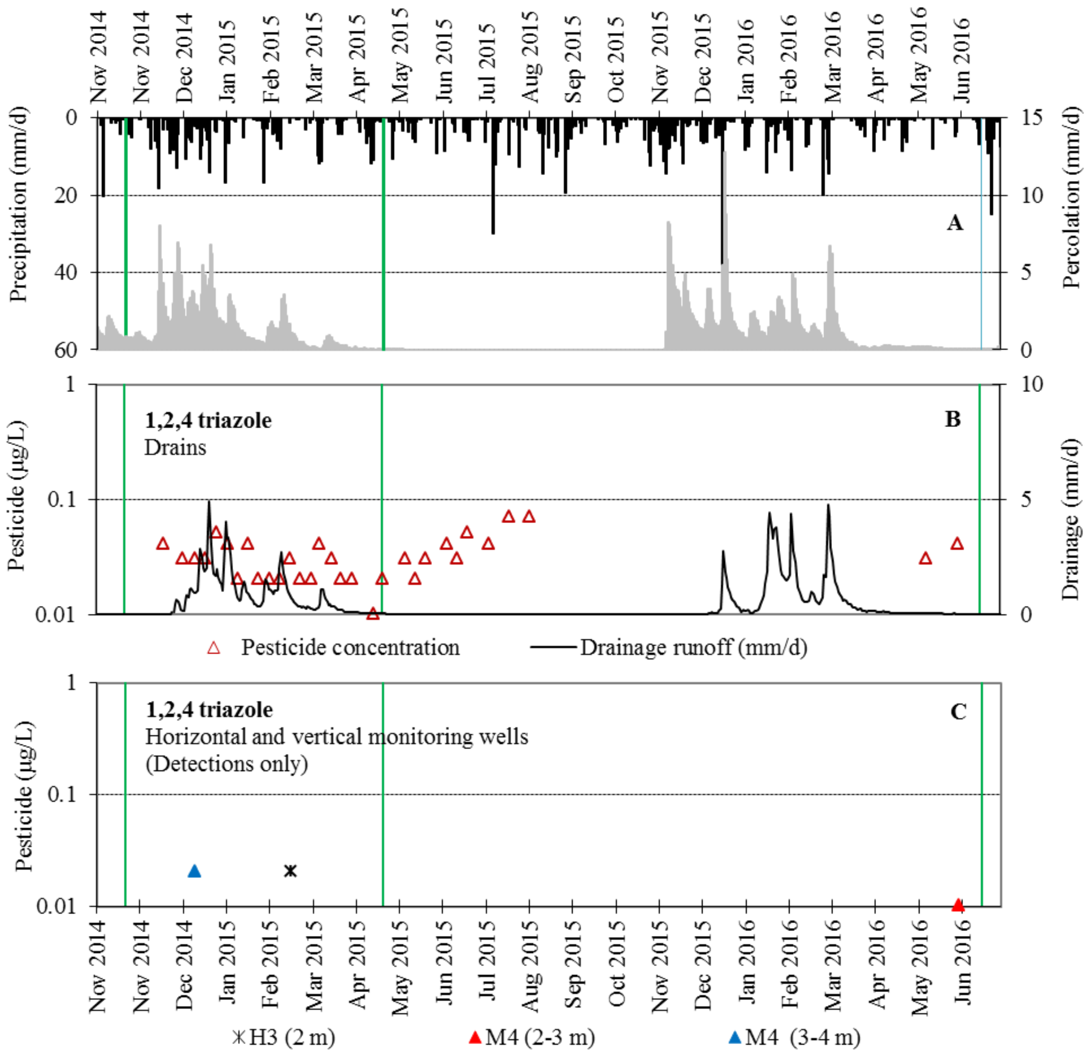

Figure 6.7. **1,2,4-triazole** detections at **Faardrup**: Precipitation and simulated percolation 1 m b.g.s. (A) together with the concentration of 1,2,4-triazole in water samples collected drainage (B) and groundwater (C). The green vertical lines indicate the date of tebuconazole application.

7 Pesticide analysis quality assurance

Reliable results and scientifically valid methods of analysis are essential for the integrity of the present monitoring programme. Consequently, the field monitoring work has been supported by intensive quality assurance entailing continuous evaluation of the analyses employed. Two types of sample are used in the quality control 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 2015 to June 2016 are presented below, while those for the preceding monitoring periods are given in previous monitoring reports (available on http://pesticidvarsling.dk/monitor_uk/index.html).

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.

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^{-1}. 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 2015 to June 2016, two external control samples per test field were analysed at the laboratory 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/LGC, 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 cold and dark until use. For the preparation of stock solutions, e.g. 150 µl (for low level sample when 3L groundwater is available) or 350 µl (for high level sample when 3L groundwater is available) of the pesticide mixtures, 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 1.0, 2.0, or 3.0 L measuring flask – depending on the available water in the groundwater well (determined before preparation of the standard solutions). The standard solution was transferred to the measuring flaks, diluted and the volume in the flask adjusted to the mark with groundwater from a defined groundwater well in each field. After thorough mixing, the control sample was decanted to a sample bottle similar to the monitoring sample bottles, labelled, 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^{-1} for the spiked low level control sample, and 0.117 µg L^{-1} for the high level sample. The pesticides included, their concentration in the initial ampoule and in the final QC solutions are 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 1.7.2015-30.6.2016. Concentrations in both the original ampoules and in the final high-level and low-level external control samples used.

Compound	Ampoule concentration (µg L^{-1})	Ampoules	High-level control (µg L^{-1})	Low-level control (µg L^{-1})
1,2,4-triazole	1000	3	0.117	0.050
AMBA	1000	1	0.117	0.050
AMPA	1000	2	0.117	0.050
Bentazone	1000	1	0.117	0.050
CGA 192155	1000	1	0.117	0.050
CGA 339833*	1000	1*	0.117	0.050
CyPM	1000	1	0.117	0.050
Glyphosate	1000	2	0.117	0.050
IN-JV460	1000	1	0.117	0.050
IN-KC576	1000	1	0.117	0.050

*CGA 339833 was found to be unstable in solution after included in the ampoule and was not further evaluated.

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 results. 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 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 19 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 the average of all compounds the mean variation S_w was 0.013, S_b 0.017 and S_t was 0.021, levels that are considered suitable when relating to the residue limit for pesticides (0.1 µg L^{-1}).

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 shows that S_b/S_w ratios greater than two were observed for only three compounds this year (azoxystrobin S_b/S_w ratio 2.3, bentazone S_b/S_w ratio 2.5, and IN-JV 460 S_b/S_w ratio 3.6). For these compounds, the results indicate that day-to-day variation makes a significant contribution. The compound triazinamin also has a S_b/S_w ratio > 2 (S_b/S_w ratio 3.6), but as the compound was added late in the reporting period, the statistics only rely on two duplicate samples and will not be further evaluated in this report.

Among the four compounds meeting the normality requirement, only one had a ratio above two (azoxystrobin). In general, all S_b/S_w ratios have decreased and less compounds have S_b/S_w ratios above two compared to ratios in the previous reports.

Azoxystrobin: the compound has a ratio above two (2.3), but this high S_b/S_w ratio is caused by the between-day deviation (S_b: 0.005) being relatively high compared to the very low S_w (0.002). However, as both S_w and S_b are still very low, this actually indicates an analytical procedure in good control, although there is still room for improvement of the analytical method.

MNBA: The compound does not meet the normality criterion again this year, but the between-day standard deviation (S_b) has decreased over the last couple of years and thus lowered the S_b/S_w ratio significantly from 3.0 to 0.2 during the last two years, and now this year increased again to 1.1. The between-day (S_b) has slightly increased since last year, but the within-day (S_w) and the total standard (S_t) deviation have, however, decreased compared to last year, indicating that it may be possible to improve the analytical procedure for this compound even further to bring down these deviations.

AE-F092944, AE-F130619, Flupyrsulfuron-methyl, Foramsulfuron, IN-JV460, IN-KC576 and IN-KY374 are all new compounds in the analytical programme and included for the first time in this report.

IN-JV460: The compound does not meet the normality and S_b/S_w ratio criteria. The high S_b/S_w ratio is due to the relatively high between-day standard deviation (S_b – 0.029) compared to the within-day deviation (S_w – 0.008), indicating that it may be possible to improve the analytical procedure for this compound to bring down these deviations.

AE-F092944, AE-F130619, CGA 192155, CGA 339833, IN-KC576, IN-KY374 fulfil the S_b/S_w ratio criterion and CGA 339833 and IN-KY374 additionally fulfil the criterion for normality. All the compounds have, however, relatively high total standard deviation (S_t > 0.020), indicating that it may be possible to improve the analytical procedure for these compounds to bring down the deviations.

When all compounds are considered, no compounds have S_b/S_w ratios higher than 3.6 (observed for IN-JV460), and in total only three compounds had ratios > 2.0, which is an improvement compared to last year's report, where it was five compounds. This year's high S_b/S_w ratios are due to relatively high between-day deviations (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. The ratios > 2 in this year's report, are due to very low within day deviation and relatively higher between-day deviations. None of the between-day contributions are, however, significant on the 0.05 significance level.

Table 7.2. Internal QA of pesticide analyses carried out in the period 1.7.2015-30.6.2016. Results of the test for normality, one-way analysis of variance (ANOVA), the estimated values of standard deviations (w: within-day, b: between-day, t: total – see text for details), pesticide concentration in internal QA sample (Conc.) and number of duplicate samples (n) are given for each pesticide. For test the P value α=0.05 was used.

Compound	Normal Distribut. α=0.05	Significant S_b Between day contribut. ANOVA α=0.05	S_w (µg L^{-1})	S_b (µg L^{-1})	S_t (µg L^{-1})	Ratio S_b/S_w	n	Conc. (µg L^{-1})
1,2,4-triazole*	-	-	0.004	0.006	0.007	1.3	58	0.03
AE-F092944*	-	-	0.018	0.026	0.032	1.4	42	0.1
AE-F130619*	-	-	0.015	0.020	0.025	1.4	41	0.1
AMBA*	-	-	0.035	0.031	0.047	0.9	37	0.1
AMPA*	Yes	-	0.002	0.003	0.004	1.4	40	0.03
Azoxystrobin	Yes	-	0.002	0.005	0.005	2.3	40	0.05
Bentazone	-	-	0.001	0.003	0.004	2.5	40	0.05
CGA 192155*	-	-	0.012	0.019	0.023	1.6	11	0.05
CGA 339833*	Yes	-	0.018	0.022	0.028	1.3	11	0.05
CyPM*	-	-	0.009	0.010	0.013	1.1	38	0.05
Flupyrsulfuron-methyl	-	-	0.011	0.019	0.022	1.7	39	0.1
Foramsulfuron	-	-	0.020	0.020	0.028	1.0	40	0.1
Glyphosate	-	-	0.003	0.004	0.006	1.3	41	0.03
IN-JV460*	-	-	0.008	0.029	0.030	3.6	39	0.1
IN-KC576*	-	-	0.011	0.019	0.022	1.7	42	0.1
IN-KY374*	Yes	-	0.025	0.027	0.037	1.1	37	0.1
MNBA*	-	-	0.025	0.028	0.038	1.1	38	0.1
Mesotrione	-	-	0.020	0.015	0.025	0.7	40	0.1
Triazinamin[a]	Yes	-	0.002	0.009	0.009	3.6	2	0.1

**Degradation product.*

[a] *Data represents only two duplicate samples - compound included late in the reporting period.*

The total standard deviation (S_t) of the various analyses of pesticides and degradation products lie within the range 0.004-0.047 µg L^{-1}, the highest value observed for AMBA. In general, the data suggest that the analytical procedure used for the quantification of the compounds is good and in general has improved or in line with last year's report, but there is still room for improvement and optimisation of, especially, the between-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 32 blank samples made from HPLC water were analysed and no compounds were detected in any of these analysed blank samples. Based on 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 1.7.2015-30.6.2016. 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 %		Jyndevad %		Silstrup %		Estrup %		Faardrup %		Average %	n_{low}/ n_{high}	$n_{total\ analysed}$
	Low	High	Low	High	Low	High	Low	High	Low	High			
1,2,4-triazole	**140**	117	**193**	**137**			**140**	105	120	120	135	10/10	20
AMBA					92	83	**42**	**54**			68	6/6	12
AMPA					108	111	113	98			107	4/4	8
Bentazone	**130**	**128**	**132**	94			93	94			107	4/4	8
CGA 192155	101	92	102	90							96	4/4	8
CyPM					88	87	108	114			99	6/6	12
Glyphosate					100	94	108	94			99	4/4	8
IN-JV460			74	73					**152**	**160**	114	6/6	12
IN-KC576			72	**54**					100	108	83	6/6	12

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 38 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 AMBA, bentazone, and IN-JV460, points to the need of keeping track of these particular compounds.

The metabolite CGA339833 was initially included in the ampoule no. 1, but the compound was later found out to be unstable in solution and thus not recovered in the external QA samples.

Last year, a new procedure was implemented in the QA programme. Now every year upon arrival of the new ampoule, the concentration of the most critical compounds are confirmed at the commercial laboratory before the ampoule is used in the QA control sample program. This procedure was implemented due to the previous experience with flawed production of AMPA and glyphosate ampoules.

In general, all recoveries of the low external QA (concentration in QA_{low} is 0.05 µg L^{-1}) are within the acceptable range, except for 1,2,4-triazole, AMBA, bentazone, and IN-JV460. The degradation product 1,2,4-triazole has an elevated recovery of up to 193%, which seems to reflect the background concentration (ranging from 0.01 to 0.07 µg L^{-1}) of the compound in the water from the monitoring wells used for preparation of the spiked samples. This year's recoveries of 1,2,4-triazole relies on 20 samples and in combination with the internal QA samples, the QA program confirms that the analytical method is acceptable.

The recoveries of AMBA and IN-JV460 in both the external spiked QA_{low} and QA_{high} samples are slightly lower than acceptable and we will have extra focus on these compounds in the future.

Except for CGA339833, all the compounds included in the spiking procedure (Table 7.1) were detected in the commercial laboratory.

During the 2015/2016 monitoring period a total of four pesticides (azoxystrobin, bentazone, mesotrione, foramsulfuron) and four degradation products (1,2,4-triazole, AE-F130619, CyPM, MNBA) 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 analytes included in this year's analytical program are presented 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 similar to last year, with total standard deviation (S_t) in the range 0.004-0.047 µg L^{-1}.

- As demonstrated by the external QA, recovery was generally good in externally spiked samples. Last year's effort on the ampoule procedures and optimisation of the analytical methods for AMPA and glyphosate has solved the problems and now recoveries for both AMPA and glyphosate lie within the criteria for the external QA program.

- The external QA recovery of 1,2,4-triazole was higher than the set criteria but the discrepancy relates to the background content of 1,2,4-triazole in the water from the monitoring wells used for preparation of the spiked external QA samples. Both the QA program and the analytical method is good control.

- 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/monitor_uk/index.html). Pesticide detections in samples from the drainage systems, suction cups and groundwater monitoring wells are detailed in Appendix 5. The monitoring data in 1 m depth (water collected from drainage 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 depth is defined as root zone leaching exceeding an average concentration of 0.1 µg L^{-1} within the first season after application. On sandy and clayey till soils, leaching is determined as the weighted average concentration in water collected from suction cups and drainage, 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^{-1} and detections of the pesticide (or its degradation products) exceeding 0.1 µg L^{-1} (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.

Until June 2016, 115 pesticides and/or degradation products (51 pesticides and 64 degradation products) have been analysed in PLAP, comprising five agricultural fields (1.2 to 2.4 ha) cultivated with different crops. The 64 degradation products degrade from 37 pesticides of which three have not been tested in PLAP (fludioxonil, mancozeb and tribenuron-methyl). Of the 54 pesticides (51+3), 17 resulted in detections in groundwater samples in concentrations exceeding 0.1 µg L^{-1} of the pesticide and/or its degradation products (Table 8.3 and 8.4). 15 of these 17 pesticides resulted in detections in samples from 1 m depth exceeding 0.1 µg L^{-1} (Table 8.1 and 8.2). Only five of the 17 pesticides resulted in detections indicating a high leaching risk through sandy soils (fludioxonil, metalaxyl-M, metribuzin, rimsulfuron and tebuconazole), whereas the others plus tebuconazole revealed a leaching risk through fractured clayey tills (azoxystrobin, bentazone, bifenox, ethofumesate, fluazifop-P-butyl, glyphosate, mesotrione, metamitron, propyzamide, pyridate and terbuthylazine).). Here it should be emphasised that the presented leaching risk for tebuconazole is due to the presence of 1,2,4-triazole at both sandy soils and fractured clayey tills, and that this can be the result of other applied fungicides including the use as seed treatment. This is evaluted further in PLAP and a 1,2,4-triazol screening is initiated in the Danish National Groundwater Monitoring Programme (GRUMO). The following 11 pesticides did not result in any detection of the pesticide and/or its degradation product being tested in water samples collected from the variably-saturated zone (via drains and suction cups) or saturated zone (via groundwater well screens situated at 1.5-4.5 m depth); Aclonifen, boscalid, chlormequat, cyazofamid, florasulam, iodosulfuron-methyl, linuron, metsulfuron-methyl, thiacloprid, thiamethoxam and tribenuron-methyl. Both the number of detections at 1 m depth (water from suction cups and drainage) and in groundwater, emphasize that clayey till soils are more vulnerable to leaching compared to sandy soils (Table 8.1-8.4). In particular, the presence of fractures facilitates transport of compounds to the groundwater. By including a new clayey till field (Lund) in PLAP the representability of vulnerable soils will increase and hereby improve the early warning in relation to leaching through vulnerable soils.

An evaluation of the pesticides resulting in detections indicating a high leaching risk will be given in the following:

- **Azoxystrobin**, and in particular its degradation product CyPM, leached from the root zone (1 m depth) in relatively high average concentrations at the clayey till fields Silstrup and Estrup. CyPM leached into the drainage in average concentrations exceeding 0.1 µg L^{-1} at both the Silstrup and Estrup fields. Following the May 2014 application at Silstrup azoxystrobin was for the first time detected in concentrations exceeding 0.1 µg L^{-1} in water from drainage (0.11 µg L^{-1}). Such a concentration level has previously been monitored at Estrup (Table 8.1 and 8.2). At both fields, leaching of azoxystrobin has mostly been confined to the depth of the drainage system, and it has rarely been detected in groundwater (Table 8.3 and 8.4). However, detection of CyPM in water from the groundwater monitoring wells has gradually increased over time with highest numbers of detection found after the latest applications (2009/2013/2014 at Silstrup, Figure 4.6 and 2008/2012/2014 at Estrup, Figure 5.6). Out of 738 (Silstrup) + 726 (Estrup) groundwater samples taken at Silstrup and Estrup, 100 (Silstrup) + 38 (Estrup) samples contained CyPM, whereof 14 (Silstrup) + 5 (Estrup) exceeded 0.1 µg L^{-1}. 10/14 (Silstrup) and 4/5 (Estrup) of these samples were collected after the application in 2014, with a maximal concentration of 0.52 µg L^{-1} at Silstrup and 0.46 µg L^{-1} at Estrup. Many of the CyPM detections were in water collected from the horisontal wells in 2 m depth, which became operational in early 2012 – Particularly at Estrup the low permeable layer seems to minize the hydraulic connection from the surface to the vertical well screens but not to the new horizontal well screens, which could be caused by a spatial variation in the presence of the low permeable layer or more dominant vertical hydraulic active macropores intersecting the horisontal well compared to the vertical well – causes, which are cases for further research. Possible causal relationships to these findings are under evaluation in PLAP. At the clayey till field Faardrup, azoxystrobin and CyPM were detected in four samples from the drainage before 2007, and in no samples from the sandy Jyndevad field during the period 2005-2007 (Appendix 5). At all three clayey till fields, azoxystrobin was generally only detected during the first couple of months following application, while CyPM leached for a longer period of time and at higher concentrations (Jørgensen *et al.*, 2012).

Table 8.1. Degree of leaching to drainage and suction cups at **1 m depth** (detections on water from suction cups and drainagey) of pesticides and/or their degradation products at the five PLAP fields. Pesticides applied in spring 2016 are not included in the table. (+) indicates that the pesticide and/or its degradation product is included in the monitoring programme July 2014 – June 2016.

Risk	**Pesticid**	**Sand**		**Clayey till**		
		Tylstrup	Jyndevad	Silstrup	Estrup	Faardrup
High	Azoxystrobin (+)	Grey	Grey	Red	Red	Blue
	Bentazone (+)	Grey	Red	Red	Red	Red
	Bifenox	Grey	Grey	Red	Red	Red
	Diflufenican (+)		Grey	Blue	Red	
	Ethofumesate			Blue	Red	Blue
	Fluazifop-P-butyl (+)	Grey	Grey	Red		Blue
	Fluroxypyr (+)	Grey	Grey	Grey	Red	Blue
	Glyphosate (+)		Grey	Red	Red	Blue
	Mesotrione (+)		Grey	Red	Red	
	Metalaxyl-M (+)	Red	Red			
	Metamitron			Blue	Red	Blue
	Metribuzin	Red	Red			
	Picolinafen		Grey		Red	
	Pirimicarb	Grey	Grey	Blue	Red	Blue
	Propyzamide (+)	Grey		Red		Red
	Rimsulfuron	Blue	Red	Grey		
	Tebuconazole (+)*	Blue	Blue	Grey	Red	Blue
	Terbuthylazine	Blue	Blue	Red	Red	Red
Low	Amidosulfuron		Blue	Grey	Grey	
	Bromoxynil (+)	Grey	Grey	Grey	Blue	Grey
	Clomazone (+)	Grey	Grey		Grey	Blue
	Dimethoate	Grey	Grey	Blue	Grey	Grey
	Epoxiconazole	Grey	Grey	Grey	Blue	Grey
	Flamprop-M-isopropyl	Grey		Blue	Blue	Grey
	Floramsulfuron (+)			Blue	Blue	
	Flupyrsulfuron-methyl (+)		Blue			Grey
	Ioxynil (+)	Grey	Grey	Grey	Blue	Grey
	MCPA		Grey	Grey	Blue	Blue
	Mancozeb (+)	Blue	Grey			
	Mesosulfuron-methyl		Grey		Blue	
	Metrafenone (+)				Blue	Grey
	Pendimethalin	Grey	Grey	Blue	Grey	Grey
	Phenmedipham			Grey		Blue
	Propiconazole	Grey	Grey	Blue	Blue	Grey
	Prosulfocarb (+)	Grey		Blue		Grey
	Pyridate		Grey	Blue		
	Triflusulfuron-methyl			Blue		Grey
None	Aclonifen	Grey	Grey			
	Aminopyralid (+)	Grey			Grey	
	Boscalid	Grey				
	Chlormequat		Grey	Grey	Grey	
	Clopyralid	Grey		Grey	Grey	
	Cyazofamid	Grey	Grey			
	Desmedipham			Grey		Grey
	Fenpropimorph	Grey	Grey	Grey	Grey	Grey
	Florasulam		Grey		Grey	
	Fludioxonil (+)	Grey	Grey			
	Iodosulfuron-methyl			Grey	Grey	
	Linuron	Grey				
	Metsulfuron-methyl			Grey	Grey	
	Thiacloprid				Grey	
	Thiamethoxam	Grey				Grey
	Triasulfuron (+)	Grey		Grey	Grey	
	Tribenuron-methyl	Grey	Grey	Grey	Grey	Grey

Red	The pesticide (or its degradation products) leached at 1 m depth in average concentrations exceeding 0.1 µg L^{-1} within the first season after application.
Blue	The 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^{-1}; average concentration (1 m depth) below 0.1 µg L^{-1} within the first season after application.
Grey	The pesticide either not detected or only detected in very few samples in concentrations below 0.1µg L^{-1}.

* These numbers can include 1,2,4-triazole degraded from the pesticides: epoxiconazole and prothioconazole.

Table 8.2. Number of samples (N) from drainage and suction cups at **1 m depth** in which the various pesticides and/or their *degradation products* were detected in either several (more than three) consecutive samples or in a single sample exceeding 0.1 µg L^{-1} for each field with max conc. M (µg L^{-1}). Pesticides resulting in no detections are not included. The pesticide and *degradation products* are listed, if analysed, under Analyte.

Risk	**Pesticide**	**Analyte**	**Tylstrup**		**Jyndevad**		**Silstrup**		**Estrup**		**Faardrup**	
			N	M	N	M	N	M	N	M	N	M
High	Azoxystrobin	Azoxystrobin	0	-	0	-	23	0.11	141	1.40	0	-
		CyPM	0	-	0	-	152	0.56	357	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	80	2.00	45	6.40	226	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	0	-	0	-	5	0.34	0	-	6	0.16
	Diflufenican	*AE-B107137*			0	-	5	0.13	18	0.09		
		Diflufenican			0	-	11	0.12	27	0.49		
	Ethofumesate	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	203	0.35	499	1.60	15	0.11
		Glyphosate			0	-	108	4.70	343	31.00	5	0.09
	Mesotrione	*AMBA*			1	0.01	0	-	4	0.04		
		MNBA			0	-	5	0.09	8	0.46		
		Mesotrione			0	-	9	1.10	25	3.3		
	Metalaxyl-M	*CGA 108906*	93	4.80	68	3.70						
		CGA 62826	35	0.12	73	1.20						
		Metalaxyl-M	4	0.03	11	0.04						
	Metamitron	*Desamino-metamitron*					58	0.67	49	5.55	16	2.50
		Metamitron					45	0.55	42	26.37	12	1.70
	Metribuzin	*Desamino-diketo-metribuzin*	63	2.10	0	-						
		Diketo-metribuzin	184	0.62	3	0.09						
	Picolinafen	*CL 153815*			0	-			31	0.50		
		Picolinafen			1	0.02			17	0.07		
	Pirimicarb	Pirimicarb	0	-	0	-	14	0.05	40	0.08	7	0.06
		Pirimicarb-desmethyl	0	-	1	0.01	1	0.05	0	-	6	0.05
		Pirimicarb-desmethyl-formamido	0	-	0	-	0	-	26	0.38	3	0.04
	Propyzamide	Propyzamide	0	-			23	1.60			4	0.51
		RH-24580	0	-			2	0.02			0	-
		RH-24644	0	-			15	0.05			4	0.02
		RH-24655	0	-			0	-			1	0.02
	Rimsulfuron	*PPU*	153	0.09	194	0.29	0	-				
		PPU-desamino	45	0.03	123	0.18	0	-				
	Tebuconazole	*1,2,4-triazole* *	5	0.06	14	0.16			76	0.45	31	0.07
		Tebuconazole	0	-	0	-	2	0.08	41	2.00	4	0.05
	Terbuthylazine	*2-hydroxy-desethyl-terbuthylazine*	5	0.02			28	0.11	87	6.30	8	1.00
		Desethyl-terbuthylazine	2	0.01	20	0.06	108	1.08	146	8.20	89	8.30
		Desisopropylatrazine	17	0.04			43	0.04	71	0.44	25	0.36
		Hydroxy-terbuthylazine	1	0.04			26	0.04	88	0.99	21	0.58
		Terbuthylazine	0	-	0	-	60	1.55	112	11.00	41	10.00

* These numbers can include 1,2,4-triazole degraded from the pesticides: epoxiconazole and prothioconazole.

Table 8.2 (Continued). Number of samples (N) from drainage and suction cups at **1 m depth** in which the various pesticides and/or their *degradation products* were detected in either several (more than three) consecutive samples or in a single sample exceeding 0.1 µg L^{-1} for each field with max conc. M (µg L^{-1}). Pesticides with no detections are omitted. The pesticide and *degradation products* are listed, if analysed, under Analyte.

Risk	Pesticide	Analyte	Tylstrup		Jyndevad		Silstrup		Estrup		Faardrup	
			N	M	N	M	N	M	N	M	N	M
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
	Flupyrsulfuron-methyl	*IN-KY374*			1	0.09					0	-
	Foramsulfuron	*AE-F092944*					0	-	1	0.01		
		AE-F130619					7	0.02	2	0.02		
		Foramsulfuron					7	0.24	16	0.32		
	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				
	Triflusulfuron-methyl	*IN-E7710*					5	0.01			0	-

Table 8.3. Detections of pesticides and/or their degradation products in water samples from the **groundwater monitoring screens** at the five PLAP fields (see Table 8.4 for details). (+) indicates that a pesticide and/or its degradation product is included in the monitoring programme July 2014 – June 2016.

Risk	Pesticide	Tylstrup	Jyndevad	Silstrup	Estrup	Faardrup
High	Azoxystrobin (+)	Grey	Grey	Red	Red	Blue
	Bentazone (+)	Grey	Blue	Red	Blue	Red
	Bifenox	Grey	Blue	Red	Red	Red
	Diflufenican (+)		Grey	Red	Grey	
	Ethofumesate			Blue	Grey	Red
	Fluazifop-P-butyl (+)	Grey	Grey	Red		Red
	Fludioxonil (+)	Grey	Red			
	Glyphosate (+)		Blue	Blue	Red	Blue
	Mesotrione (+)		Grey	Grey	Red	
	Metalaxyl-M (+)	Red	Red			
	Metamitron			Red	Grey	Red
	Metribuzin	Red	Red			
	Propyzamide (+)	Grey		Red		Blue
	Pyridate		Grey	Red		
	Rimsulfuron	Blue	Red			
	Tebuconazole (+)*	Blue	Red	Grey	Red	Blue
	Terbuthylazine	Blue	Blue	Red	Blue	Red
Low	Aminopyralid (+)	Blue			Grey	
	Clopyralid	Grey		Blue		Grey
	Desmediphan			Blue		Grey
	Dimethoate	Grey	Grey	Blue	Grey	Grey
	Epoxiconazole	Grey	Blue	Grey	Grey	Grey
	Fenpropimorph	Grey	Blue	Grey	Grey	Blue
	Flamprop-M-isopropyl	Grey		Blue	Grey	Grey
	Fluroxypyr (+)	Grey	Grey	Grey	Blue	Blue
	Foramsulfuron (+)			Blue	Grey	
	Ioxynil	Grey	Grey	Grey	Grey	Blue
	MCPA		Grey	Grey	Blue	Grey
	Mancozeb (+)	Blue				
	Metrafenone (+)				Blue	Grey
	Phenmedipham			Grey		Blue
	Pirimicarb	Grey	Grey	Blue	Blue	Blue
	Propiconazole	Grey	Grey	Grey	Blue	Blue
	Prosulfocarb (+)	Blue		Blue		Grey
	Triasulfuron (+)	Grey		Grey	Blue	
	Triflusulfuron-methyl			Blue		Grey
None	Aclonifen	Grey	Grey			
	Amidosulfuron		Grey		Grey	
	Boscalid	Grey				
	Bromoxynil (+)	Grey	Grey	Grey	Grey	Grey
	Chlormequat		Grey	Grey	Grey	
	Clomazone (+)	Grey	Grey	Grey	Grey	Grey
	Cyazofamid	Grey	Grey			
	Florasulam		Grey		Grey	
	Flupyrsulfuron-methyl (+)		Grey			Grey
	Iodosulfuron-methyl			Grey	Grey	
	Linuron	Grey				
	Mesosulfuron-methyl		Grey		Grey	
	Metsulfuron-methyl			Grey	Grey	
	Pendimethalin	Grey	Grey	Grey	Grey	Grey
	Picolinafen		Grey		Grey	
	Thiacloprid				Grey	
	Thiamethoxam	Grey				Grey
	Tribenuron-methyl	Grey	Grey	Grey	Grey	Grey

- Red: The pesticide (or its degradation products) leached to groundwater in a concentration exceeding 0.1 µg L^{-1} within the first season after application.
- Blue: The pesticide (or its degration products) was detected in more than three consecutive samples or in a single sample in concentrations exceeding 0.1 µg L^{-1}; concentrations (groundwater) below 0.1 µg L^{-1} within the first season after application.
- Grey: The pesticide was either not detected or only detected in very few samples in concentrations below 0.1 µg L^{-1}.

*This information can include 1,2,4-triazole degraded from the pesticides: epoxiconazole and prothioconazole.

Table 8.4. Number of samples (N) from the **groundwater monitoring screens** in which the various pesticides and/or their *degradation products* were detected at each field with the max conc. M (µg L^{-1}). Only high and low risk are included. Hence, pesticides resulting in no detections are omitted. The pesticide and *degradation products* are mentioned, if analysed, under Analyte.

Risk	Pesticide	Analyte	Tylstrup		Jyndevad		Silstrup		Estrup		Faardrup	
			N	M	N	M	N	M	N	M	N	M
High	Azoxystrobin	Azoxystrobin	0	-	0	-	8	0.03	2	0.04	0	-
		CyPM	0	-	0	-	100	0.52	38	0.46	0	-
	Bentazone	*2-amino-N-isopropyl-benzami*de	0	-	0	-	0	-	1	0.03	0	-
		Bentazone	0	-	1	0.01	29	0.44	44	0.05	21	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
		Nitrofen	0	-	0	-	0	-	0	-	0	-
	Diflufenican	*AE-B107137*			0	-	1	0.02	2	0.03		
		Diflufenican			0	-	1	0.47	0	-		
	Ethofumesate	Ethofumesate					5	0.04	0	-	31	1.40
	Fluazifop-P-	*Fluazifop-P*	0	-	0	-	1	0.07			6	0.17
	butyl	*TFMP*	0	-	0	-	87	0.29			0	-
	Fludioxonil	*CGA 192155*	0	-	1	0.05						
		CGA 339833	0	-	1	0.37						
	Glyphosate	*AMPA*			2	0.02	40	0.08	8	0.07	2	0.03
		Glyphosate			0	-	40	0.05	53	0.67	5	0.03
	Mesotrione	*MNBA*			0	-	0	-	1	0.02		
		Mesotrione			0	-	0	-	3	0.13		
	Metalaxyl-M	*CGA 108906*	288	1.50	278	2.70						
		CGA 62826	17	0.04	174	0.68						
		Metalaxyl-M	21	0.08	88	1.30						
	Metamitron	*Desamino-metamitron*					30	0.19	0	-	48	1.30
		Metamitron					29	0.17	0	-	24	0.63
	Metribuzin	*Desamino-diketo-metribuzin*	239	0.20	20	1.83						
		Diketo-metribuzin	453	0.55	26	1.37						
		Metribuzin	1	0.01	0	-						
	Propyzamide	Propyzamide	0	-			9	0.14			1	0.03
		RH-24644	0	-			2	0.03			0	-
	Pyridate	*PHCP*			0	-	14	0.31				
	Rimsulfuron	*PPU*	58	0.05	374	0.23						
		PPU-desamino	9	0.03	98	0.09						
	Tebuconazole	*1,2,4-triazole*[*]	60	0.05	111	0.15			110	0.26	4	0.04
		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

[*] These numbers can include 1,2,4-triazole degraded from the pesticides: epoxiconazole and prothioconazole.

Table 8.4 (*Continued*). Number of samples (N) from the **groundwater monitoring screens** in which the various pesticides and/or their *degradation products* were detected at each field with the max conc. M (µg L^{-1}). Only high and low risk are included. Hence, pesticides resulting in no detections are omitted. The pesticide and *degradation products* are mentioned, if analysed, under Analyte.

Risk	Pesticide	Analyte	Tylstrup		Jyndevad		Silstrup		Estrup		Faardrup	
			N	M	N	M	N	M	N	M	N	M
Low	Aminopyralid	Aminopyralid	2	0.06					0	-		
	Clopyralid	Clopyralid	0	-			1	0.03			0	-
	Desmedipham	Desmedipham					1	0.03			0	-
	Dimethoate	Dimethoate	0	-	0	-	1	0.09	0	-	0	-
	Epoxiconazole	Epoxiconazole	0	-	1	0.01	0	-	0	-	0	-
	Fenpropimorph	Fenpropimorph	0	-	1	0.03	0	-	0	-	1	0.02
	Flamprop-M-isopropyl	Flamprop-M-isopropyl	0	-			1	0.02	0	-	0	-
	Fluroxypyr	Fluroxypyr	0	-	0	-	0	-	1	0.06	1	0.07
	Foramsulfuron	*AE-F130619*					7	0.03	0	-		
		Foramsulfuron					4	0.04	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
	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
	Propiconazole	Propiconazole	0	-	0	-	0	-	2	0.02	1	0.04
	Prosulfocarb	Prosulfocarb	4	0.03			1	0.03			0	-
	Triasulfuron	*Triazinamin*	0	-			0	-	1	0.04		
	Triflusulfuron-methyl	*IN-M7222*					1	0.05			0	-

- **Bentazone** leached through the root zone (1 m b.g.s.) in average concentrations exceeding 0.1 µg L^{-1} to the drainage system at the clayey till 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 water from monitoring screens (Appendix 5). On the sandy soils, bentazone leached at Jyndevad, but was only detected once 1 m b.g.s. at Tylstrup. At Jyndevad many high concentrations (exceeding 0.1 µg L^{-1}) 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 detected in the monitoring wells. Although leached in high average concentrations (>0.1 µg L^{-1}) at four fields, bentazone 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^{-1} 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 water from 1 m depth at Jyndevad, once in drainage at Estrup and Faardrup (Table 8.2), and once in water from a horizontal well at Estrup (Table 8.4). Bentazone has until May 2013 been applied 17 times to the five tests fields. Bentazone was in the period from 2001 to 2015 detected in four groundwater samples from Silstrup in 2003 and in 2005 in four groundwater samples from Faardrup in concentrations ≥0.1 µg L^{-1}. Bentazone has been detected in 105 groundwater samples out of 2877 analysed samples. In total bentazone has been analysed in 4014 water samples from drainage and groundwater. Especially application of bentazone on pea at Silstrup and maize at Faardrup have resulted in a large number of detections and also detections in the groundwater exceeding 0.1 µg L^{-1} (Rosenbom *et al.*, 2013; Pea: 21% detections in groundwater with 1% above 0.1 µg L^{-1}; Maize: 5% detections in groundwater with 2% exceeding 0.1 µg L^{-1}). In May 2016, bentazone was applied to spring barley at both Tylstrup and Jyndevad to test, whether bentazone and three of its degradation products not tested in PLAP before (6-hydroxy-bentazone, 8-hydroxy-bentazone and N-methyl-bentazone) pose a contamination risk to the groundwater. Monitoring of bentazone and these three degradation products 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^{-1} at the clayey till 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^{-1} 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^{-1} (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 from Faardrup, often in low concentrations, but 0.16 µg L^{-1} was detected in one drainage sample in November 2010. In Silstrup, 0.34 and 0.22 µg L^{-1} was detected in two drainage 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, and always in concentrations less than 0.1 µg L^{-1}. The monitoring results thus reveal that the very toxic degradation product nitrofen can be formed in soil after application of bifenox. Detections of nitrofen in water from drainage resulted in the Danish EPA announcing bifenox to be banned in Denmark. The manufacturer immediately removed bifenox from the Danish market before the ban was finally issued in Denmark. Monitoring of bifenox stopped in December 2012.

- **Diflufenican** and the degradation product AE-B107137 and AE-B05422291 have been analysed after application at Jyndevad in 2011 and at Silstrup and Estrup in 2012 and 2013. None of the compounds were detected at Jyndevad, whereas both diflufenican and AE-B107137 were detected frequently in samples from drainage at the clayey till fields. Diflufenican was detected in one groundwater sample (0.47 µg L^{-1}) from Silstrup and AE-B107137 was detected in one and two groundwater samples from Silstrup (0.02 µg L^{-1}) and Estrup (max. 0.03 µg L^{-1}), respectively. Monitoring stopped in April 2015.

- In the clayey till field Estrup, **ethofumesate**, **metamitron**, and its degradation product desamino-metamitron leached through the root zone (1 m b.g.s.) into the drainage in average concentrations exceeding 0.1 µg L^{-1} (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 samples were not as high as at Estrup, although concentrations exceeding 0.1 µg L^{-1} were detected in water from both drainage and groundwater monitoring screens during a period of one to six months 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^{-1} of ethofumesate and 2.100 g ha^{-1} 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^{-1} 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^{-1} 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^{-1}, neither ethofumesate nor metamitron was detected in the analysed water samples. The monitoring of ethofumesate and metamitron stopped in June 2011.

- **Fluazifop-P-butyl** has been included in the monitoring programme several times at Jyndevad, Tylstrup, Silstrup and Faardrup. As fluazifop-P-butyl rapidly degrades, monitoring has until July 2008 only focused on its degradation product fluazifop-P (free acid). Except for one detection below 0.1 µg L^{-1} in groundwater at Silstrup and 17 detections with eight exceeding 0.1 µg L^{-1} at Faardrup (four drainage samples, three soil water samples from the variably-saturated zone and one groundwater sample, Table 8.2 and 8.4), leaching was not pronounced. At Faardrup, fluazifop-P-butyl was applied May 2011 in a reduced dose and another degradation product of fluazifop-P-butyl (TFMP) was included in the monitoring programme. TFMP was not detected in drainage or groundwater. TFMP 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^{-1} were found within a ten-month period, following application (Table 8.3 and 8.4). At the onset of drainage in September, TFMP was detected in all the drainage samples at concentrations exceeding 0.1 µg L^{-1}. The average TFMP concentration in drainage was 0.24 µg L^{-1} in 2008/09. The leaching pattern of TFMP indicates pronounced preferential flow, also in periods with a relatively dry variably-saturated zone. In 2009 the Danish EPA restricted the use of fluazifop-P-butyl regarding dosage, crop types and frequency of applications. After use in low doses at Silstrup in May 2011 no leaching was observed. The fifth application in April 2012 caused a sharp increase in concentrations in drainage as well as groundwater, reaching 0.64 µg L^{-1} and 0.22 µg L^{-1}, respectively. The last detections of TFMP in drainage water was 0.022 µg L^{-1} on 30 October 2013 and in groundwater 0.023 µg L^{-1} on 15 May 2013. This relatively high leaching potential of TFMP following the 2012 application compared to the 2011 application seems to be caused by heavy precipitation events shortly after the application (Vendelboe *et al.*, 2016). Since October 2013 TFMP has been detected in low concentrations in both groundwater and drainage. Untill now the pesticide has been applied ten times at four PLAP fields. Monitoring of TFMP stopped in March 2015.

- **Fludioxoxil** was applied to potatoes at Tylstrup and Jyndevad (sandy soils) in April 2014. To evaluate the leaching risk related to such application the degradation products CGA 192155 and CGA 339833 were included in the PLAP-monitoring programme for the fields. Both compounds were detected only once during the monitoring period extending to April 2016. This was in a groundwater sample from 1.5-2.5 m depth of the vertical well M1 collected 15 October 2015 (CGA 192155: 0.05 µg L^{-1}; CGA 339833: 0.37 µg L^{-1}).

- **Fluroxypyr** has been analysed on all test fields. Fluroxypyr was detected in three samples collected from drainage at Estrup, twice the concentration was 1.4 µg L^{-1} and in one sample from Faardrup; 0.19 µg L^{-1} (Table 8.2). One groundwater sample from each of the two fields contained more than 0.05 µg L^{-1} (Table 8.4). The monitoring of fluroxypyr itself was stopped in June 2008. In May 2015 fluroxypyr was applied to spring barley at Faardrup to evaluate the leaching potential of its two degradation products fluroxypyr-methoxypyridine and fluroxypyr-pyridinol. None of the two compounds were detected in water from drainage or groundwater. Monitoring at Faardrup is ongoing.

- **Glyphosate** and its degradation product AMPA were found to leach through the root zone in high average concentrations through clayey till soils. At the clayey till fields Silstrup and Estrup, glyphosate has been applied eleven and ten times (in 2000, 2001, 2002, 2003, 2005, 2007, 2011, 2012, 2013 and 2014) within the total monitoring period. All applications have resulted in detectable leaching of glyphosate and AMPA into the drainage, often at concentrations exceeding 0.1 µg L^{-1} several months after application. Higher leaching levels of glyphosate and AMPA have mainly been confined to the depth of the drainage system and were rarely 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^{-1}, more than two years after the application (Figure 5.7D). Numbers of detections exceeding 0.1 µg L^{-1} in groundwater monitoring wells is, however, very limited (only a few samples). Glyphosate and AMPA were also detected in drainage water at the clayey till 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 clayey till 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^{-1} in drainage from Silstrup, but not in concentrations in groundwater exceeding 0.1 µg L^{-1}. After application in August 2013 glyphosate was detected in drainage in low concentrations up to 0.036 µg L^{-1}, and AMPA in concentrations up to 0.054 µg L^{-1}. Glyphosate and AMPA was detected in low concentrations in nine groundwater samples in concentrations up to 0.052 µg L^{-1}. Glyphosate and its degradation product AMPA were detected frequently in high concentrations ≥0.1 µg L^{-1} in drainage from Estrup after application in October 2011 and in August 2013, and glyphosate was detected in one groundwater sample in concentration ≥0.1 µg L^{-1} (0.13 µg L^{-1}) after the 2012 application. Neither AMPA nor glyphosate were detected in groundwater from Estrup after the August 2013 application. A more detailed study of the detections at Estrup reveals that the leaching of glyphosate and AMPA were highly *climate driven*, controlled by the timing and intensity of the first rainfall event after glyphosate application (Nørgaard *et al.* 2014). Monitoring at Faardrup of glyphosate stopped August 2012. The Silstrup and Estrup field was sprayed in July 2014, 23 and 10 days, respectively, before the harvest of winter wheat. In the first sampling of drainage at Silstrup on 27 August 2014 the concentration of glyphosate was 0.27 µg L^{-1} and the concentration of AMPA was 0.089 µg L^{-1}. An additional 21 samples contained glyphosate (0.01 to 0.14 µg L^{-1}; Figure 4.8B). AMPA was detected in 53 of a total 65 samples (0.012 to 0.14 µg L^{-1}; Figure 4.8C). Glyphosate and AMPA were only detected in 15 and 16 groundwater samples, respectively, all having concentrations below 0.1 µg L^{-1} and for glyphosate all were sampled before April 2015 (Figure 4.8D-E). Following the latter application at Estrup in July 2014 glyphosate was detected in 26 drainage samples out of 68 with two samples having concentrations of 0.13 and 0.32 µg L^{-1}. Only six detections of glyphosate were obtained on groundwater samples with the two highest concentrations being 0.09 µg L^{-1} in September 2015 and 0.13 µg L^{-1} in March 2016. As observed before in PLAP, these detections seem to be weather driven, in this case by heavy rain and snowmelt events, respectively. Following the July 2014 application AMPA was not detected in the groundwater samples but in 60 samples out of 68 samples from drainage with nine exceeding 0.1 µg L^{-1} (max. conc. 0.21 µg L^{-1}; Figure 5.7). Monitoring at Silstrup and Estrup ended May 2016.

- The herbicide **mesotrione** was applied to maize in 2012 at Jyndevad and at Silstrup and Estrup in May and June 2015 plus twice in June 2016. At all three fields, mesotrione and two degradation products AMBA and MNBA were included in the monitoring. The same detection pattern was observed at Silstrup and Estrup. None of the three compounds were detected in the background samples collected before application. Within the two last hydrological years AMBA is only detected in low concentrations (max 0.04 µg L^{-1}) four times in the variably-saturated zone but not in the saturated zone. Both mesotrione and MNBA has been detected in drainage (1 m depth) in concentrations exceeding 0.1 µg L^{-1} 13 times (max 3.30 µg L^{-1}) and once (0.46 µg L^{-1}), respectively (Table 8.5). The two compounds were also detected in the groundwater. Mesotrione was detected only once in a concentration exceeding 0.1 µg L^{-1}, in water collected from the horizontal well at 3.5 m depth at Estrup. Monitoring at Silstrup and Estrup is ongoing.

- The fungicide **metalaxyl-M** was applied at both Jyndevad and Tylstrup on potatoes in July 2010. At Jyndevad, the compound itself as well as the two degradation products CGA 62826 and CGA 108909 could still be detected in the groundwater five years after the application. Whereas metalaxyl-M, with a single exception, was found only in the vertical monitoring well M7 upstream the PLAP field, both degradation products were detected in water from both suction cups 1.0 m b.g.s., the vertical wells up- and downstream the field, as well as the horizontal well beneath the field. Regarding CGA 62826 the only exceedance of the regulatory limit was 0.15 µg L^{-1} found in the horizontal well 2.5 m b.g.s. on 15 July 2014. CGA 108909, however, was in total at or above the limit six times downstream the field and once upstream (it was also detected in irrigation water in September 2014 – 0.029 µg L^{-1}). Highest concentration was 0.34 µg L^{-1} in the uppermost screen of M5.1 (Table 3.2). As both degradation products were detected in water from the suction cups 1 m b.g.s. the leaching seems to have peaked, but is still continuing June 2015. During the period April 2010 to June 2015 at Tylstrup, CGA 108906 was detected in 82% of the total 506 analysed water samples: One sample of the irrigated water had no detection, the 153 samples from the variably-saturated zone had 84% detections and the 352 samples from the saturated zone showed 82% detections. In 13% of the groundwater samples, which were found to be collected only from vertical screens, concentrations exceed 0.1 µg L^{-1} having a maximum concentration of 1.5 µg L^{-1}. The maximum concentration level detected in water collected from the horizontal groundwater screens of H1 only reached 0.099 µg L^{-1} since sampling was only initiated in March 2012, which was some months after a pulse of CGA 108906 had been detected in samples from 1 and 2 m depth at both S1 and S2 and at the downstream vertical screens. 1% (4/352) of the 13% (47/352) groundwater samples were collected from the screens of the upstream well M1. Here, samples were collected from the three lowest screens M1.2, M1.3 and M1.4 with a level of detections being 17%, 11% and 94%, respectively. These detections were primarily done in the beginning of the period, except for samples taken from M1.4 at 5-6 m depth, where detections were present throughout the whole monitoring period. This clearly indicates the earlier mentioned groundwater contribution of CGA 108906 from upstream fields, which was present before the metalaxyl-M application at the PLAP field in June 2010. With a background concentration of CGA 108906 ranging from 0.02–0.3 µg L^{-1}, detected in the vertical groundwater monitoring wells, it is difficult to determine, to which extent the elevated concentrations observed in the downstream monitoring wells are due to the metalaxyl-M applied on the PLAP field in 2010 or to applications on the upstream fields. Detections of CGA 108906 in water from suction cups and the horizontal well H1, which is situated just beneath the fluctuating groundwater, clearly indicate that CGA 109806 does leach through the PLAP field in high concentrations and hence contribute to the detections in water samples from the vertical groundwater screens downstream the PLAP-field. The monitoring results confirmed the pronounced leaching potential of the two degradation products reported in the EU-admission directive for metalaxyl-M from 2002. At the national approval of metalaxyl-M in Denmark in 2007 the Danish EPA was aware of the degradation products and asked for test in potatoes in PLAP as soon as possible with regard to the planned crop rotation. As a consequence of the monitoring results, metalaxyl-M was banned in Denmark in December 2013 and was recently included in the revised analysis program of the National Groundwater Monitoring (GRUMO) and for drinking water wells in the Waterworks Drilling Control. In the latter, CGA 108906 is already the second most frequently detected compound. Results from PLAP were also sent to EFSA in connection with the re-evaluation of metalaxyl-M in EU. The monitoring of the parent and the two degradation products in PLAP stopped in March 2015.

- 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^{-1} 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^{-1} were seen as late as three years after application. Evidence was also found that their degradation products might be present in the groundwater at least six years after application, most likely because metribuzine and its degradation products have long-term sorption and dissipation characteristics (Rosenbom *et al.*, 2009). Long-term sorption is currently not well described in the groundwater models, but new guidance on how to do this is expected to be published within the next year. In Denmark the conservative Danish approach to groundwater modelling assures that compounds with a high leaching risk are not approved. 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 as the use of it was banned in Denmark. The monitoring of metribuzine and degradation products stopped in February 2011.

- At Estrup, CL 153815 (degradation product of **picolinafen**) leached through the root zone and into the drainage water in average concentrations exceeding 0.1 µg L^{-1} (Appendix 5). CL 153815 was not detected in deeper monitoring screens (Table 8.3). Leaching of CL 153815 was also not detected in the sandy soil Jyndevad after application in October 2007 (Table 8.1, 8.3 and Appendix 5). Monitoring stopped in March 2010.

- **Pirimicarb** together with its two degradation products pirimicarb-desmethyl and pirimicarb-desmethyl-formamido, were included in the monitoring programme for all five fields. All of the three compounds were detected, but only pirimicarb-desmethyl-formamido leached in average concentrations exceeding 0.1 µg L^{-1} through the root zone (1 m b.g.s.) into the drainage system (Table 8.1) at Estrup. Comparable high levels of leaching of pirimicarb-desmethyl-formamido were not 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) were 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 clayey till fields at Silstrup and Faardrup, and entered the drainage system at average concentrations exceeding 0.1 µg L^{-1} (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, concentrations in the groundwater from the screens were always less than 0.1 µg L^{-1} (Appendix 5, Table 8.3 and 8.4). The monitoring at Silstrup ended in March 2008. Propyzamide was applied on 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 at Faardrup stopped in April 2015.

- **Pyridate** was applied to maize at Jyndevad and Silstrup in May 2001. Only its degradation product PHCP was included in the monitoring programme for the two fields. The compound was not detected at Jyndevad, whereas it was detected at Silstrup in water from 1 m depth four times out of 62 samples all exceeding 0.1 µg L^{-1} and with a maximum concentration of 2.69 µg L^{-1} and 14 times out of 175 groundwater samples with four exceeding 0.1 µg L^{-1} and having a max concentration of 0.31 µg L^{-1}. Monitoring stopped in July 2003 at Jyndevad and July 2004 at Silstrup.

- 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^{-1} 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^{-1}) were detected in the soil water sampled 1 and 2 m b.g.s. (Table 8.1 and 8.2). PPU was occasionally detected in groundwater and three samples exceeded 0.1 µg L^{-1} at Jyndevad in 2011/2012, whereas PPU was detected in low concentration <0.1 µg L^{-1} at Tylstrup (Table 8.3 and 8.4). 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^{-1} 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^{-1}. 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). The Danish EPA has withdrawn the approval of rimsulfuron based on the persistence of PPU supported by these monitoring data. Monitoring stopped in December 2012.

- **Tebuconazole** was applied in autumn 2007 at Tylstrup, Jyndevad, Estrup and Faardrup. Only on the clayey till soil of Estrup did the compound leach through the root zone (1 m b.g.s.) and into the drainage in average concentrations exceeding 0.1 µg L^{-1} in an average yearly concentration of 0.44 µg L^{-1} (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 a groundwater monitoring well in concentrations exceeding 0.1 µg L^{-1} (Table 8.3 and 8.4). None of the applications at the three other PLAP fields caused tebuconazole to be detected in similar high concentrations in the variably saturated zone, though concentrations below 0.1 µg L^{-1} were detected in a few samples from the groundwater monitoring screens (Table 8.3 and 8.4). Monitoring of tebuconazole stopped in December 2012. To evaluate on the leaching potential of its degradation product 1,2,4-triazole, tebuconazole was applied in 2014 on cereals at Estrup in May (Table 5.2) and at Tylstrup, Jyndevad and Faardrup in November (Table 2.2, 3.2 and 4.2). The monitoring results of 1,2,4-triazole from Tylstrup (Figure 2.7), Jyndevad (Figure 3.8), Estrup (Figure 5.10) and Faardrup (Figure 6.7) reveal:
    - an in PLAP unprecedented high background concentration level of 1,2,4-triazole in water samples collected from the groundwater at all fields except for Faardrup. The concentration declined with depth, which indicates a source coming from the field surface.

- a 1,2,4-triazole contribution to the groundwater from the variably-saturated (1m depth) caused by the actual application at the two sandy field, whereas this contribution is unclear at the clayey till fields (Estrup and Faardrup) since it was not possible to obtain a drainage sample before application.

With the background concentration level in the groundwater at Tylstrup, Jyndevad and Estrup it is, however, clear that the source resulting in the many detections can not only be the tebuconazole application, but an outcome of earlier applications of fungicides or use of seed dressing having 1,2,4-triazole as a degradation product or even other sources. To evaluate the leaching of 1,2,4-triazole as a result of the application of other parent fungicides the following fungicides were applied:

- epoxiconazole to winter wheat in May 2015 at Jyndevad,
- prothioconazole to winter wheat in May 2015 at Tylstrup and to spring barley in June 2015 at Jyndevad and in May 2015 at Faardrup
- propiconazole (in ½ maximum allowed dose) to spring barley in June 2016 at both Jyndevad and Faardrup.

Following the epoxiconazole and prothioconazole application in 2015, an increase in the concentration of 1,2,4-triazole in water collected from 1 m depth and groundwater monitorings wells was detected. At Faardrup only one detection (0.01 µg/L) was found following the period September 2015 to May 2016 during which monitoring was temporarily stopped due to analysis expenses. At Jyndevad the applications resulted in a concentration level at 1 m depth exceeding 0.1 µg L^{-1} (Figure 3.8). The outcome reveals that 1,2,4-triazole leaching through the variably saturated zone (1 m depth) at both of the sandy fields but also the fractured clayey till field Faardrup, where no 1,2,4-triazole is detected in drainage samples just prior to the 2015 applications. Monitoring of 1,2,4-triazole is ongoing.

- **Terbuthylazine** as well as its degradation products leached through the root zone (1 m b.g.s.) at high average concentrations on clayey till soils. At the three clayey till 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^{-1} (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 exceed 0.1 µg L^{-1}. 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^{-1} during a two 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^{-1}) 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^{-1}) at Jyndevad (Table 8.4, Kjær *et al.*, 2004). Pronounced leaching of terbuthylazine was also seen at two of the three clayey till 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^{-1}. 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 low concentrations. The monitoring of terbuthylazine ended in June 2009.

The monitoring results generally revealed that:

- 19 pesticides resulted in detections in water samples from 1 m depth in average concentration within a year after application being below 0.1 µg L^{-1} (Table 8.1).
- 17 pesticides resulted in no detections at 1 m depth (Tabel 8.1).
- 19 pesticides resulted in detection in groundwater samples in concentrations below 0.1 µg L^{-1}. (Tabel 8.3).
- 18 pesticides resulted in no detections in groundwater; here among 11, which were not detected in samples from 1 m depth (Table 8.3).

The leaching patterns from the sandy and clayey till fields are further illustrated in Figure 8.1 and 8.2A-C showing the frequency of detection in samples 1 m b.g.s. (suction cups on sandy soils and drainage on clayey till soils) and the deeper located groundwater monitoring screens.

At the clayey till fields several pesticides were often detected in water from the drainage system, whereas the frequency of detection in water from 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 Estrup, leaching of pesticides has mainly been confined to the depth of the drainage system.

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, is 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 clayey till fields, the number of water samples collected from drainage 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 the smallest.

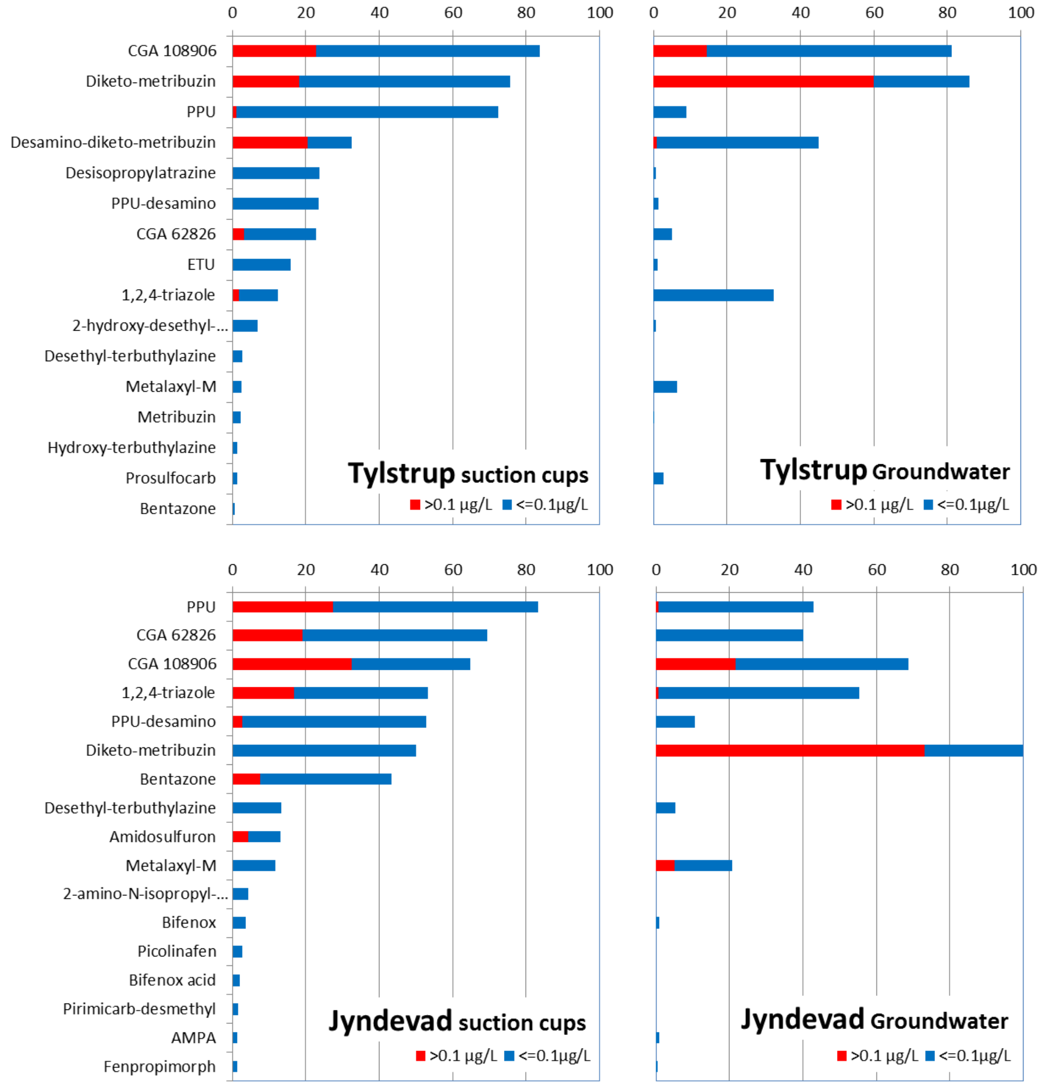

Figure 8.1. Frequency of detection in samples from the suction cups (left) and groundwater monitoring screens located deeper than the suction cups (right) at the **sandy fields: Tylstrup** and **Jyndevad.** Frequency is estimated for the entire monitoring period up to July 2016. The time the different pesticides have been included in the programme and the number of analysed samples varies. The figure includes pesticides detected in water from suction cups and groundwater.

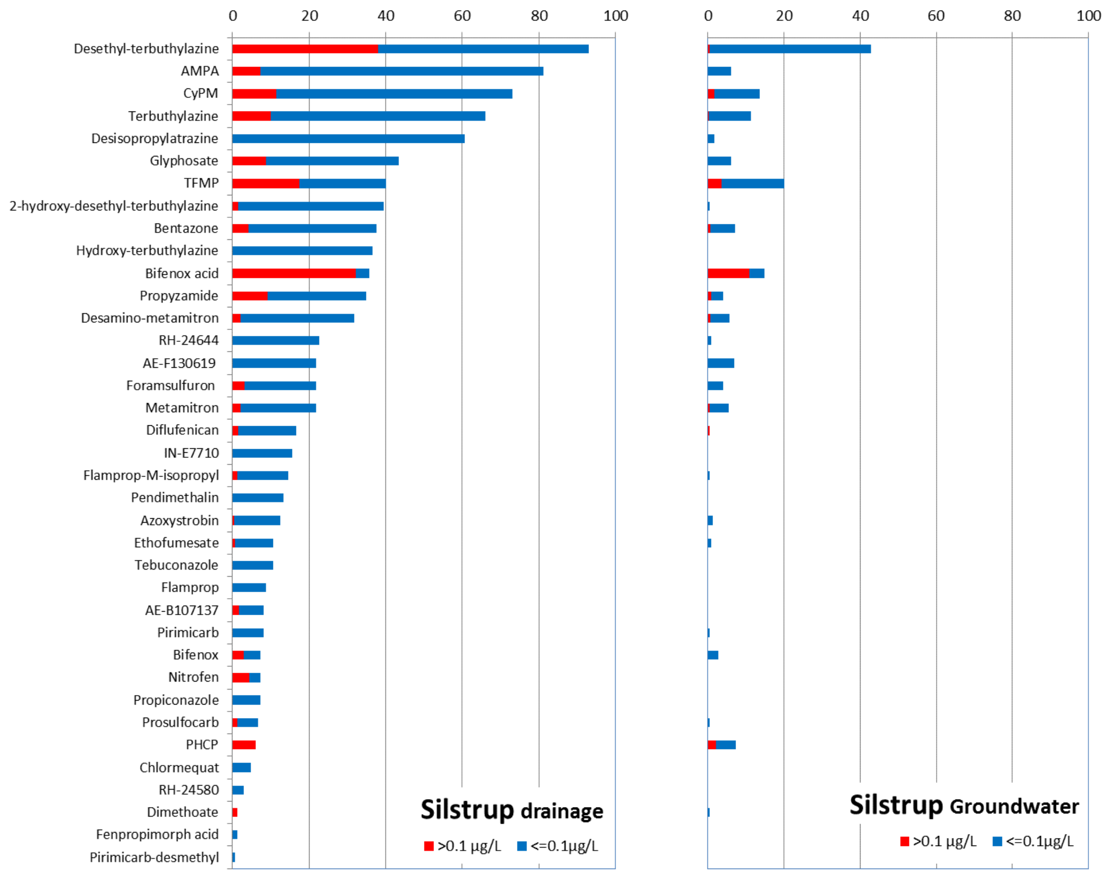

Figure 8.2A. Frequency of detection in samples from the drainage system (left) and groundwater monitoring screens located deeper than the drainage system (right) at the **clayey till field Silstrup**. Frequency is estimated for the entire monitoring period up to July 2016. The time the different pesticides have been included in the programme and the number of analysed samples varies. The figure includes pesticides detected in drainage and groundwater.

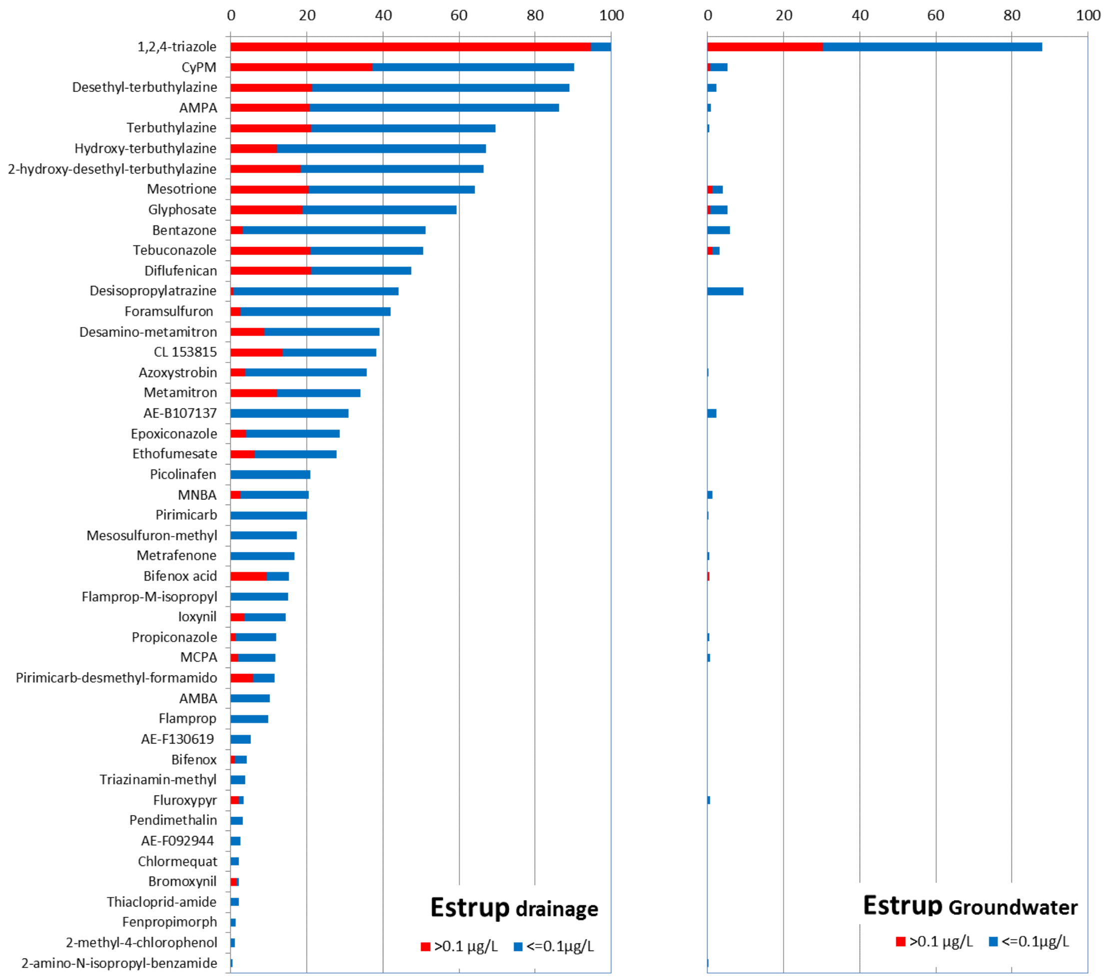

Figure 8.2B. Frequency of detection in samples from the drainage system (left) and groundwater monitoring screens located deeper than the drainage system (right) at the **clayey till field Estrup**. Frequency is estimated for the entire monitoring period up to July 2016. The time the different pesticides have been included in the programme and the number of analysed samples varies. The figure includes pesticides detected in drainage and groundwater.

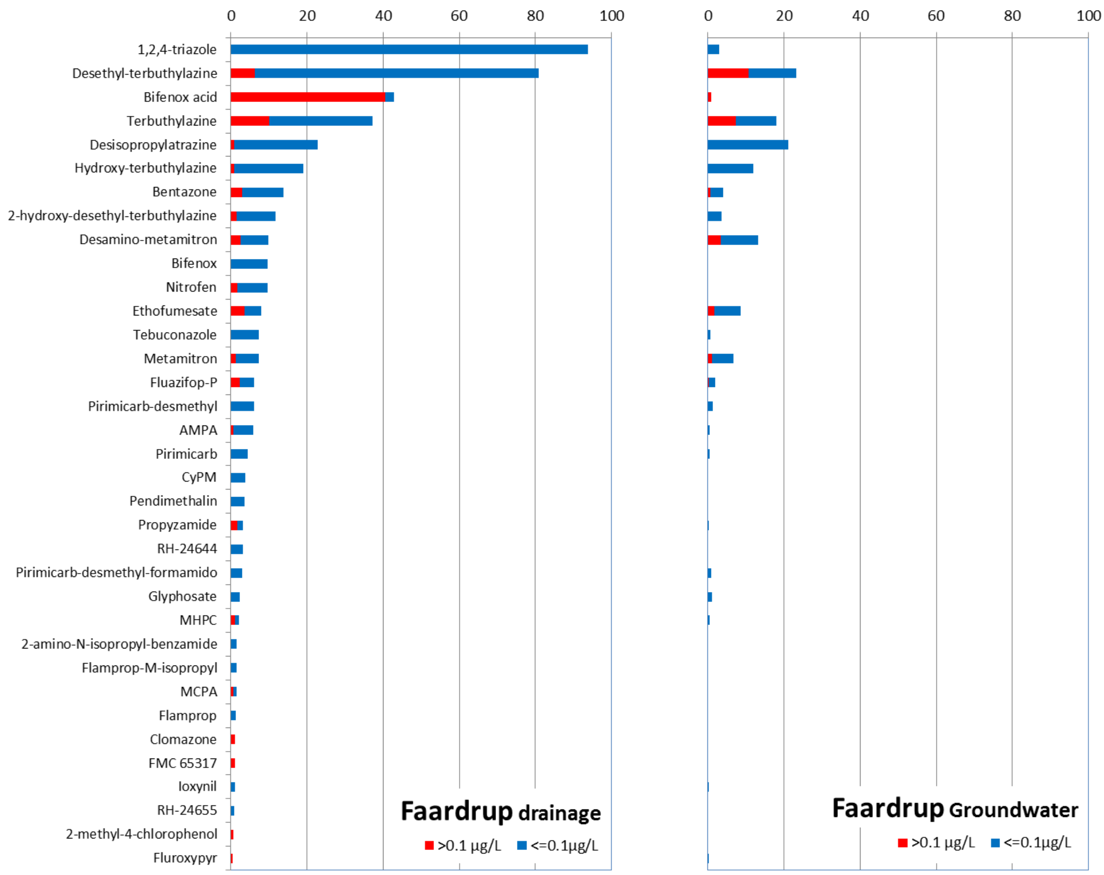

Figure 8.2C. Frequency of detection in samples from the drainage system (left) and groundwater monitoring screens located deeper than the drainage system (right) at the **clayey till field Faardrup**. Frequency is estimated for the entire monitoring period up to July 2016. The time the different pesticides have been included in the programme and the number of analysed samples varies. The figure includes pesticides detected in drainage and groundwater.

This PLAP-report, presents the results of the monitoring period July 2014–June 2016. A total of 9,921 single analyses have now been 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). Within this period, PLAP has evaluated the leaching risk of 15 pesticides and 28 degradation products after the applicaton of the maximum allowed dose of the specific pesticides in connection with the specific crops. The 43 compounds include 12 compounds not evaluated in any previous PLAP reports (marked in red in Table 8.5).

Results covering the period May 1999–June 2015 have been reported previously (Kjær *et al.*, 2002, Kjær *et al.*, 2003, Kjær *et al.*, 2004, Kjær *et al.*, 2005c, Kjær *et al.*, 2007, Kjær *et al.*, 2008, Kjær *et al.*, 2009, Rosenbom *et al.*, 2010b, Kjær *et al.*, 2011, and Brüsch *et al.*, 2013a, Brüsch *et al.*, 2013b, Brüsch *et al.*, 2014, Brüsch *et al.*, 2015, Brüsch *et al.*, 2016; Rosenbom *et al.*, 2016). 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 July 2014-June 2016. All reports and associated peer-reviewed articles can be found at: http://pesticidvarsling.dk/monitor_uk/index.html.

Table 8.5 ***(Same as Table 0.1)*** 15 pesticides and 28 *degradation products* have been analysed in PLAP in the period July 2014-June 2016 of which 12compounds were not evaluated in the latest PLAP-report (in red). The number of water samples analysed collected from the Variably-saturated Zone (VZ; drains and suction cups), Saturated Zone (SZ; groundwater screens) and irrigated water (Irrigation) are presented together with the results of analysis on samples from VZ and SZ given as number of detections (Det.), detections > 0.1 µg L^{-1} and maximum concentration (Max conc). For water used for irrigation, the detected concentration in µg L^{-1} is presented in brackets. (-) indicate no detections.

Pesticide	**Analyte**	**Number of samples from:**			**Results of analysis**					
					VZ			**SZ**		
		VZ	**SZ**	**Irrigation**	**Det.**	**>0.1 µg L^{-1}**	**Max conc.**	**Det.**	**>0.1 µg L^{-1}**	**Max conc.**
Aminopyralid	Aminopyralid	54	103	1 (0.05)	0	0	-	2	0	0.06
Azoxystrobin	Azoxystrobin	129	290		25	1	0.11	7	0	0.03
	CyPM	129	290		123	32	1.00	69	13	**0.52**
Bentazone	Bentazone	118	219	3 (0.01;-;-)	39	0	0.06	14	0	0.02
	6-hydroxy-bentazone	10	53	2(-)	0	0	-	0	0	-
	8-hydroxy-bentazone	10	53	2(-)	0	0	-	0	0	-
	N-methyl-bentazone	10	53	2(-)	0	0	-	0	0	-
Bromoxynil	Bromoxynil	24	70		0	0	-	0	0	-
Clomazone	Clomazone	45	118	1 (-)	0	0	-	0	0	-
	FMC 65317	45	118	1 (-)	0	0	-	0	0	-
Diflufenican	Diflufenican	52	100		6	0	0.02	0	0	-
	AE-05422291	52	100		0	0	-	0	0	-
	AE-B107137	50	109		4	0	0.03	2	0	0.03
Fluazifop-P-buthyl	*TFMP*	39	124		0	0	-	0	0	-
Fludioxonil	*CGA 192155*	88	366	4 (-)	0	0	-	1	0	0.05
	CGA 339833	88	355	4 (-)	0	0	-	1	1	**0.37**
Flupyrsulfuron-methyl	**Flupyrsulfuron-methyl**	58	345	2 (-)	0	0	-	0	0	-
	IN-JV460	58	345	2 (-)	0	0	-	0	0	-
	IN-KC576	58	345	2 (-)	0	0	-	0	0	-
	IN-KY374	58	345	2 (-)	4	3	0.45	0	0	-
Foramsulfuron	**Foramsulfuron**	70	174		23	2	0.32	4	0	0.04
	AE-F092944	70	174		1	0	0.01	0	0	-
	AE-F130619	70	174		9	0	0.02	7	0	0.03
Glyphosat	Glyphosate	134	273		48	5	0.32	21	1	**0.13**
	AMPA	134	273		114	10	0.21	16	0	0.06
Ioxynil	Ioxynil	24	70		0	0	-	0	0	-
Mancozeb	*EBIS*	30	152	2 (-)	0	0	-	0	0	-
Mesotrione	Mesotrione	89	267	1 (-)	34	13	3.30	3	1	**0.13**
	AMBA	89	267	1 (-)	4	0	0.04	0	0	-
	MNBA	89	265	1 (-)	13	1	0.46	1	0	0.02
Metalaxyl-M	Metalaxyl-M	44	152	2 (-)	0	0	-	30	1	**0.11**
	CGA 108906	43	152	2 (0.029;-)	21	2	0.20	98	9	**0.34**
	CGA 62826	43	152	2 (0.071;-)	8	0	0.03	44	1	**0.15**
Metrafenone	Metrafenone	43	84		0	0	-	0	0	-
Propyzamid	Propyzamide	15	54		0	0	-	0	0	-
	RH-24580	15	54		0	0	-	0	0	-
	RH-24644	15	54		0	0	-	0	0	-
	RH-24655	15	54		0	0	-	0	0	-
Prosulfocarb	Prosulfocarb	27	65	1 (-)	0	0	-	0	0	-
Tebuconazole 2014 Epoxiconazole 2015 Prothioconazole 2015	*1,2,4-triazole*	195	590	4 (-)	130	78	0.45	278	38	**0.26**
Fluroxypyr	***Fluroxypyr-methoxypyridine***	1	16		0	0	-	0	0	-
	Fluroxypyr-pyridinol	1	16		0	0	-	0	0	-
Triasulfuron	*Triazinamin*	3	16		0	0	-	0	0	-
Sub total	43-45 (15-17 Pesticides; 28 *Degradation products*)	2434	7449	38	**606**	**147**		**598**	**65**	
Percent		25%	75%	0.4%	**25%**	**6%**		**8%**	**1%**	
Total			**9921**							

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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.

Pesticide	P/M	Analyte	CAS no.	Systematic name	Latest analysis	N
Aclonifen	P	Aclonifen	74070-46-5	2-chloro-6-nitro-3-phenoxyaniline	18.06.13	471
Amidosulfuron	P	Amidosulfuron	120923-37-7	N-[[[[(4,6-dimethoxy-2-pyrimidinyl)amino]carbonyl]-amino]sulfonyl]-N-methylmethanesulfonamide	01.03.06	562
Amidosulfuron	M	Desmethyl-amidosulfuron	-	3-(4-hydroxy-6-methoxypyrimidin-2-yl)-1-(N-methyl-N-methylsulfonyl-aminosulfonyl)-urea (AEF101630)	01.03.06	129
Aminopyralid	P	Aminopyralid	150114-71-9	4-amino-3,6-dichloropyridine-2-carboxylic acid	17.06.14	446
Azoxystrobin	P	Azoxystrobin	131860-33-8	Methyl (E)-2-{2-[(6-(2-cyanophenoxy)-4-pyrimidin-4-yloxy]phenyl}-3-methoxyacrylate	29.06.16	3339
Azoxystrobin	M	CyPM	1185255-09-7	E-2-(2-[6-cyanophenoxy)-pyrimidin-4-yloxy]-phenyl) – 3-methoxyacrylic acid	29.06.16	3492
Bentazone	P	Bentazone	25057-89-0	3-(1-methylethyl)-1H-2,1,3-benzothiadiazin-4(3H)-one 2,2 dioxide	09.06.16	4704
Bentazone	M	2-amino-N-isopropyl-benzamide	30391-89-0	2-amino-N-isopropylbenzamide	28.06.07	2139
Bentazone	M	N-methyl-bentazone	61592-45-8	3-isopropyl-1-methyl-1H-2,1,3-benzothiadiazin-4(3H)-one 2,2-dioxide	09.06.16	72
Bentazone	M	6-hydroxy-bentazone	60374-42-7	6-Hydroxy-3-isopropyl-1H-2,1,3-benzothiadiazin-4(3H)-one 2,2-dioxide	09.06.16	72
Bentazone	M	8-hydroxy-bentazone	60374-43-8	8-Hydroxy-3-(1-methylethyl)-1H-2,1,3-benzothiadiazin-4(3H)-one 2,2-dioxide	09.06.16	72
Bifenox	P	Bifenox	42576-02-3	methyl 5-(2,4-dichlorophenoxy)-2-nitrobenzoate	27.12.12	1190
Bifenox	M	Bifenox acid	53774-07-5	5-(2,4-dichlorophenoxy)-2-nitrobenzoic acid	27.12.12	1109
Bifenox	M	Nitrofen	1836-75-5	2,4-dichlorophenyl 4'-nitrophenyl ether	27.12.12	1190
Boscalid	P	Boscalid	188425-85-6	2-chloro-N-(4'-chlorobiphenyl-2-yl)nicotinamide	11.12.12	190
Bromoxynil	P	Bromoxynil	1689-84-5	3,5-dibromo-4-hydroxybenzonitrile	03.06.14	1888
Chlormequat	P	Chlormequat	999-81-5	2-chloroethyltrimethylammonium chloride	10.07.08	335
Clomazone	P	Clomazone	81777-89-1	2-[(2-chlorphenyl)methyl]-4,4-dimethyl-3-isoxazolidione	08.04.15	1124
Clomazone	M	FMC 65317	-	(N-[2-chlorophenol)methyl]-3-hydroxy-2,2-dimethylpropanamide, (Propanamide-clomazone)	08.04.15	1090
Clopyralid	P	Clopyralid	1702-17-6	3,6-Dichloropyridine-2-carboxylic acid	12.03.09	843
Cyazofamid	P	Cyazofamid	120116-88-3	4-chloro-2-cyano-N,N-dimethyl-5-p-tolylimidazole-1-sulfonamide	12.06.12	417
Desmedipham	P	Desmedipham	13684-56-5	Ethyl 3-(phenylcarbamoyloxy)phenylcarbamate	24.06.03	973
Desmedipham	M	EHPC	7159-96-8	Carbamic acid, (3-hydroxyphenyl)-ethyl ester	24.06.03	652
Diflufenican	P	Diflufenican	83164-33-4	2',4'-difluoro-2-(α,α,α-trifluoro-m-tolyloxy)nicotinanilide	08.04.15	662
Diflufenican	M	AE-B107137	36701-89-0	2-[3-(trifluoromethyl)phenoxy]pyridine-3-carboxylic acid	08.04.15	690
Diflufenican	M	AE-05422291	-	2-[3-(trifluoromethyl)phenoxy]pyridine-3-carboxamide	08.04.15	662
Dimethoate	P	Dimethoate	60-51-5	O,O-dimethyl S-methylcarbamoylmethyl-phosphorodithioate	13.06.05	2038
Epoxiconazole	P	Epoxiconazole	106325-08-0	(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	26225-79-6	(±)-2-ethoxy-2,3-dihydro-3,3-dimethylbenzofuran-5-yl-methanesulfonate	30.06.11	1826
Fenpropimorph	P	Fenpropimorph	67564-91-4	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	63782-90-1	Isopropyl N-benzoyl-N-(3-chloro-4-flourophenyl)-D-alaninate	13.06.05	1987
Flamprop-M-isopropyl	M	Flamprop	58667-63-3	N-benzoyl-N-(3-chloro-4-flourophenyl)-D-alanine	13.06.05	1996
Florasulam	P	Florasulam	145701-23-1	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-fluro-5-hydroxy[1,2,4]triazolo[1,5-c]pyrimidine-2-sulfonamide	19.06.08	275
Fluazifop-P-buthyl	P	Fluazifop-P-butyl	79241-46-6	butyl (R)-2-{4-[5-(trifluoromethyl)-2-pyridyloxy]phenoxy}propionate	24.06.03	402
Fluazifop-P-buthyl	M	Fluazifop-P	83066-88-0	(R)-2-(4-((5-(trifluoromethyl)-2-pyridinyl)oxy)phenoxy-propanoic acid	28.03.12	1769
Fluazifop-P-buthyl	M	TFMP	33252-63-0	5-trifluoromethyl-pyridin-2-ol	08.04.15	1010
Fludioxonil	M	CGA 192155	126120-85-2	2,2-difluoro-benzo[1,3]dioxol-4-carbocyclic acid	05.04.16	569

Pesticide	P/M	Analyte	CAS no.	Systematic name	Latest analysis	N
Fludioxonil	M	CGA 339833	-	3-carbamoyl-2-cyano-3-(2,2-difluoro-benzo[1,3]dioxol-4-yl)-oxirane-2-carbocyclic acid	05.04.16	558
Flupyrsulfuron-methyl	P	Flupyrsulfuron-methyl	144740-54-5		09.06.16	443
Flupyrsulfuron-methyl	M	IN-JV460	-	1-(4,6-dimethoxypyrimidine-2-yl)-2,4-diketo-7-trifluoro-methyl-1,2,3,4-tetrahydropyridol(2,3-d)pyrimidine	09.06.16	443
Flupyrsulfuron-methyl	M	IN-KC576	-		09.06.16	443
Flupyrsulfuron-methyl	M	IN-KY374	-	N-(4,6-dimethoxypyrimidine-2-yl)-N-(3-methoxycarbonyl-6-trifluoromethylpyridine-2-yl)-amine	09.06.16	443
Fluroxypyr	P	Fluroxypyr	69377-81-7	(4-amino-3,5-dichloro-6-fluro-2-pyridinyl)oxy]acetic acid	12.06.08	2047
Fluroxypyr	M	Fluroxypyr-methoxypyridine	35622-80-1	4-amino-3,5-dichloro-6-fluoro-2-pirydynil-2-methoxypyridine	01.06.16	19
Fluroxypyr	M	Fluroxypyr-pyridinol	94133-62-7	4-amino-3,5-dichloro-6-fluoro-2-pyridinol	01.06.16	19
Foramsulfuron	P	Foramsulfuron	173159-57-4		29.06.16	270
Foramsulfuron	M	AE-F092944	36315-01-2	2-amino-4,6-dimethoxypyrimidine	29.06.16	270
Foramsulfuron	M	AE-F130619	-	4-amino-2-[3-(4,6-dimethoxypyrimidin-2-yl)ureidosulfonyl]-N, N-dimethylbenzamide	29.06.16	270
Glyphosate	P	Glyphosate	1071-83-6	N-(phosphonomethyl)glycine	04.05.16	4189
Glyphosate	M	AMPA		Amino-methylphosphonic acid	04.05.16	4188
Iodosulfuron-methyl-natrium	P	Iodosulfuron-methyl-natrium	144550-36-7	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
Ioxynil	P	Ioxynil	1689-83-4	4-hydroxy-3,5-diiodobenzonitrile	31.03.15	1994
Iinuron	P	Linuron	330-55-2	3-(3,4-dichlorophenyl)-1-methoxy-1-methylurea	13.09.01	389
Mancozeb	M	EBIS	33813-20-6	ethylene bisisothiocyanate sulfide	19.03.15	238
Mancozeb	M	ETU	96-45-7	Ethylenethiourea	03.04.01	278
MCPA	P	MCPA	94-74-6	(4-chloro-2-methylphenoxy)acetic acid	29.06.06	1465
MCPA	M	2-methyl-4-chlorophenol	1570-64-5	2-methyl-4-chlorophenol	29.06.06	1458
Mesosulfuron-methyl	P	Mesosulfuron-methyl	208465-21-8	Methyl 2-[3-(4,6-dimethoxypyrimidin-2-yl)ureidosulfonyl]-4-methanesulfonamidomethylbenzoate	02.12.09	647
Mesosulfuron-methyl	M	Mesosulfuron	400852-66-6	2-[[[[(4,6-dimethoxy-2-pyrimidinyl)amino]carbonyl]amino]sulfonyl]-4-[[(methylsulfonyl)amino]methyl]benzoic acid	02.12.09	270
Mesotrione	P	Mesotrione	104206-82-8	2-(4-mesyl-2-nitrobenzoyl)cyclohexane-1,3-dione	29.06.16	625
Mesotrione	M	MNBA	110964-79-9	methylsulfonyl-2-nitrobenzoic acid	29.06.16	623
Mesotrione	M	AMBA	393085-45-5	2-amino-4-methylsulfonylbenzoic acid	29.06.16	625
Metalaxyl-M	P	Metalaxyl-M	70630-17-0	methyl N-(methoxyacetyl)-N-(2,6-xylyl)-D-alaninate	19.03.15	1117
Metalaxyl-M	M	CGA 62826	75596-99-5	2-[(2,6-dimethylphenyl)(methoxyacetyl)amino]propanoic acid	19.03.15	1127
Metalaxyl-M	M	CGA 108906	104390-56-9	2-[(1-carboxyethyl)(methoxyacetyl)amino]-3-methylbenzoic acid	19.03.15	1124
Metamitron	P	Metamitron	41394-05-2	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	220899-03-6	3'-bromo-2,3,4,6'-tetramethoxy-2',6-dimethylbenzophenone	08.04.15	608
Metribuzin	P	Metribuzin	21087-64-9	4-amino-6-tert-butyl-4,5-dihydro-3-methylthio-1,2,4-triazine-5-one	28.05.02	577
Metribuzin	M	Desamino-metribuzin	35045-02-4	6-(1,1-dimethylethyl)-3-(methylthio)- 1,2,4-triazin-5-(4H)-one	28.05.02	542
Metribuzin	M	Diketo-metribuzin	56507-37-0	4-amino-6-tert-butyl-4,5-dihydro-1,2,4-triazine-3,5-dione	09.03.11	977
Metribuzin	M	Desamino-diketo-metribuzin	52236-30-3	6-tert-butyl-4,5-dihydro-3-methylthio-1,2,4-triazine-3,5-dione	09.04.08	891
Metsulfuron-methyl	P	Metsulfuron-methyl	74223-64-6	Methyl-2-(4-methoxy-6-methyl-1,3,5-triazin-2-ylcarbamoylsulfamoyl)benzoate	22.12.10	1346
Pendimethalin	P	Pendimethalin	40487-42-1	N-(1-ethyl)-2,6-dinitro-3,4-xynile	10.12.09	2881
Phenmedipham	P	Phenmedipham	13684-63-4	3-[(methoxycarbonyl)amino]phenyl (3-methylphenyl)carbamate	24.06.03	974
Phenmedipham	M	3-aminophenol	137641-05-5	1-amino-3-hydroxybenzene	26.02.02	391
Phenmedipham	M	MHPC	13683-89-1	Methyl-N-(3-hydoxyphenyl)-carbamate	24.06.03	968
Picolinafen	P	Picolinafen	137641-05-5	4'-fluoro-6-(a,a,a-trifluoro-m-tolyloxy)pyridine-2-carboxanilide	30.03.10	352
Picolinafen	M	CL153815	137640-84-7	6-(3-trifluoromethylphenoxy)-2-pyridine carboxylic acid	30.03.10	352
Pirimicarb	P	Pirimicarb	23103-98-2	2-(dimethylamino)-5,6-dimethyl-4-pyrimidinyldimethylcarbamate	26.06.07	3432
Pirimicarb	M	Pirimicarb-desmethyl-formamido	27218-04-8	2-methylformamido-5,6-dimethylpyrimidine-4-yl dimethylcarbamate	26.06.07	2678
Pirimicarb	M	Pirimicarb-desmethyl	30614-22-3	2-(dimethylamino)-5,6-dimethyl-4-pyrimidinylmethylcarbamate	26.06.07	3078
Propiconazol	P	Propiconazole	60207-90-1	1-[[2-(2,4-dichlorophenyl)-4-propyl-1,3-dioxolan-2-yl]methyl]-1H-1,2,4-triazole	22.03.05	3421

Pesticide	**P/M**	**Analyte**	**CAS no.**	**Systematic name**	**Latest analysis**	**N**
Propyzamide	P	Propyzamide	23950-58-5	3,5-dichloro-N-(1,1-dimethylprop-2-ynyl)benzamide	12.06.14	1158
Propyzamide	M	RH-24644	-	2-(3,5-dichlorophenyl)-4,4-dimethyl-5-methylene-oxazoline	12.06.14	1158
Propyzamide	M	RH-24655	-	3,5-dichloro-N-(1,1-dimethylpropenyl)benzamide	12.06.14	1059
Propyzamide	M	RH-24580	-	N-(1,1-dimethylacetonyl)-3,5-dichlorobenzamide	12.06.14	1158
Prosulfocarb	P	Prosulfocarb	52888-80-9	N-[[3-(4-methoxy-6-methyl-1,3,5-triazin-2-yl)-3-[2-(3,3,3,- trifluro=propyl)phenylsulfonyl]urea	19.03.15	921
Pyridate	P	Pyridate	55512-33-9	O-6-chloro-3-phenylpyridazin-4-yl S-octyl thiocarbonate	03.09.02	183
Pyridate	M	PHCP	40020-01-7	3-phenyl-4-hydroxy-6-chloropyridazine	02.06.04	571
Rimsulfuron	P	Rimsulfuron	122931-48-0	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	138724-53-5	N-(4,6-dimethoxy-2-pyrimidinyl-N-((3-ethylsulfonyl)-2-pyridinyl)urea (IN70941)	11.12.12	2311
Tebuconazole	P	Tebuconazole	107534-96-3	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-triazole	288-88-0	1,2,4-triazole	26.06.16	888
Terbuthylazin	P	Terbuthylazine	5915-41-3	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	Desisopropylatrazine	1007-28-9	6-chloro-N-ethyl-1,3,5-triazine-2,4-diamine	25.03.09	1618
Terbuthylazin	M	Desethyl-terbuthylazine	30125-63-4	6-chloro-N-(1,1-dimethylethyl)-1,3,5,triazine-2,4-diamine	10.06.09	2619
Terbuthylazin	M	Hydroxy-terbuthylazine	66753-07-9	6-hydroxy-N-(1,1-dimethylethyl)-N´-ethyl-1,3,5,triazine-2,4-diamine	19.06.08	1520
Thiacloprid	P	Thiacloprid	111988-49-9	(Z)-3-(6-chloro-3-pyridylmethyl)-1,3-thiazolidin-2-ylidenecyanamide	28.03.12	168
Thiacloprid	M	Thiacloprid-amide	676228-91-4	(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-{carbamoyl[(6-chloropyridin-3-yl)-methyl]amino}-ethanesulfonic acid	28.03.12	176
Thiamethoxam	P	Thiamethoxam	153719-23-4	3-(2-cholro-thiazol-5-ylmethyl)-5-methyl[1,3,5]oxadiazinan-4ylidene-N-nitroamine	18.06.08	559
Thiamethoxam	M	CGA 322704	210880-92-5	[C(E)]-N-[(2-chloro-5-thiazolyl)methyl]-N'-methyl-N'-nitroguanidine	18.06.08	559
Triasulfuron	P	Triasulfuron	82097-50-5	1-[2-(2-chloroethoxy)phenylsulfonyl]-2-(4-methoxy-6-methyl-1,3,5-triazine-2-yl)-urea	04.03.03	445
Triasulfuron	M	Triazinamin	1668-54-8	2-amino-4-methoxy-6-methyl-1,3,5-triazine	29.06.16	1745
Tribenuron-methyl	P	Tribenuron-methyl	101200-48-0	Methyl-2-[4-methoxy-6-methyl-1,3,5-triazin-2-yl(methyl)-carbamoylsulfamoyl]benzoate	09.06.01	3
Tribenuron-methyl	M	Triazinamin-methyl	5248-39-5	4-methoxy-6-methyl-1,3,5-triazin-methylamine	29.08.12	2386
Triflusulfuron-methyl	P	Triflusulfuron-methyl	126535-15-7	Methyl-2-[4-dimethylamino-6-(2,2,2-trifluoroethoxy)-1,3,5-triazin-2-ylcarbamoylsulfamoyl]-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 fields, 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 clayey till fields, 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 clayey till fields, 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.

Field	Monthly monitoring (Intensive)	Half-yearly monitoring (Extensive)	Not monitored
Tylstrup	M4, M5, S1a, S2a, H1 ^{m}	M1, M3, M4, M5, S1a, S2a, S1b*, S2b*	M2, **M6**, M7
Jyndevad	M1, M4, S1a, S2a, H1 ^{m}	M2, M5, M7	M3, **M6**, S1b, S2b
Silstrup	M5, H1.2, H2 ^{m}	M9, M10. M12, H1.1, H1.3	M1, M2, M4, **M6**, M8, M7, M11, **M13**, **H2.1, H2.2, H2.3**
Estrup	M4, H1.2, H2 ^{m}	M1, M5, M6, H1.1 H1.3	M2, **M3, M7**
Faardrup	M4, M5, H2.3, H2 ^{m}	M6, H2.1, H2.5	M1, **M2, M3, M7, H1.1**, H1.2, **H1.3**

S1a and S1b refer to suction cups installed 1 and 2 m b.g.s., respectively, at location S1, whereas S2a and S2b refer to suction cups installed 1 and 2 m b.g.s., respectively, at location S2. ^{m}- Mixed water samples from three screens.
**At Tylstrup suctions cups installed 2 m b.g.s.are monitored four times a year (see text).*
From september2014 some wells and some deeper wells are monitored more frequent and some of the horizontal wells are monitored every month in water samples form the 3 screens, replacing mixed samples.This 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 clayey till fields, sampling from the suction cups for inorganic analysis, from one-two monitoring wells per field, and one horizontal well at Silstrup (H2) and Faardrup (H1) was suspended. On the sandy fields, 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 fields were sampeled monthly. Each horizontal well contain three screens and water sampels form 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 analysis 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 flow-proportional sampler (µg L^{-1}). ND are included as 0 µg L^{-1} calculating average concentrations.

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

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

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

where:
n = Number of weeks within the period of continuous drainage runoff
V_i= Weekly accumulated drainage runoff (mm/week)
Vf_i = Drainage runoff accumulated during a “flow event” (mm/storm event)
Cf_i= Pesticide concentration in the “event samples” collected by means of the flow-proportional sampler (µg L^{-1})
Ct_i= Pesticide concentration in the weekly samples collected by means of the time-proportional sampler (µg L^{-1})

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 2016 growing seasons. The active ingredients of the various pesticides are indicated in parentheses.

Date	Management practice and growth stages – **Tylstrup**
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^{-1}
19-04-2011	Seed bed preparation, 8 cm depth
19-04-2011	Spring barley sown, cv.TamTam, seeding rate 180 kg ha^{-1}, 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^{-1} (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^{-1} (epoxiconazole not analysed)
05-07-2011	BBCH stage 75
08-07-2011	BBCH stage 77
08-07-2011	Biomass 1175.9 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^{-1} - 85% DM
18-08-2011	Straw remowed, yield 34.6 hkg ha^{-1} - 100% DM
22-03-2012	Ploughed - depth 24 cm
24-03-2012	Spring barley sown, cv. TamTam, seeding rate 185 kg ha^{-1}, 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^{-1}
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^{-1}
25-05-2012	Mustang forte (aminopyralid/florasulam/2,4-D) - weeds - 0.75 L ha^{-1}
25-05-2012	BBCH stage 29
31-05-2012	BBCH stage 32
31-05-2012	Irrigation 24 mm. Started 31/05. Ended 01/05
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 + epoxiconazole) - fungi - 1.5 L ha^{-1} (epoxiconazole not analysed)
02-07-2012	BBCH stage 61
10-07-2012	BBCH stage 79
10-07-2012	Biomass 1138.3 g m^{-2} - 100% DM
24-07-2012	BBCH stage 83

Date	Management practice and growth stages – **Tylstrup**
06-08-2012	BBCH stage 86
13-08-2012	BBCH stage 88
13-08-2012	Glyfonova 450 Plus (glyphosate) - weeds - 2.4 L ha^{-1} (not analysed)
27-08-2012	BBCH stage 89
27-08-2012	Harvest of spring barley. Tubbleheight 15 cm, grain yield 62.0 hkg ha^{-1} - 85% DM. Straw remowed, yield 37.3 hkg ha^{-1} - 100% DM
31-08-2012	Tracer (potasium bromide), 30 kg ha^{-1}
20-09-2012	Ploughed - depth 22 cm
23-09-2012	Winter rye sown, cv. Magnifico, seeding rate 64.0 kg ha^{-1}, 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^{-1}
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^{-1}
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^{-1}
07-05-2013	BBCH stage 31
08-05-2013	Starane XL (fluroxypyr) - weeds - 1.2 L ha^{-1}
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 1275.2 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. Stubleheight 15 cm, grainyield 77.4 hkg ha^{-1} - 85% DM. Straw remowed, yield 33.8 hkg ha^{-1} - 100% DM
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^{-1}
03-04-2014	Fertilisation - 100 K, kg ha^{-1}
15-04-2014	Maxim 100 FS (fludioxonil) - fungi - 250 ml ton^{-1} potatoes ~ 625 mL ha^{-1} a 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^{-1} (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^{-1} (not included in monitoring)
17-05-2014	BBCH stage 9 – emergence
22-05-2014	Titus WSB (rimsulfuron) + U46 M (MCPA) - weeds - 20 g ha^{-1} + 100 mL ha^{-1} (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

Date	Management practice and growth stages – **Tylstrup**
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^{-1}
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^{-1}
14-07-2014	BBCH stage 69
14-07-2014	Dithane NT (mancozeb) - fungi - 2.0 L ha^{-1}
23-07-2014	BBCH stage 75?
23-07-2014	Irrigation 24 mm. Started 23/07. Ended 23/07
24-07-2014	Dithane NT (mancozeb) - fungi - 2.0 L ha^{-1}
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^{-1}
11-08-2014	BBCH stage 90?
11-08-2014	Dithane NT (mancozeb) - fungi - 2.0 L ha^{-1}
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^{-1}
25-08-2014	BBCH stage 92
25-08-2014	Dithane NT (mancozeb) - fungi - 2.0 L ha^{-1}
12-09-2014	Harvest of potatoes. Tuber yield 107.1 hkg ha^{-1} - 100% DM
15-09-2014	Liming - 4.0 t ha^{-1}
20-09-2014	Disk harrowed - depth 10 cm
20-09-2014	Stubble cultivated - depth 25 cm
22-09-2014	Sowing winter wheat, cv. Mariboss, sowing depth 3.0 cm, seeding rate 190 kg ha^{-1}, row distance 12.5 cm, final plantnumber 248 m^{-2}
22-09-2014	BBCH stage 00
29-09-2014	BBCH stage 07-08
29-09-2014	Fertilisation - 24.5 N, kg ha^{-1}
02-10-2014	BBCH stage 09 – emergence
09-10-2014	BBCH stage 11
13-10-2014	BBCH stage 12
22-10-2014	BBCH stage 13
30-10-2014	BBCH stage 13
30-10-2014	Lexus 50 WG (flupyrsulfuron) - weeds - 10 g ha^{-1} (i.e. 4.6 g a.i. ha^{-1})
14-11-2014	BBCH stage 14-15
14-11-2014	Orius 200 EW (tebuconazole) - fungi – 1.25 L ha^{-1} (i.e. 250 g a.i. ha^{-1})
17-12-2014	BBCH stage 22
17-12-2014	Biomass 16.1 g m^{-2} - 100% DM
24-03-2015	BBCH stage 22
24-03-2015	Fertilisation - 49.6 N, 7.1 P, 23.6 K, kg ha^{-1}
09-04-2015	BBCH stage 24
09-04-2015	Lexus 50 WG (flupyrsulfuron) - weeds - 10 g ha^{-1} (i.e. 4.6 g a.i. ha^{-1})
22-04-2015	BBCH stage 30
30-04-2015	BBCH stage 31
05-05-2015	BBCH stage 31
05-05-2015	Fertilisation - 105 N, 15 P, 50 K, kg ha^{-1}
14-05-2015	BBCH stage 32
14-05-2015	Starane XL (fluroxypyr + florasulam) - weeds - 1.2 L ha^{-1} (i.e.120 g a.i. ha^{-1} + 3 g a.i. ha^{-1})
14-05-2015	Proline EC 250 (prothioconazole) - fungi - 0.8 L ha^{-1} (i.e. 200 g a.i. ha^{-1})
26-05-2015	BBCH stage 33
12-06-2015	BBCH stage 49
12-06-2015	Proline EC 250 (prothioconazole) - fungi - 0.8 L ha^{-1} (i.e. 200 g a.i. ha^{-1})
15-06-2015	BBCH stage 51
15-06-2015	Biomass 890.1 g m^{-2} - 100% DM
13-07-2015	BBCH stage 71
21-07-2015	BBCH stage 75
21-07-2015	Irrigation 26 mm. Started 21/7 20:00. Ended 22/7 07:00
13-08-2015	BBCH stage 82

Date	Management practice and growth stages – **Tylstrup**
13-08-2015	Biomass 1673 g m^{-2} – 100% DM
20-08-2015	BBCH stage 88
20-08-2015	Broadsown a catchcrop of oil seed rape cv. Akiro, 16 kg ha^{-1} (on top of the soil)
20-08-2015	Glyphogan (glyhosate) - weeds - 2.7 l ha^{-1} (sprayed simultaniously with the sowing of the catchcrop) (i.e. 972 g a.i. ha^{-1})
01-09-2015	BBCH stage 09 – emergence of catch crop
08-09-2015	BBCH stage 90
08-09-2015	Harvest of winter wheat. Stubleheight 14 cm, grainyield 74.0 hkg ha^{-1} 85% DM
10-09-2015	Straw remowed, yield 46.4 hkg ha^{-1} - 100% DM
22-03-2016	Ploughed - depth 23 cm
15-04-2016	Spring barley sown, cv.Evergreen, seeding rate 155 kg ha^{-1}, sowing depth 2.8 cm, row distance 13 cm. Final plantnumber 272 m^{-2} Sown with rotorharrow combine sowing machine
15-04-2016	BBCH stage 0
18-04-2016	Fertilization – 168 N, 24 P, 80 K, kg ha^{-1}
21-04-2016	Undersowing of clover grass catch crop (AgrowGrass 350 MidiMaize) seeding rate 13 kg ha^{-1}, sowing depth 1 cm, row distance 12 cm
01-05-2016	BBCH stage 9
10-05-2016	BBCH stage 12
19-05-2016	BBCH stage 23
19-05-2016	Biomass 47.8 g m^{-2} – 100% DM
19-05-2016	Fighter 480 (bentazone) - weeds- 1.5 L ha^{-1} (i.e. 720 g a.i. ha^{-1})
19-05-2016	Catchcrop – BBCH stage 11-12
02-06-2016	BBCH stage 36
09-06-2016	BBCH stage 50
09-06-2016	Irrigation 27 mm. Started 21/7 20:00. Ended 22/7 07:00
10-06-2016	BBCH stage 50
10-06-2016	Biomass 414.8 g m^{-2} – 100% DM
24-06-2016	BBCH stage 54

Table A3.2. Management practice at **Jyndevad** during the 2009 to 2016 growing seasons. The active ingredients of the various pesticides are indicated in parentheses.

Date	Management practice and growth stages – **Jyndevad**
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^{-1}, 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^{-1}
05-04-2011	BBCH stage 9
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^{-1} (not analysed)
26-04-2011	DFF (diflufenican) - 0.25 L ha^{-1} - weeds
02-05-2011	BBCH stage 26
02-05-2011	Irrigation - 30 mm ha^{-1}. 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^{-1} - manganese 0.368 kg ha^{-1} + N 0.035 kg ha^{-1}
18-05-2011	BBCH stage 37
23-05-2011	BBCH stage 40
23-05-2011	Irrigation - 32 mm ha^{-1}. 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^{-1}. 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^{-1} - 85% DM, stubble height 15 cm
25-08-2011	Remowal of straw, straw yield 30.2 hkg ha^{-1} - 100% DM
30-03-2012	Ploughed. Depth 22 cm
02-04-2012	Rolled with concrete roller
30-04-2012	Fertilization 120 K, kg ha^{-1}
30-04-2012	Fertilization 140 N, 17.7 P, 65.3 K, kg ha^{-1}
03-05-2012	Sowing maize - cultivare Atrium - seed distance 12 cm, row distance 75 cm, depth 6 cm. Seedrate 111,000 seeds ha^{-1}, final plant number 12.8 m^{-2}
03-05-2012	Fertilization 29.4 N, 14.7 P, kg ha^{-1}
07-05-2012	Tracer (potasium bromide), 30.54 kg ha^{-1}
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^{-1}
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 (mesotrione) - weeds - 1.5 L ha^{-1}
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^{-1} + 0.06 L ha^{-1} - 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 2182.3 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 8241.8 g m^{-2} - 100% DM
20-08-2012	BBCH stage 68

Date	Management practice and growth stages – **Jyndevad**
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%
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^{-1} - 100% DM. Stubble height 25 cm
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^{-1},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 (bentazone) + Stomp (pendimethalin) 0.4 L ha^{-1} + 0.6 L ha^{-1} - 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 (bentazone) + Stomp (pendimethalin) 0.5 L ha^{-1} + 0.6 L ha^{-1} - weeds (pendimethalin not analysed)
17-05-2013	Fertilization 16.0 P, 83.2 K, kg ha^{-1}
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^{-1}. 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^{-1}. 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^{-1} (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^{-1} - 86% DM. Strawyield 30.1 hkg ha^{-1} - 100% DM, stubble height 10 cm. Straw shreddet at harvest
14-08-2013	Harvest of the eastern half of the field - straw shreddet at harvest
20-08-2013	Stuble cultivation - 8 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^{-1}
10-04-2014	Fertilization 19.7 N, kg ha^{-1}
15-04-2014	Planting potatoes. Cv. Oleva, Rowdistance 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^{-1} 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}+ 1.5 L ha^{-1}
06-05-2014	BBCH stage 08 (crop not emerged yet)
06-05-2014	Titus WSB (rimsulfuron) - weeds - 10 g ha^{-1} (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^{-1} (not included in monitoring)
02-06-2014	BBCH stage 29
10-06-2014	BBCH stage 38

Date	Management practice and growth stages – **Jyndevad**
12-06-2014	BBCH stage 39
12-06-2014	Dithane NT (mancozeb) - fungi - 2.0 L ha^{-1}
14-06-2014	BBCH stage 47
14-06-2014	Irrigation - 20 mm ha^{-1}. Started on eastside 14/06. Ended on westside15/06
16-06-2014	BBCH stage 48
18-06-2014	BBCH stage 50
18-06-2014	Dithane NT (mancozeb) - fungi - 2.0 L ha^{-1} + Mospilan SG (acetamiprid) - pests - 150 g ha^{-1} (not included)
18-06-2014	Microcare - 1.0 L ha^{-1} - manganese 0.368 kg ha^{-1} + N 0.035 kg ha^{-1}
19-06-2014	BBCH stage 50
19-06-2014	Irrigation - 25 mm ha^{-1}. 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^{-1} + Mospilan SG (acetamiprid) - pests - 150 g ha^{-1} (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^{-1}
08-07-2014	BBCH stage 69
12-07-2014	Dithane NT (mancozeb) - fungi - 2.0 L ha^{-1}
12-07-2014	BBCH stage 70
18-07-2014	BBCH stage 72
18-07-2014	Dithane NT (mancozeb) - fungi - 2.0 L ha^{-1}
18-07-2014	Microcare - 1.0 L ha^{-1} - manganese 0.368 kg ha^{-1} + N 0.035 kg ha^{-1}
21-07-2014	BBCH stage 79
21-07-2014	Irrigation - 25 mm ha^{-1}. 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^{-1}
29-07-2014	BBCH stage 82
29-07-2014	Irrigation - 25 mm ha^{-1}. Started on eastside 29/07. Ended on westside 30/07
30-07-2014	Ranman (cyazofamid) - fungi - 0.2 L ha^{-1}
30-07-2014	BBCH stage 85
04-08-2014	BBCH stage 86
04-08-2014	Irrigation - 25 mm ha^{-1}. 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^{-1}
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^{-1}
01-09-2014	Rotor harrowed - 6 cm depth
16-09-2014	Harrowed diagonally - depth 6 cm.
18-09-2014	Winterwheat drilled directly in the potato stuble
26-09-2014	BBCH 09 – emergence
29-09-2014	BBCH 10
08-10-2014	BBCH 13
22-10-2014	BBCH 14
22-10-2014	Lexus 50 WG (flupyrsulfuron) - weeds - 10 g ha^{-1} (i.e. 4.6 g a.i. ha^{-1})
24-10-2014	BBCH 14
27-10-2014	BBCH 15
11-11-2014	BBCH 20
11-11-2014	Orius 200 EW (tebuconazole) - fungi – 1.25 L ha^{-1} (i.e. 250 g a.i. ha^{-1})
17-11-2014	BBCH 20
27-11-2014	BBCH 21
09-03-2015	BBCH 22
17-03-2015	BBCH 22
18-03-2015	Fertilization 120.0 N, 15 P, 56 K, kg ha^{-1}
20-03-2015	BBCH 22
20-03-2015	Lexus 50 WG (flupyrsulfuron) - weeds - 10 g ha^{-1} (i.e. 4.6 g a.i. ha^{-1})
07-04-2015	BBCH 23
15-04-2015	BBCH 30
15-04-2015	Biomass 64.5 g m^{-2} - 100% DM
16-04-2015	Fertilization 4 P, 20 K, kg ha^{-1}
17-04-2015	Fertilization 50.0 N, kg ha^{-1}

Date	Management practice and growth stages – **Jyndevad**
20-04-2015	BBCH 31
28-04-2015	BBCH 32
04-05-2015	BBCH 33
08-05-2015	BBCH 34
	Opus + Comet (epoxiconazole+pyraclostrobin) - fungi - 1.0 L ha^{-1}+1.0 L ha^{-1} (i.e 125g a.i. ha^{-1}+250g a.i. ha^{-1})
13-05-2015	BBCH 35
18-05-2015	BBCH 37
26-05-2015	BBCH 43
01-06-2015	BBCH 47
09-06-2015	BBCH 55
09-06-2015	Biomass 949.1 g m^{-2} - 100% DM
11-06-2015	BBCH 57
11-06-2015	Irrigation - 27 mm ha^{-1}. Started on eastside 11/06. Ended on westside 12/06
16-06-2015	BBCH 59
17-06-2015	Proline 250 EC (prothioconazole) - fungi - 0.8 L ha^{-1} (i.e. 200 g a.i. ha^{-1})
23-06-2015	BBCH 60
29-06-2015	BBCH 65
30-06-2015	BBCH 65
30-06-2015	Irrigation - 30 mm ha^{-1}. Started on eastside 30/06. Ended on westside 01/07
06-07-2015	BBCH 75
08-07-2015	BBCH 75
08-07-2015	Biomass 1358.8 g m^{-2} - 100% DM
13-07-2015	BBCH 79
13-07-2015	Irrigation - 30 mm ha^{-1} started on eastside 13/7 ended on westside 14/7
14-07-2015	BBCH 79
21-07-2015	BBCH 81
03-08-2015	BBCH 83
10-08-2015	BBCH 87
20-08-2015	Harvest of winter wheat. Grain yield 79.7 hkg ha^{-1} 85% DM, straw yield 71.5 hkg ha^{-1} 100% DM, stubbleheight 15 cm. Straw shredded (left in field) at harvest.
20-08-2015	Rotor harrowed, 5-6 cm depth
07-03/2016	Ploughing - 22 cm depth
21-03-2016	Sowing spring barley cv. KWS Irena, depth 4.0 cm, rowdistance 12 cm, seed rate 170 kg ha^{-1}, final plantnumber 345 m^2 - using a combine drill
21-03-2016	Rolled with concrete roller
21-03-2016	BBCH stage 0
30-03-2016	BBCH stage 9
04-04-2016	BBCH stage 10
05-04-2016	BBCH stage 11
05-04-2016	Fertilization 136.0 N, 17 P, 63 K, kg ha^{-1}
20-04-2016	BBCH stage 12
20-04-2016	Sowing catch crop of grass and clover (Foragemax 42)
27-04-2016	BBCH stage 13
03-05-2016	BBCH stage 16
03-05-2016	Fighter 480 (bentazone) - weeds - 1.5 L ha^{-1}
10-05-2015	BBCH stage 20
10-05-2016	Emergence of catch crop – BBCH stage 09
12-05-2016	Biomass 27.7 g m^{-2} - 100% DM
17-05-2016	BBCH stage 27
23-05-2016	BBCH stage 32
31-05-2016	BBCH stage 37
02-06-2016	BBCH stage 50
02-06-2016	Bumper 25 EC (propiconazole) -fungi - 0.5 L ha^{-1} (i.e. 125 g a.i.ha^{-1})
03-06-2016	Irrigation - 30 mm ha^{-1} started on eastside 4/6 ended on westside 3/6
03-06-2016	BBCH stage 50
03-06-2016	Biomass 721.7 g m^{-2} - 100% DM
06-06-2016	BBCH stage 53
08-06-2016	BBCH stage 56
08-06-2016	Irrigation - 30 mm ha^{-1} started on eastside 8/6 ended on westside 9/6
13-06-2016	BBCH stage 57
20-06-2016	BBCH stage 58
27-06-2016	BBCH stage 67

Table A3.3. Management practice at **Silstrup** during the 2009 to 2016 growing seasons. The active ingredients of the various pesticides are indicated in parentheses.

Date	Management practice and growth stages – **Silstrup**
22-07-2010	Red fescue - 2. season
16-03-2011	Fertilization 50 N, 7 P, 24 K, kg ha^{-1}
15-04-2011	Hussar OD (iodosulfuron) - weeds - 0.05 L ha^{-1} (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^{-1}
04-05-2011	BBCH stage 35
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^{-1} - 87% DM
30-07-2011	Straw removed - straw yield 45.8 hkg ha^{-1} - 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^{-1}
29-09-2011	Trimming of grass - 5-6 cm height
05-10-2011	Pig slurry application - surface applied - 29.0 t ha^{-1} - 122,1 Total-N, 72.8 NH4-N,30.2 P, 52.2 K, 14,9 Mg, kg ha^{-1}, 908 g ha^{-1} CU, (VAP no. 36552)
15-03-2012	Fertilization 60 N, 32 S kg ha^{-1}
13-04-2012	DFF (diflufenican) - weeds - 0.15 L ha^{-1}
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^{-1}
10-05-2012	BBCH stage 41
15-05-2012	BBCH stage 51
18-05-2012	BBCH stage 52
18-05-2012	Folicur (tebuconazole) - fungi - 1.0 L ha^{-1}
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^{-1} - 87% DM
25-07-2012	Straw removed - straw yield 48.3 hkg ha^{-1} - 100% DM, stubble height 12 cm
25-07-2012	BBCH stage 89
10-09-2012	Tracer (potasium bromide) 30.0 kg ha^{-1}
10-09-2012	Glyfonova 450 Plus (glyphosate) - weeds (killing the red fescue) - 4.8 L ha^{-1}
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^{-1}, 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^{-1} +0.2 Lha^{-1}
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^{-1}
03-05-2013	Sowing spring barlye cv. Quenc, replacing winter wheat injured by frost. Depth 3.8 cm, seeding rate 175 kg ha^{-1}, 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^{-1}

Date	Management practice and growth stages – **Silstrup**
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^{-1}
11-06-2013	BBCH stage 30
25-06-2013	BBCH stage 47
25-06-2013	Amistar (azoxystrobin) - fungi - 1.0 L ha^{-1}
01-07-2013	Folicur 250 EC (tebuconazole) - fungi - 1.0 L ha^{-1}
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 1332.1 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^{-1}
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^{-1} - 85% DM, straw yield 46.0 hkg ha^{-1} - 100% DM, stubbleheight 14 cm. Straw shredded at harvest
20-09-2013	Liming 3.2 t ha^{-1}
23-09-2013	Ploughed - depth 24 cm – packed
25-09-2013	Sowing winter wheat cv. Hereford. Depth 4 cm, seeding rate 190 kg ha^{-1}, 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	Oxitril CM (bromoxynil + ioxynil) + DFF (diflufenican) - weeds – 0.08 L ha^{-1}+ 0.2 L ha^{-1} (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^{-1}
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^{-1}
18-06-2014	BBCH stage 63
23-06-2014	BBCH stage 68
02-07-2014	Biomass 1776.5 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^{-1}
15-08-2014	BBCH stage 90
16-08-2014	Harvest of winter wheat. Grain yield 83.5 hkg ha^{-1} - 85% DM, straw yield 113.8 hkg ha^{-1} - 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)
28-04-2015	Pig slurry application - accidified at application - hose applied at surface - 28.3 t ha^{-1} – 126.2 Total-N, 75.6 NH4-N, 44.2 P, 46.7 K, kg ha^{-1}, DM of slurry 5.33%
28-04-2015	Ploughed - 24 cm depth
30-04-2015	Fertilization 112.5 K kg ha^{-1}

Date	Management practice and growth stages – **Silstrup**
30-04-2015	Seedbed preparation, 5-8 cm depth
02-05-2015	Sowing maiz cv. Ambition, depth 3.5 cm, rowdistance 75 cm, seed distance 14 cm seeding rate 10 m^2. final plantnumber 7.4 m^2 (seeds werer coated with thirame, fludioxonil and metalaxyl-M)
02-05-2015	Fertilization 30 N, 12.9 P, kg ha^{-1} (placed at sowing)
03-05-2015	BBCH 1
12-05-2015	BBCH 5
19-05-2015	BBCH 7
27-05-2015	BBCH 9
27-05-2015	Callisto (mesotrione) + Harmony SX (thifensulfuron-methyl) - weeds - (0.75 L ha^{-1}+ 5.625 g ha^{-1}) (i.e. 75 g a.i. ha^{-1} + 2.813 g a.i. ha^{-1}
06-06-2015	BBCH 12
09-06-2015	BBCH 12
09-06-2015	Callisto (mesotrione) + MaisTer (foramsulfuron+iodosulfuron) - weeds - (0.75 L ha^{-1} + 100 g ha^{-1}) (i.e. 75 g a.i. ha^{-1} + 30 g a.i. ha^{-1} + 1 g a.i. ha^{-1})
18-06-2015	BBCH 14
23-06-2015	BBCH 15
23-06-2015	MaisTer (foramsulfuron+iodosulfuron) - weeds - (50 g ha^{-1}) (i.e. 15 g a.i. ha^{-1} + 0,5 g a.i. ha^{-1})
03-07-2015	BBCH 17-18
03-07-2015	Biomass 5.8 g m^{-2} - 100% DM
14-07-2015	BBCH 19
22-07-2015	BBCH 31
12-08-2015	BBCH 51
13-08-2015	BBCH 51
13-08-2015	Biomass 303.8 g m^{-2} - 100% DM
19-08-2015	BBCH 54
26-08-2015	BBCH 65
09-09-2015	BBCH 70
23-09-2015	BBCH 72
30-09-2015	BBCH 73
05-10-2015	BBCH 74
05-10-2015	Biomass 1086.2 g m^{-2} - 100% DM
21-10-2015	BBCH 77
28-10-2015	BBCH 80
31-10-2015	Harvest of maiz. Stubble height 25 cm. Total harvested yield 64.98 hkg ha^{-1}100% DM.
05-11-2015	Maiz stubble chrushed with a cutter
28-04-2016	Stuble cultivated - depth 6 cm
09-05-2016	Pig slurry application – acidified at application – trail hose applied at surface – 34 t ha^{-1} - 150.6 Total-N, 85.0 NH4-N, 70.7 P, 73.4 K, kg ha^{-1}, DM of slurry 4.79%
10-05-2016	Ploughed - 24 cm depth - packed with a ring roller
11-05-2016	Fertilization 89.6 K kg ha^{-1}
12-05-2016	Rotary cultivated - depth 5.0 cm
13-05-2016	Fertilization 33.4 N, 17.5 P, kg ha^{-1} (placed at sowing)
13-05-2016	Sowing maiz cv. Activate, depth 3.5 cm, rowdistance 75 cm, seeddistance 14.7 cm seeding rate 10 m^2. final plantnumber 8 m^2 (seeds werer coated Mesurol FS 500 - thirame, fludioxonil and metalaxyl-M)
13-05-2016	BBCH stage 01
25-05-2016	BBCH stage 07
30-05-2016	BBCH stage 09 – emergence
02-06-2016	BBCH stage 12
06-06-2016	BBCH stage 13-14
06/06/2016	Callisto (mesotrion) + Harmony SX (thifensulfuron-methyl) - weeds - (0.75 L ha^{-1} + 5.625 g ha^{-1}) (i.e. 75 g a.i. ha^{-1} + 2.813 g a.i. ha^{-1}
08-06-2016	BBCH stage 14
08-06-2016	Biomass 3.3 g m^{-2} - 100% DM
22-06-2016	BBCH stage 16-17
22/06/2016	Callisto (mesotrion) + MaisTer (foramsulfuron+iodosulfuron) - weeds - (0.75 L ha^{-1} + 150 g ha^{-1}) (i.e. 75 g a.i. ha^{-1} + 45 g a.i. ha^{-1} + 1,5 g a.i. ha^{-1})
27-06-2016	BBCH stage 17-18
29-06-2016	BBCH stage 19-21

Table A3.4. Management practice at **Estrup** during the 2009 to 2016 growing seasons. The active ingredients of the various pesticides are indicated in parentheses.

Date	Management practice and growth stages – **Estrup**
06-09-2010	Rotor harrowed - depth 5 cm
14-09-2010	Ploughed - depth 20 cm - packed with a ring roller
14-09-2010	Seedbed preparation - depth 5 cm
14-09-2010	Winter wheat sown cv. Frument. Depth 4.0 cm, rowdistance 12 cm, seeding rate 210 kg ha^{-1}. Final plantnumber 370 m^{-2}
25-09-2010	BBCH stage 09 – emergence
30-09-2010	BBCH stage 10
30-09-2010	Express ST (tribenuron-methyl) - weeds - 1 tablet ha^{-1}
07-10-2010	BBCH stage 11
14-10-2010	BBCH stage 12
28-10-2010	BBCH stage 13
11-11-2010	BBCH stage 20
11-11-2010	Fertilization manganes sulfate (32%) - 3.0 L ha^{-1}
18-11-2010	BBCH stage 21
17-03-2011	BBCH stage 21
17-03-2011	Fertilization 70 N, 9 P, 33 K, kg ha^{-1}
07-04-2011	BBCH stage 22
07-04-2011	Biomass 37.1 g m^{-2} - 100% DM
14-04-2011	BBCH stage 22
14-04-2011	Pig slurry application - trail hose (surface) - 42.4 t ha^{-1}, 124 total-N, 90 NH4N, 56 P ha^{-1}, 19 K, kg ha^{-1}
19-04-2011	BBCH stage 23
26-04-2011	BBCH stage 29
26-04-2011	Fox 480 SC (bifenox) - weeds - 1.2 L ha^{-1}
02-05-2011	BBCH stage 31
02-05-2011	Fertilization manganes sulfate (32%) - 3.0 L ha^{-1}
05-05-2011	BBCH stage 30
09-05-2011	BBCH stage 31
09-05-2011	Flexity (metrafenon) - fungi - 0.5 L ha^{-1}
12-05-2011	BBCH stage 32
18-05-2011	BBCH stage 37
25-05-2011	BBCH stage 43
31-05-2011	BBCH stage 45
31-05-2011	Biomass 731.6 g m^{-2} - 100% DM
07-06-2011	BBCH stage 58
07-06-2011	Flexity (metrafenon) - fungi - 0.5 L ha^{-1}
08-06-2011	BBCH stage 58
16-06-2011	BBCH stage 65
23-06-2011	BBCH stage 68
28-06-2011	BBCH stage 70
28-06-2011	Biomass 1201.1 g m^{-2} - 100% DM
30-06-2011	BBCH stage 70
14-07-2011	BBCH stage 77
21-07-2011	BBCH stage 83
28-07-2011	BBCH stage 87
04-08-2011	BBCH stage 89
22-08-2011	Harvest of winter wheat. Stubleheight 12 cm, grainyield 66.3 hkg ha^{-1} 85% DM,
22-08-2011	Straw shredded at harvest - 53.8 hkg ha^{-1} 100% DM
03-10-2011	Roundup Max (glyphosate) - weeds - 2.0 kg ha^{-1}
09-11-2012	Ploughed - depth 20 cm - packed with a Dalbo ring roller
22-03-2012	Fertilization 117 N, 15 P, 55 K, kg ha^{-1}
29-03-2012	Rotor harrowed - depth 4 cm
30-03-2012	Spring barley sown, cv. Keops, seeding rate 159 kg ha^{-1}, sowing depth 4.3 cm, row distance 12 cm. Final plantnumber 330 m^{-2}
03-04-2012	Rolled with a Cambridge roller
22-04-2012	BBCH 9 – emergence
23-04-2012	BBCH stage 10
26-04-2012	BBCH stage 11
01-05-2012	BBCH stage 12
15-05-2012	BBCH stage 22
15-05-2012	Biomass 30.5 g m^{-2} - 100% DM
15-05-2012	Fox 480 SC (bifenox) - weeds - 1.2 L ha^{-1}
18-05-2012	BBCH stage 23
18-05-2012	Mustang forte (aminopyralid/florasulam/2,4-D) - weeds - 0.75 L ha^{-1}

Date	Management practice and growth stages – **Estrup**
21-05-2012	BBCH stage 30
21-05-2012	Fertilization manganes nitrate (23,5%) - 2.0 L ha^{-1}
29-05-2012	BBCH stage 37
29-05-2012	Fertilization manganes nitrate (23,5%) - 2.0 L ha^{-1}
06-06-2012	BBCH stage 40
13-06-2012	BBCH stage 50
13-06-2012	Amistar (azoxystrobin) - fungi - 1.0 L ha^{-1}
14-06-2012	BBCH stage 50
14-06-2012	Biomass 528.5 g m^{-2} - 100% DM
20-06-2012	BBCH stage 56
27-06-2012	BBCH stage 61
02-07-2012	BBCH stage 70
02-07-2012	Biomass 914.6 g m^{-2} - 100% DM
11-07-2012	BBCH stage 73
18-07-2012	BBCH stage 77
25-07-2012	BBCH stage 83
01-08-2012	BBCH stage 86
13-08-2012	BBCH stage 89
13-08-2012	Harvest of spring barley. Stuble height 12 cm, grainyield 62.9 hkg ha^{-1} 85% DM.
13-08-2012	Straw shredded at harvest - 41.0 hkg ha^{-1} 100% DM
26-09-2012	Tracer (potasium bromide) - 30 kg ha^{-1}
08-03-2013	Ploughed - depth 20 cm - packed with a Dalbo ring roller
05-04-2013	Fertilization 16 P, 84 K, kg ha^{-1}
23-04-2013	Seedbed preparation - depth 5 cm
23-04-2013	Sowing peas - cultivare Alvesta - depth 5 cm, rowdistance 12 cm, seeding rate 230 kg ha^{-1}. Final plantnumber 82 m^{-2}
23-04-2013	Rolled with a Cambridge roller
25-04-2013	BBCH stage 0
25-04-2013	Command CS (clomazone) - weeds - 0.25 L ha^{-1}
04-05-2013	BBCH 9 – emergence
16-05-2013	BBCH stage 12
16-05-2013	Fighter 480 (bentazone) - weeds - 1.0 L ha^{-1}
16-05-2013	Cyperb (cypermethrin) - pests - 0.3 L ha^{-1} (not analysed)
22-05-2013	BBCH stage 31
27-05-2013	BBCH stage 33
27-05-2013	Biomass 42.3 g m^{-2} - 100% DM
06-06-2013	BBCH stage 37
12-06-2013	BBCH stage 40
21-06-2013	BBCH stage 60
21-06-2013	Biomass 357.7 g m^{-2} - 100% DM
26-06-2013	BBCH stage 62
09-07-2013	BBCH stage 66
12-07-2013	BBCH stage 68
12-07-2013	Biomass 718.1 g m^{-2} - 100% DM
13-07-2013	BBCH stage 68
13-07-2013	Pirimor G (pirimicarb) - pests - 0.25 kg ha^{-1}
17-07-2013	BBCH stage 79
31-07-2013	BBCH stage 83
05-08-2013	BBCH stage 83
05-08-2013	Biomass 985.3 g m^{-2} - 100% DM
13-08-2013	BBCH stage 87
20-08-2013	BBCH stage 90
21-08-2013	Glyphonova 450 Plus (glyphosate) - weeds - 2.4 L ha^{-1}
27-08-2013	BBCH stage 93
06-09-2013	Harvest of peas. Stubble height 10 cm, seed yield 49.8 hkg ha^{-1}- 86% dry matter.
06-09-2013	Straw shedded at harvest - 24.38 hkg ha^{-1} 100% DM
13-09-2013	Winter wheat sown cv. Herford. Depth 4.0 cm, rowdistance 12 cm, seeding rate 180 kg ha^{-1}. Final plantnumber 365 m^{-2} using a combined powerharrow sowing equipment
21-09-2013	BBCH 9 – emergence
25-09-2013	BBCH stage 11
09-10-2013	BBCH stage 12
14-10-2013	BBCH stage 20
14-10-2013	Fertilization manganes nitrate (23.5%) - 2.0 kg ha^{-1}
30-10-2013	BBCH stage 21
11-11-2013	BBCH stage 24

Date	Management practice and growth stages – **Estrup**
11-11-2013	Oxitril CM (bromoxynil + ioxynil) + DFF (diflufenican) - weeds - 0.2 L ha^{-1} + 0.24 L ha^{-1} (bromoxynil and ioxynil not included)
13-11-2013	BBCH stage 24
02-04-2014	BBCH stage 30
04-04-2014	BBCH stage 30
04-04-2014	Fertilization 150 N, 16 P, 60 K, kg ha^{-1} (liquid fertilizer - applied 1000 L ha^{-1} with a sprayer)
22-04-2014	BBCH stage 32
22-04-2014	Fluxyr 200 EC - (fluroxypyr) - weeds - 0.7 L ha^{-1} (not included)
22-04-2014	Fertilization manganes nitrate (23,5%) - 2.0 kg ha^{-1}
07-05-2014	BBCH stage 34
07-05-2014	Biomass 54.0 g m^{-2} - 100% DM
15-05-2014	BBCH stage 36
15-05-2014	Primus (florasulam) - weeds - 50 mL ha^{-1}
20-05-2014	BBCH stage 38
20-05-2014	Folicur 250 EC (tebuconazole) - fungi - 1.0 L ha^{-1}
27-05-2014	BBCH stage 50
02-06-2014	BBCH stage 59
02-06-2014	Biomass 497.3 g m^{-2} - 100% DM
02-06-2014	Amistar (azoxystrobin) - fungi - 1.0 L ha^{-1}
11-06-2014	BBCH stage 67
18-06-2014	BBCH stage 71
24-06-2014	BBCH stage 72
24-06-2014	Cyperb (cypermethrin) - pests - 0.25 L ha^{-1} (not analysed)
02-07-2014	BBCH stage 74
07-07-2014	BBCH stage 75
07-07-2014	Biomass 1557.7 g m^{-2} - 100% DM
16-07-2014	BBCH stage 82
26-07-2014	BBCH stage 87
26-07-2014	Glyphonova 450 Plus (glyphosate) - weeds – 2.4 L ha^{-1}
06-08-2014	BBCH stage 90
06-08-2014	Harvest of winter wheat. Stubleheight 11 cm, grainyield 69.3 hkg ha^{-1} 85% DM
12-08-2014	Harrowed to 5 cm depth and sown a catch crop of oilseed radish 12 kg ha^{-1} seed on soil surface
06-08-2014	Straw shredded at harvest - 48.7 hkg ha^{-1}, 100% DM
12-08-2014	Liming 3.5 t ha^{-1} magnesium limestone
29-04-2015	Pig slurry application - accidified at application from pH 7,15 til 6,82- hose applied at surface - 28.0 t ha^{-1} - 117.3 Total-N, 76.44 NH4-N, 39.2 P, 47.9 K, kg ha^{-1}, DM of slurry 5.43%
29-04-2015	Ploughed - depth 20 cm
11-05-2015	Seedbed preparation - depth 5 cm using a Rabewerke rotary cultivator
11-05-2015	Fertilization 30.8 N, 4.7 P, 19.0 K, kg ha^{-1} (placed at sowing)
11-05-2015	Sowing maize cv. Ambition, depth 4 cm, rowdistance 75 cm, seeddistance 12.1 cm seeding rate 11 m^2. Final plantnumber 10.5 m^2
13-05-2015	Fertilization 55.3 N, 8.5 P, 34.0 K, kg ha^{-1} (applied with a field sprayer - luiquid fertilizer
27-05-2015	BBCH 09
27-05-2015	Callisto (mesotrione) + Harmony SX (thifensulfuron-methyl) - weeds - (0.75 L ha^{-1}+ 5.625 g ha^{-1}) (i.e. 75 g a.i. ha^{-1} + 2.813 g a.i. ha^{-1}
03-06-2015	BBCH 12
06-06-2015	BBCH 13
06-06-2015	Callisto (mesotrione) + MaisTer (foramsulfuron+iodosulfuron) - weeds - (0.75 L ha^{-1} + 100 g ha^{-1}) (i.e. 75 g a.i. ha^{-1} + 30 g a.i. ha^{-1} + 1 g a.i. ha^{-1})
08-06-2015	BBCH 13
08-06-2015	Biomass 0.4 g m^{-2} - 100% DM
18-06-2015	BBCH 14
23-06-2005	BBCH 16
30-06-2015	BBCH 18
30-06-2015	MaisTer (foramsulfuron+iodosulfuron) + Lodin 200 EC (fluroxypyr) - weeds - (50 g ha^{-1} + 1.0 L ha^{-1}) (i.e. 15 g a.i. ha^{-1} + 0,5 g a.i. ha^{-1} + 180 g a.i. ha^{-1})
01-07-2015	BBCH 19
09-07-2015	BBCH 22
16-07-2015	BBCH 33
23-07-2015	BBCH 43
30-07-2015	BBCH 51
04-08-2015	BBCH 51
04-08-2015	Biomass 1794 g m^{-2} - 100% DM
05-08-2015	BBCH 60
13-08-2015	BBCH 65
08-06-2015	Biomass 4159 g m^{-2} - 100% DM

Date	Management practice and growth stages – **Estrup**
20-08-2015	BBCH 69
01-09-2015	BBCH 72
15-09-2015	BBCH 73
22-09-2015	BBCH 74
06-10-2015	BBCH 75
13-10-2015	BBCH 78
23-10-2015	BBCH 81
23-10-2015	Harvest of maiz. Stubble height 25 cm. Total harvested yield 105.98 hkg ha^{-1} 100% DM.
04-05-2016	Pig slurry application - accidified at application trail hose applied at surface - 21.0 t ha^{-1} - 86.5 Total-N, 56.3 NH4-N, 11.6 P, 29.6 K, kg ha^{-1}, DM of slurry 3.58 %
05-05-2016	Ploughed - depth 20 cm
06-05-2016	Seedbed preparation - depth 5 cm using a Rabewerke rotary cultivator
06-05-2016	Fertilization 150 N, 20 P, 60 K, kg ha^{-1} (20% thereof placed at sowing and 80% harowed into the soil before the sowing)
06-05-2016	Sowing maiz cv. Ambition, depth 4 cm, rowdistance 75 cm, seed distance 12.1 cm, seeding rate 11 m^2. Final plantnumber 10.5 m^2
14-05-2016	BBXH stage 09
14-05-2016	BBCH stage 11
14-05-2016	BBCH stage 13
01-06-2016	BBCH stage 14
01-06-2016	Callisto (mesotrion) + Harmony SX (thifensulfuron-methyl) - weeds - (0.75 l ha^{-1} + 5.625 g ha^{-1}) (i.e. 75 g a.i. ha^{-1} + 2.813 g a.i. ha^{-1})
05-06-2016	BBCH stage 14
05-06-2015	Biomass 288.5 g m^{-2} - 100% DM
08-06-2016	BBCH stage 16
11-06-2016	BBCH stage 17
11-06-2016	Callisto (mesotrion) + MaisTer (foramsulfuron+iodosulfuron) - weeds - (0.75 l ha^{-1} + 100 g ha^{-1}) (i.e. 75 g a.i. ha^{-1} + 30 g a.i. ha^{-1} + 1 g a.i. ha^{-1})
15-06-2016	BBCH stage 18
16-06-2016	BBCH stage 18
16-06-2016	MaisTer (foramsulfuron+iodosulfuron) - weeds - (50 g ha^{-1}) (i.e. 15 g a.i. ha^{-1} + 0,5 g a.i. ha^{-1})
22-06-2016	BBCH stage 25-26
29-06-2016	BBCH stage 46-47

Table A3.5. Management practice at **Faardrup** during the 2009 to 2016 growing seasons. The active ingredients of the various pesticides are indicated in parentheses.

Date	Management practice and growth stages – **Faardrup**
22-08-2010	Red fescue
06-09-2010	Fertilization 58.5 N, 4.5 P, 15.8 K, kg ha^{-1}
06-09-2010	BBCH stage 24-29
25-10-2010	Fox 480 SC (bifenox) - weeds - 1.5 L ha^{-1}
25-10-2010	BBCH stage 24-29
07-03-2011	BBCH stage 26-27
07-03-2011	Fertilization 104 N, 8 P, 28 K, kg ha^{-1}
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^{-1}
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 hight 5 cm
20-07-2011	Straw removed. Straw yield 21.1 hkg ha^{-1}
20-07-2011	Threshing of grass seed. Yield 7.2 hkg ha^{-1} - 87% DM, stubble height 5 cm
03-10-2011	BBCH stage 29
03-10-2011	Glyphogan (glyphosate) - weeds - 5.0 L ha^{-1}
08-11-2011	Ploughing - depth 20 cm
26-03-2012	Fertilization 112 N, 9 P, 30 K, kg ha^{-1}
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^{-1}. Final plant number 200 m^{-2}. Undersown white clover cv. Liflex, seeding rate 2.0 kg ha^{-1}, depth 2-3 cm, row distance 13 cm
04-04-2012	Tracer (potasium bromide) 30 kg ha^{-1}
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^{-1}
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^{-1}
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 1321.7 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^{-1} - 85% DM
12-08-2012	Straw removed. Straw yield 27.62 hkg ha^{-1} - 100% DM
27-08-2012	BBCH stage 22-29 clover vegative growth - formation of side shots
29-08-2012	Trimming of stubble
26-01-2013	Kerb 400 SC (propyzamid) - fungi - 1.0 L ha^{-1}
13-05-2013	Biomass 298.2 g m^{-2} - 100% DM
14-05-2013	Fighter 480 (bentazone) - weeds - 3.0 L ha^{-1}
22-05-2013	Rolled with a concrete roller

Date	Management practice and growth stages – **Faardrup**
29-05-2013	Biomass 402.9 g m^{-2} - 100% DM
31-05-2013	Karate (Lambda-cyhalothrin) - pest - 0.3 L ha^{-1} (not analysed)
12-06-2013	Karate (Lambda-cyhalothrin) - pest - 0.3 L ha^{-1} (not analysed)
25-06-2013	Biomass 698.3 g m^{-2} - 100% DM
22-07-2013	Windrowing. Stubble height 8.0 cm
28-07-2013	Threshing of white clover. Seed yield fresh 1,560 hkg ha^{-1}. Straw yield fresh 0.96 hkg ha^{-1}
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^{-1} - 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^{-1}
09-04-2014	Fertilization 81 N, 16 P, 61 K, kg ha^{-1}
09-04-2014	BBCH 25
15-04-2014	BBCH 24
28-04-2014	Briotril (ioxynil+ bromoxynil) - weeds - 0.6 L ha^{-1} + Tomahawk 180 EC (fluroxypyr) - weeds - 0.8 L ha^{-1} (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^{-1} (not included)
04-06-2014	Biomass 1321 g m^{-2} - 100% DM
04-06-2014	BBCH 55
12-06-2014	BBCH 59
20-07-2014	BBCH 83
20-07-2014	Biomass 1995 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^{-1} (not included)
23-09-2014	Ploughing - 14 cm depth - straw 70 hkg ha^{-1} (fresh weight) incorporated
23-09-2014	Sowing winter wheat cv. Mariboss. Depth 3.5 cm, seeding rate 180 kg ha^{-1}, row distance 13.0 cm. Final plant number 375 m^{-2}
01-10-2014	BBCH 09 – emergence
20-11-2014	BBCH 23
20-11-2014	Folicur 250 (tebuconazole) - fungi - 1.0 L ha^{-1} (i.e. 250g a.i. ha^{-1})
30-11-2014	BBCH 23
30-11-2014	Lexus 50 WG (flupyrsulfuron) - weeds - 10 g ha^{-1} (i.e. 4.6 g a.i. ha^{-1})
30-11-2014	Boxer (prosulfocarb) - weeds - 3.0 L ha^{-1} (i.e. 2400 g a.i. ha^{-1})
10-03-2015	BBCH 25
10-03-2015	Biomass 44 g m^{-2} - 100% DM
13-03-2015	BBCH 25
13-03-2015	Fertilization 80 N, 18 P, 63 K, kg ha^{-1}
21-04-2015	BBCH 30
21-04-2015	Fertilization 94 N, 21 P, 74 K, kg ha^{-1}
22-04-2015	BBCH 30
22-04-2015	Lexus 50 WG (flupyrsulfuron) - weeds - 10 g ha^{-1} (i.e. 4.6 g a.i. ha^{-1})
08-05-2015	BBCH 37
12-05-2015	BBCH 37
12-05-2015	Starane XL (fluroxypur+ florasulam) - weeds - 1.2 L ha^{-1} (i.e. 120 g a.i. ha^{-1} + 3 g a.i. ha^{-1})
12-05-2015	Proline 250 EC (prothioconazole) - fungi - 0.8 L ha^{-1} (i.e. 200 g a.i. ha^{-1})
12-06-2015	BBCH 53
23-06-2015	BBCH 55
23-06-2015	Biomass 356.5 g m^{-2} - 100% DM
12-08-2015	BBCH 55
12-08-2015	Biomass 443.7 g m^{-2} – 100 % DM
28-08-2015	BBCH 89
02-09-2015	Harvest of winter wheat. Grain yield 79.7 hkg ha^{-1} 85% DM, straw yield 71.5 hkg ha^{-1} 100% DM, stubbleheight 15 cm. Straw shredded (left in field) at harvest.
11-04-2016	Rotor harrowed at the time of sowing the spring barley. Mixture of varieties. Depth 4 cm, seeding rate 155 kg ha^{-1}, row distance 12.0 cm. Final plant number 315 m^{-2}
11-04-2016	BBCH stage 0
11-04-2016	Fertilization 130 N, 26 P, 98 K, kg ha^{-1}
20-04-2016	BBCH stage 09 – emergence
02-05-2106	BBCH stage 15
13-05-2016	BBCH stage 16-21
13-05-2016	Biomass 60.7 g m^{-2} – 100% DM

Date	Management practice and growth stages – **Faardrup**
27-05-2016	BBCH stage 27
27-05-2016	Starane 180 S + Oxitril (fluroxypyr + bromoxynil and ioxynil) - weeds - 0.8 L ha^{-1} + 0.2 L ha^{-1} (i.e. 144 + 48 + 32 g a.i ha^{-1} - not included)
01-06-2016	BBCH stage 31
08-06-2016	BBCH stage 39
16-06-2016	BBCH stage 47
16-06-2016	Bumber 25 EC (propiconazole) - fungi - 0.5 L ha^{-1} (i.e. 125 g a.i. ha^{-1}) BBCH stage 65
28-06-2016	BBCH stage 65

Appendix 4

Monthly precipitation data for the PLAP fields

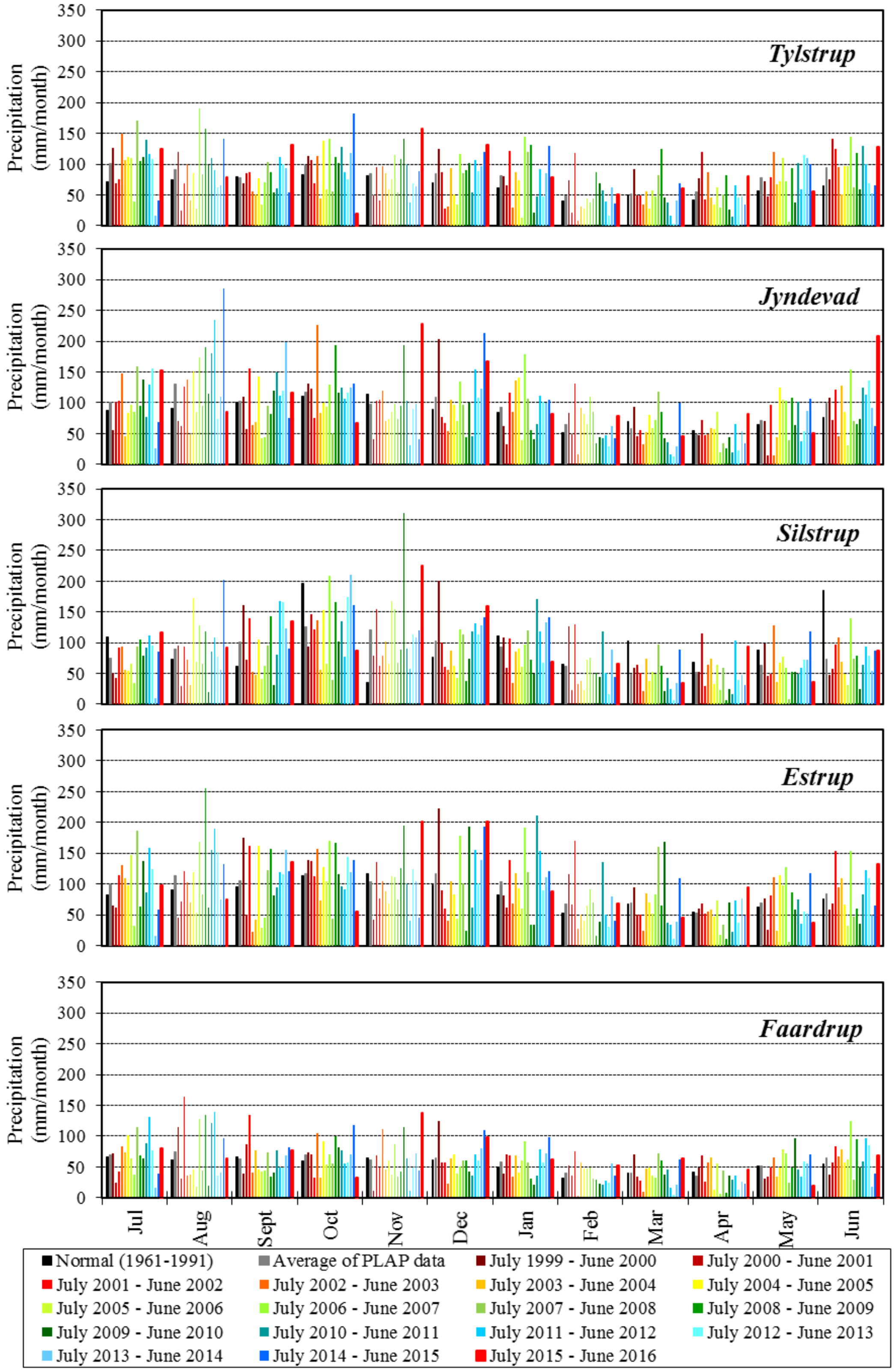

Figure A4.1. Monthly precipitation at all fields for the monitoring period July 2000–June 2016. Regional normal values (1961–1990) are included for comparison.

Appendix 5

Pesticide detections in samples from drains, suction cups and groundwater screens

Table A5.1. Number of samples, where pesticides were not detected (nd), detected in concentrations below 0.1 µg L^{-1} (≤0.1 µg L^{-1}) or detected in concentrations above 0.1µg L^{-1} (>0.1 µg L^{-1}) at **Tylstrup**. Numbers are accumulated for the monitoring period up to July 2016. All samples included.

Tylstrup		Horizontal screens			Vertical screens			Suction cups		
Parent	Compound	nd	≤ 0.1	>0.1	nd	≤0.1	>0.1	nd	≤0.1	> 0.1
Aclonifen	Aclonifen	4	-	-	123	-	-	68	-	-
Aminopyralid	Aminopyralid	27	-	-	183	2	-	91	-	-
Azoxystrobin	Azoxystrobin				216	-	-	95	-	-
	CyPM				216	-	-	95	-	-
Bentazone	2-amino-N-isopropyl-benzamide				191	-	-	72	-	-
	6-hydroxy-bentazone	2	-	-	25	-	-	8	-	-
	8-hydroxy-bentazone	2	-	-	25	-	-	8	-	-
	Bentazone	2			355	-	-	144	1	-
	N-methyl-bentazone	2	-	-	25	-	-	8	-	-
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-	Flamprop				176	-	-	65	-	-
isopropyl	Flamprop-M-isopropyl				176	-	-	65	-	-
Fluazifop-P-butyl	Fluazifop-P				178	-	-	65	-	-
	TFMP				3	-	-			
Fludioxonil	CGA 192155	22	-	-	160	-	-	65	-	-
	CGA 339833	22	-	-	160	-	-	65	-	-
Fluroxypyr	Fluroxypyr				194	-	-	70	-	-
Ioxynil	Ioxynil				198	-	-	72	-	-
Linuron	Linuron				271	-	-	67	-	-
Mancozeb	EBIS	8	-	-	70	-	-	27	-	-
	ETU				198	2	-	37	7	-
Metalaxyl-M	CGA 108906	3	25	-	61	216	47	25	93	35
	CGA 62826	27	1	-	308	16	-	119	30	5
	Metalaxyl-M	28	-	-	303	21	-	152	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	20	-	-	144	4	-	73	1	-
Rimsulfuron	PPU	9	-	-	589	58	-	74	191	3
	PPU-desamino	9	-	-	638	9	-	205	63	-
	Rimsulfuron				178	-	-	65	-	-

Tylstrup		Horizontal screens			Vertical screens			Suction cups		
Parent	Compound	nd	≤ 0.1	>0.1	nd	≤0.1	>0.1	nd	≤0.1	> 0.1
Tebuconazole	1,2,4-triazole	4	16	-	90	44	-	49	6	1
	Tebuconazole				195	1	-	77	-	-
Terbuthylazine	2-hydroxy-desethyl-terbuthylazine				190	1	-	67	5	-
	Desethyl-terbuthylazine				191	-	-	70	2	-
	Desisopropylatrazine				190	1	-	55	17	-
	Hydroxy-terbuthylazine				191	-	-	71	1	-
	Terbuthylazine				179	-	-	72	-	-
Thiamethoxam	CGA 322704				175	-	-	64	-	-
	Thiamethoxam				175	-	-	64	-	-
Triasulfuron	Triasulfuron				301	-	-	82	-	-
	Triazinamin				291	-	-	76	-	-
Tribenuron-methyl	Triazinamin-methyl				446	-	-	138	-	-

Table A5.2. Number of samples where pesticides were either not detected (nd), detected in concentrations below 0.1 µg L^{-1} (<=0.1 µg L^{-1}) or detected in concentrations above 0.1 µg L^{-1} (>0.1 µg L^{-1}) at **Jyndevad**. Numbers are accumulated for the monitoring period up to July 2016. All samples included.

Jyndevad		Horizontal screens			Vertical screens			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	-
	6-hydroxy-bentazone	2	-	-	24	-	-	2	-	-
	8-hydroxy-bentazone	2	-	-	24	-	-	2	-	-
	Bentazone	31	1	-	667	-	-	108	67	14
	N-methyl-bentazone	2	-	-	24	-	-	2	-	-
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	13	-	-	91	-	-	23	-	-
	FMC 65317	13	-	-	92	-	-	23	-	-
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	28	-	-	203	1	-	34	-	-
	CGA 339833	28	-	-	192	-	1	34	-	-
Flupyrsulfuron-methyl	Flupyrsulfuron-methyl	24	-	-	170	-	-	22	-	-
	IN-JV460	24	-	-	170	-	-	22	-	-
	IN-KC576	24	-	-	170	-	-	22	-	-
	IN-KY374	24	-	-	170	-	-	18	-	-
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	12	-	-	87	-	-	10	-	-
Mesosulfuron-methyl	Mesosulfuron				12	-	-	45	-	-
	Mesosulfuron-methyl				285	-	-	78	-	-
Mesotrione	AMBA	30	-	-	207	-	-	67	-	-
	MNBA	30	-	-	207	-	-	67	-	-
	Mesotrione	30	-	-	207	-	-	67	-	-
Metalaxyl-M	CGA 108906	2	23	6	113	171	78	37	34	34
	CGA 62826	2	20	9	217	145	-	32	53	20
	Metalaxyl-M	18	8	5	286	57	18	84	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	CL 153815				35	-	-	36	-	-
	Picolinafen				35	-	-	35	1	-
Pirimicarb	Pirimicarb				251	-	-	69	-	-

Jyndevad		Horizontal screens			Vertical screens			Suction cups		
Parent	Compound	nd	≤0.1	>0.1	nd	≤0.1	>0.1	nd	≤0.1	>0.1
	Pirimicarb-desmethyl				251	-	-	68	1	-
	Pirimicarb-desmethyl-formamido				251	-	-	69	-	-
Propiconazole	Propiconazole				291	-	-	87	-	-
Pyridate	PHCP				184	-	-	59	-	-
	Pyridate				116	-	-	39	-	-
Rimsulfuron	PPU	-	1	6	489	361	6	39	130	64
	PPU-desamino	-	7	-	765	91	-	110	117	6
	Rimsulfuron				189	-	-	52	-	-
Tebuconazole	1,2,4-triazole	8	16	-	77	94	1	14	11	5
	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^{-1} (<0.1 µg L^{-1}) or detected in concentrations above 0.1 µg L^{-1} (>=0.1 µg L^{-1}) at **Silstrup**. Numbers are accumulated for the monitoring period up to July 2016. All samples included.

Silstrup		Drainage			Horizontal screens			Vertical screens			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	162	22	1	225	3	-	393	5	-			
	CyPM	56	128	24	218	41	6	420	47	6			
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	48	-	-	66	-	-	93	-	-			
Chlormequat	Chlormequat	20	1	-	36	-	-	66	-	-			
Clopyralid	Clopyralid	44	-	-	67	-	-	124	-	-			
Desmedipham	Desmedipham	101	-	-	107	1	-	240	-	-	58	-	-
	EHPC	74	-	-	68	-	-	139	-	-	26	-	-
Diflufenican	AE-05422291	66	-	-	83	-	-	118	-	-			
	AE-B107137	56	4	1	82	-	-	118	-	-			
	Diflufenican	55	10	1	83	-	-	117	-	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	79	30	23	137	23	2	211	48	14			
Fluroxypyr	Fluroxypyr	50	-	-	74	-	-	142	-	-			
Foramsulfuron	AE-F092944	32	-	-	36	-	-	66	-	-			
	AE-F130619	25	7	-	32	4	-	63	3	-			
	Foramsulfuron	25	6	1	33	3	-	65	1	-			
Glyphosate	AMPA	47	185	18	227	14	-	380	26	-	8	-	-
	Glyphosate	141	86	22	236	5	-	371	35	-	8	-	-
Iodosulfuron-methyl	Iodosulfuron-methyl	60	-	-	85	-	-	165	-	-			
	Metsulfuron-methyl	60	-	-	85	-	-	165	-	-			
Ioxynil	Ioxynil	48	-	-	66	-	-	93	-	-			
MCPA	2-methyl-4-chlorophenol	51	-	-	67	-	-	124	-	-			
	MCPA	51	-	-	67	-	-	123	-	-			
Mesotrione	AMBA	39	4	-	31	-	-	44	-	-			
	MNBA	39	8	1	31	-	-	42	-	-			
	Mesotrione	39	25	8	31	2	1	44	-	-			
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			

Silstrup		Drainage			Horizontal screens			Vertical screens			Suction cups		
Parent	Compound	nd	≤ 0.1	>0.1	nd	≤ 0.1	>0.1	nd	≤0.1	>0.1	nd	≤0.1	>0.1
	RH-24580	64	2	-	78	-	-	149	-	-			
	RH-24644	51	15	-	77	1	-	148	1	-			
	RH-24655	66	-	-	78	-	-	149	-	-			
Prosulfocarb	Prosulfocarb	69	4	1	78	1	-	147	-	-			
Pyridate	PHCP	62	-	4	66	2	-	109	8	4			
Rimsulfuron	PPU	1	-	-									
	PPU-desamino	1	-	-									
Tebuconazole	Tebuconazole	17	2	-	15	-	-	23	-	-			
Terbuthylazine	2-hydroxy-desethyl-terbuthylazine	43	27	1	84	-	-	151	1	-			
	Desethyl-terbuthylazine	8	64	44	101	32	-	113	127	2			
	Desisopropylatrazine	28	43	-	84	-	-	148	4	-			
	Hydroxy-terbuthylazine	45	26	-	84	-	-	152	-	-			
	Terbuthylazine	31	51	9	107	5	-	173	30	1			
Triasulfuron	Triazinamin	48	-	-	79	-	-	154	-	-			
Tribenuron-methyl	Triazinamin-methyl	82	-	-	74	-	-	148	-	-	27	-	-
Triflusulfuron-methyl	IN-D8526	32	-	-	56	-	-	102	-	-			
	IN-E7710	27	5	-	56	-	-	102	-	-			
	IN-M7222	32	-	-	55	1	-	102	-	-			
	Triflusulfuron-methyl	32	-	-	56	-	-	102	-	-			

Table A5.4. Number of samples where pesticides were either not detected (nd), detected in concentrations below 0.1 µg L^{-1} (<0.1 µg L^{-1}) or detected in concentrations above 0.1 µg L^{-1} (>=0.1 µg L^{-1}) at **Estrup**. Numbers are accumulated for the monitoring period up to July 2016. 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	96	-	-	66	-	-	86	-	-			
Azoxystrobin	Azoxystrobin	254	126	15	222	1	-	503	1	-			
	CyPM	38	210	147	192	26	5	497	7	-			
Bentazone	2-amino-N-isopropyl-benzamide	237	1	-	79	1	-	271	-	-	5	-	-
	Bentazone	211	208	14	175	42	-	525	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	60	-	-	47	-	-	51	-	-			
	FMC 65317	60	-	-	47	-	-	51	-	-			
Clopyralid	Clopyralid	1	-	-									
Diflufenican	AE-05422291	57	-	-	26	-	-	45	-	-			
	AE-B107137	40	18	-	38	2	-	49	-	-			
	Diflufenican	30	15	12	26	-	-	45	-	-			
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	-			
Foramsulfuron	AE-F092944	37	1	-	30	-	-	42	-	-			
	AE-F130619	36	2	-	30	-	-	42	-	-			
	Foramsulfuron	22	15	1	30	-	-	42	-	-			
Glyphosate	AMPA	79	379	120	291	1	-	719	7	-	23	-	-
	Glyphosate	235	234	109	284	6	1	680	41	5	23	-	-
Iodosulfuron-methyl	Iodosulfuron-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	-	-			
Mesotrione	AMBA	35	4	-	32	-	-	44					
	MNBA	31	7	1	32	-	-	41	1	-			
	Mesotrione	14	17	8	30	1	1	43	1	-			
Metamitron	Desamino-metamitron	76	38	11	46	-	-	157	-	-			
	Metamitron	81	27	15	46	-	-	158	-	-			
Metrafenone	Metrafenone	100	20	-	69	-	-	119	1	-			
Pendimethalin	Pendimethalin	119	4	-	41	-	-	147	-	-	7	-	-
Picolinafen	CL 153815	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-triazole	-	4	72	-	46	9	15	26	29			
	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	-	-			

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
	Terbuthylazine	49	78	34	63	-	-	222	1	-			
Thiacloprid	M34	55	-	-	34	-	-	66	-	-			
	Thiacloprid	47	-	-	34	-	-	66	-	-			
	Thiacloprid sulfonic acid	56	-	-	34	-	-	66	-	-			
	Thiacloprid-amide	46	1	-	34	-	-	66	-	-			
Triasulfuron	Triazinamin	132	-	-	57	-	-	208	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^{-1} (<0.1 µg L^{-1}) or detected in concentrations above 0.1 µg L^{-1} (>=0.1 µg L^{-1}) at **Faardrup**. Numbers are accumulated for the monitoring period up to July 2016. 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
Azoxystrobin	Azoxystrobin	106	-	-	92	-	-	194	-	-			
	CyPM	102	4	-	92	-	-	194	-	-			
Bentazone	2-amino-N-isopropyl-benzamide	67	1	-	61	-	-	132	-	-			
	Bentazone	174	22	6	152	13	1	354	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	91	-	-	76	-	-	162	-	-			
Flupyrsulfuron-methyl	Flupyrsulfuron-methyl	36	-	-	47	-	-	104	-	-			
	IN-JV460	36	-	-	47	-	-	104	-	-			
	IN-KC576	36	-	-	47	-	-	104	-	-			
	IN-KY374	36	-	-	47	-	-	104	-	-			
Fluroxypyr	Fluroxypyr	182	-	1	146	1	-	368	-	-	73	-	-
	Fluroxypyr.methoxypyridine	1	-	-	4	-	-	12	-	-			
	Fluroxypyr-pyridinol	1	-	-	4	-	-	12	-	-			
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	59	-	-	54	-	-	114	-	-			
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	120	2	2	113	1	-	246	-	-			
	RH-24580	124	-	-	114	-	-	246	-	-			
	RH-24644	120	4	-	114	-	-	246	-	-			
	RH-24655	123	1	-	114	-	-	246	-	-			
Prosulfocarb	Prosulfocarb	78	-	-	61	-	-	126	-	-			
Tebuconazole	1,2,4-triazole	2	31	-	39	1	-	90	3	-			
	Tebuconazole	50	4	-	53	-	-	120	1	-			
Terbuthylazine	2-hydroxy-desethyl-terbuthylazine	60	7	1	60	1	-	126	6	-			
	Desethyl-terbuthylazine	21	82	7	68	21	-	149	15	30			
	Desisopropylatrazine	85	24	1	57	32	-	166	28	-			
	Hydroxy-terbuthylazine	89	20	1	85	4	-	164	30	-			
	Terbuthylazine	69	30	11	83	5	1	149	25	20			
Thiamethoxam	CGA 322704	68	-	-	58	-	-	126	-	-			
	Thiamethoxam	68	-	-	58	-	-	126	-	-			

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	Triazinamin-methyl	77	-	-	57	-	-	148	-	-			
Triflusulfuron-methyl	IN-D8526	63	-	-	38	-	-	92	-	-			
	IN-E7710	63	-	-	38	-	-	92	-	-			
	IN-M7222	63	-	-	38	-	-	92	-	-			
	Triflusulfuron-methyl	63	-	-	38	-	-	92	-	-			

Appendix 6

Laboratory internal control cards and external control sample results

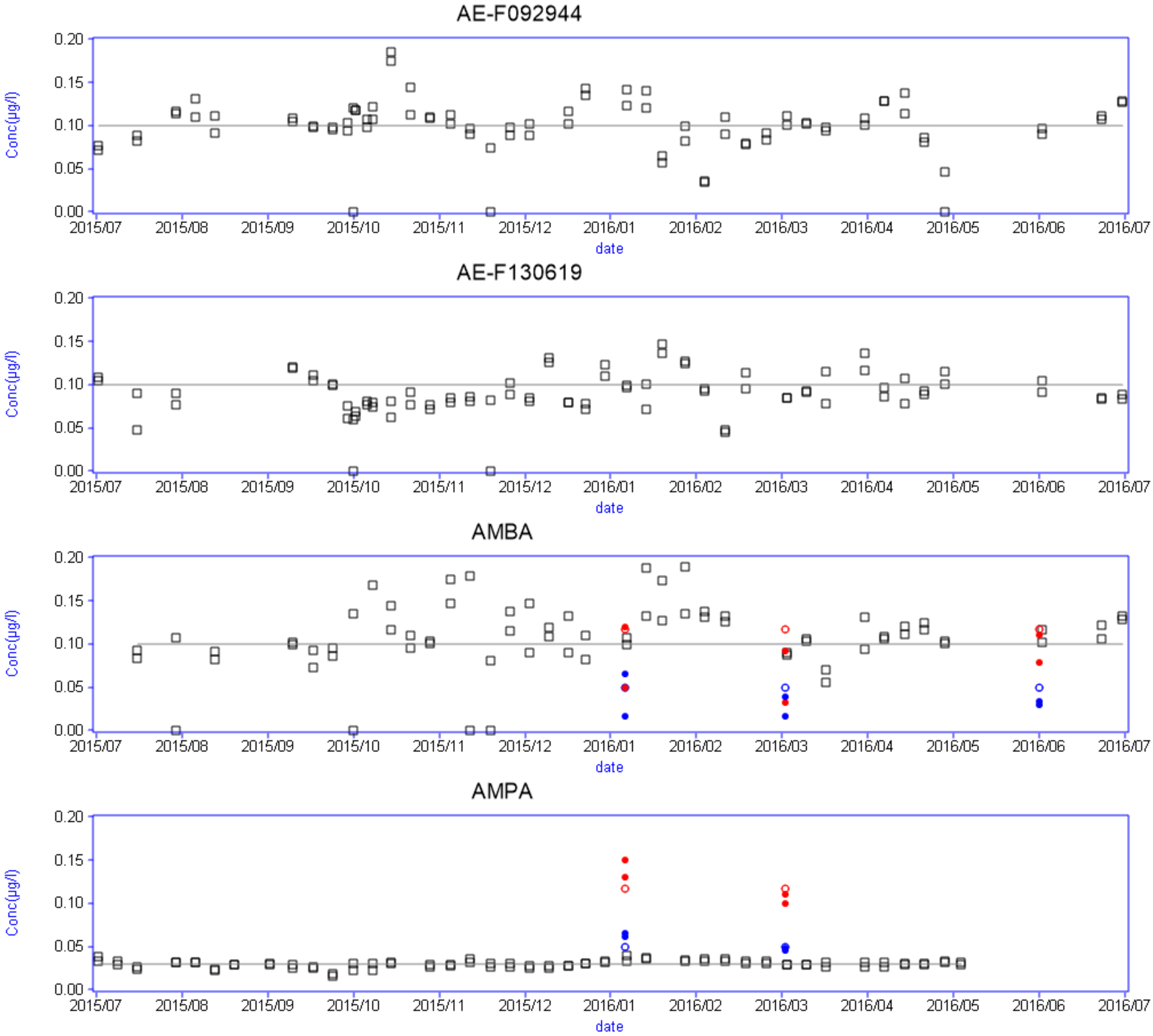

Figure A6.1. Quality control data for pesticide analysis by laboratory 1. Internal laboratory control (IQ) samples are indicated by square symbols and the nominal level is indicated by the solid grey line (□ IQ measured, — IQ nominal concentration). External control (EQ) samples are indicated by circles. Open circles indicate the nominal level (○ EQ nominal low, ○ EQ nominal high), and closed circles the measured concentration (● EQ measured low, ● EQ measured high). The spiked external QA samples with aminopyralid from Macrh 2015 are disregarded due to uncertaincies about the results.

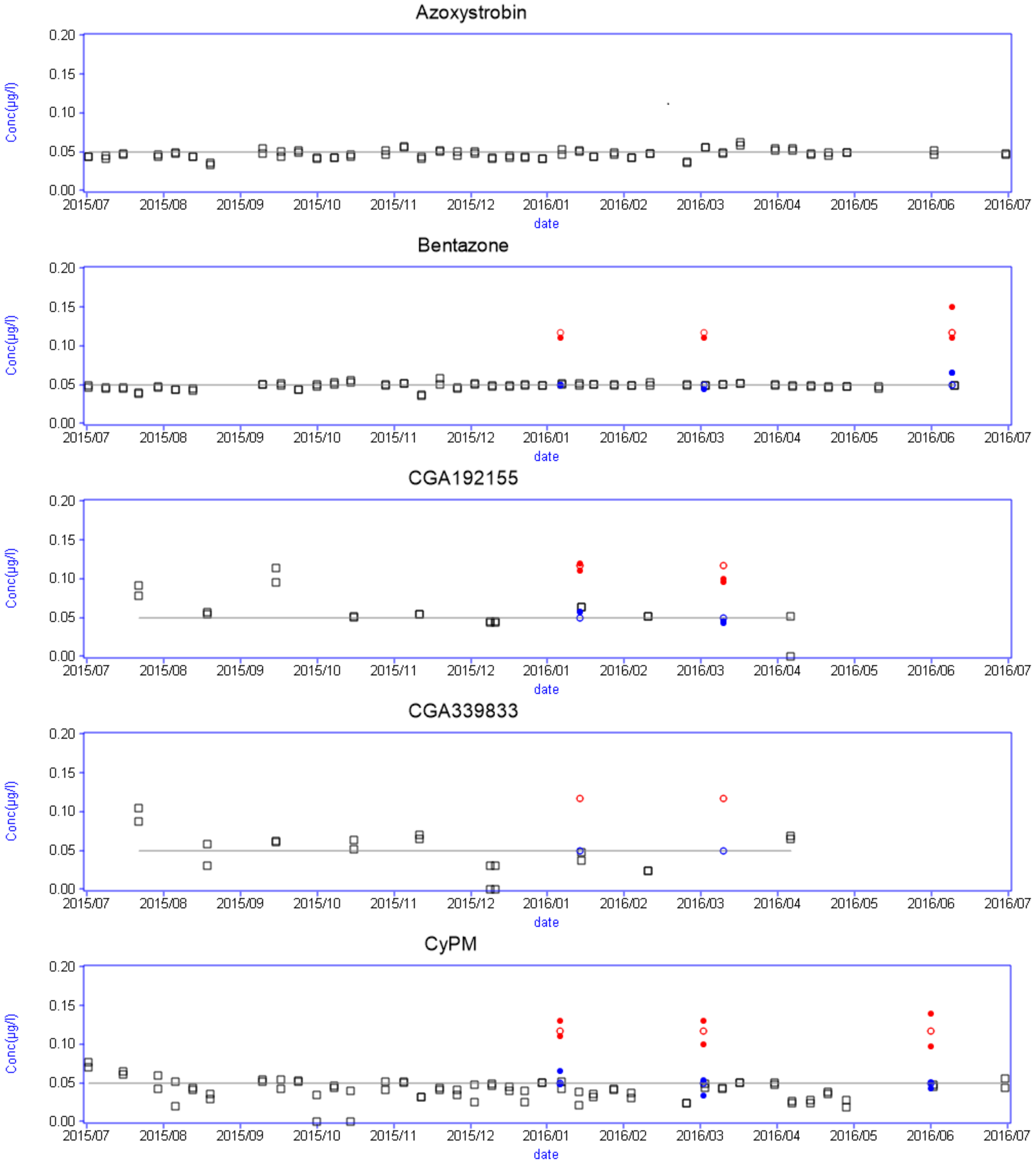

Figure A6.1 continued. Quality control data for pesticide analysis by laboratory 1. Internal laboratory control (IQ) samples are indicated by square symbols and the nominal level is indicated by the solid grey line (□ IQ measured, — IQ nominal concentration). External control (EQ) samples are indicated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

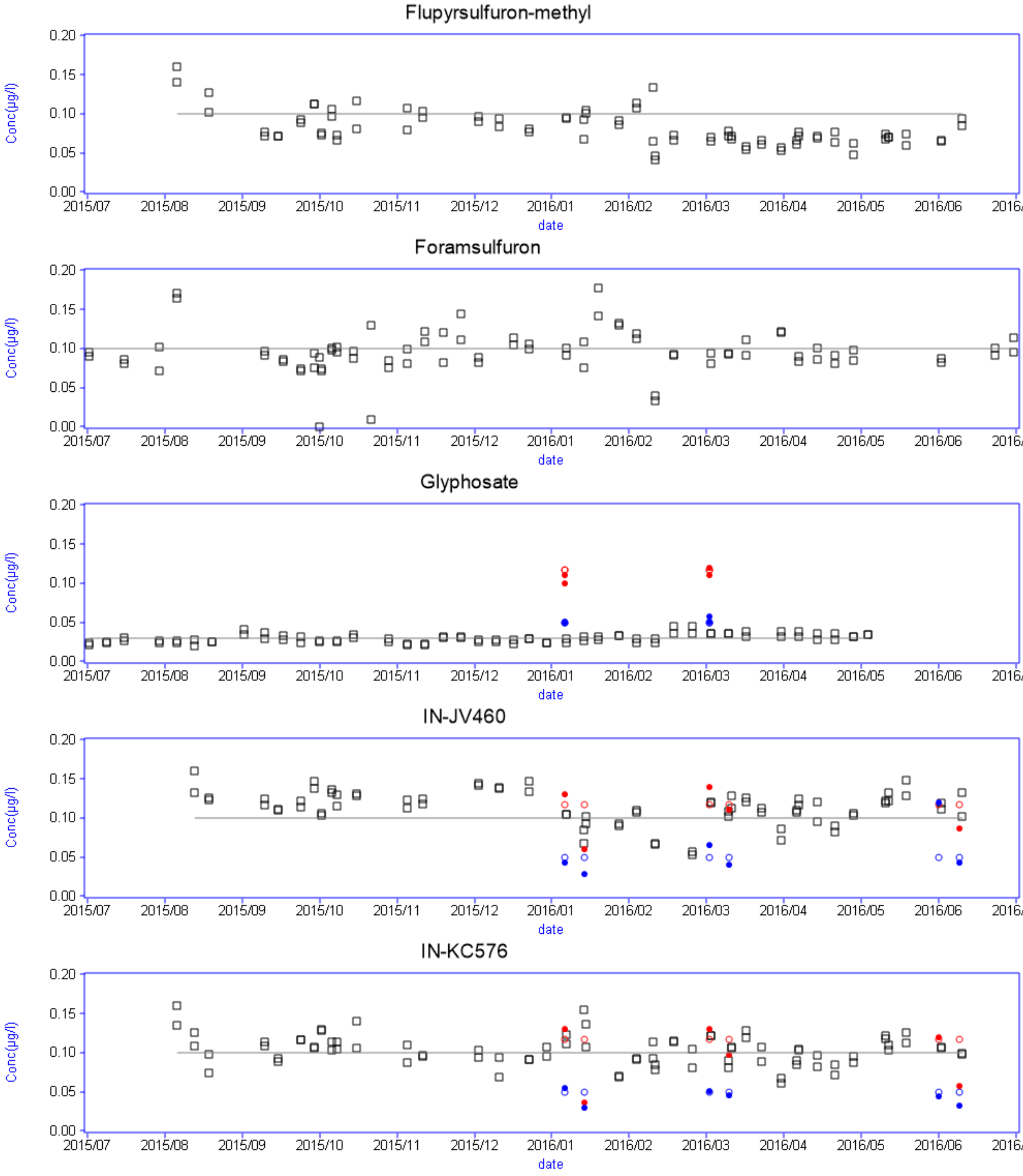

Figure A6.1 continued. Quality control data for pesticide analysis by laboratory 1. Internal laboratory control (IQ) samples are indicated by square symbols and the nominal level is indicated by the solid grey line (□ IQ measured, — IQ nominal concentration). External control (EQ) samples are indicated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

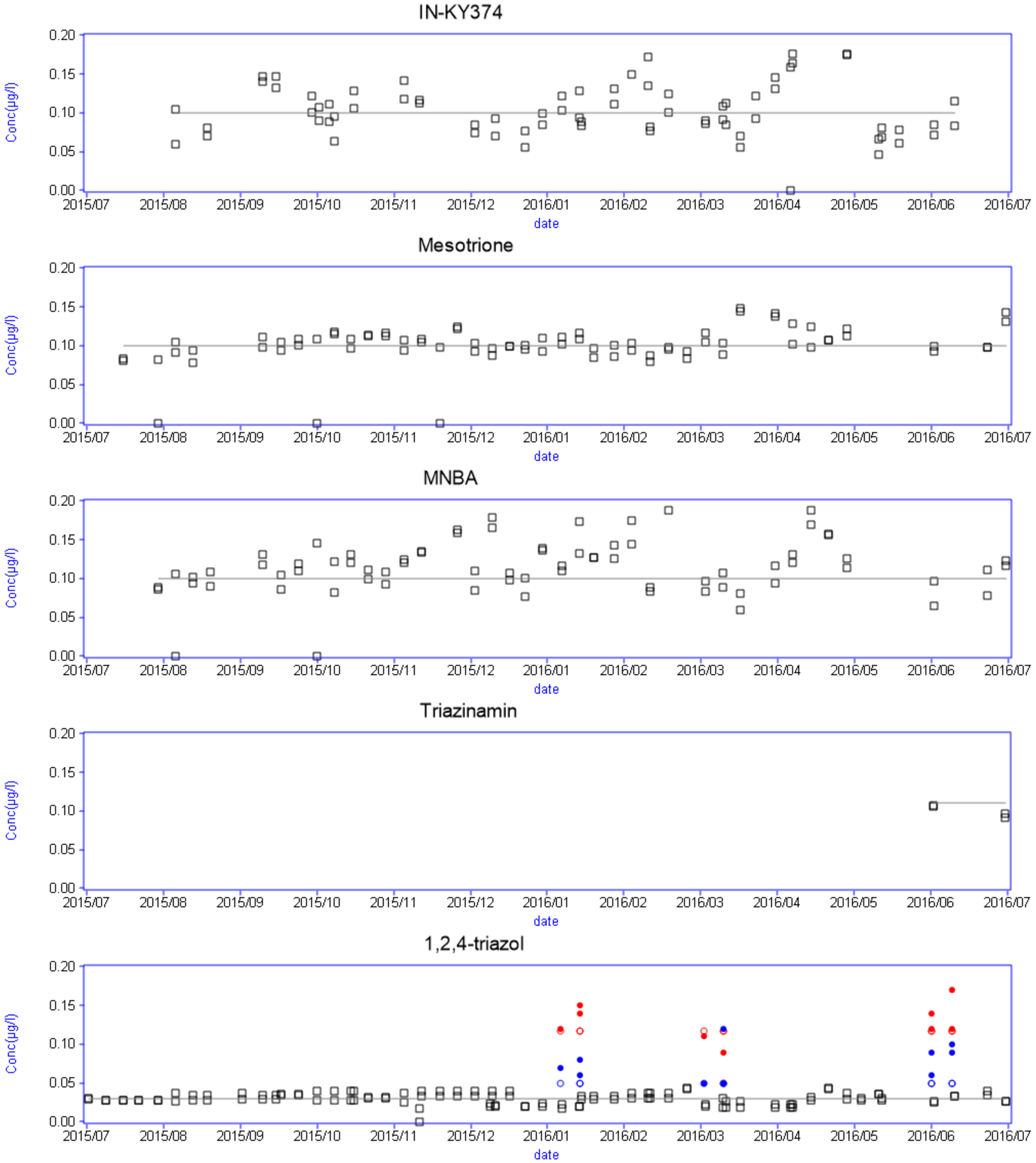

Figure A6.1 continued. Quality control data for pesticide analysis by laboratory 1. Internal laboratory control (IQ) samples are indicated by square symbols and the nominal level is indicated by the solid grey line (□ IQ measured, — IQ nominal concentration). External control (EQ) samples are indicated 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 fields in the period up to 2009/2010

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

Crop and analysed pesticides	Application date	End of monitoring	Prec. (mm)	Perc. (mm)	1st month perc. (mm)	C_{mean} (µg L^{-1})
Potatoes 1999						
Linuron (Afalon)	May 99	Jul 01	2550	1253	87	<0.01
- *ETU*[1)] (Dithane DG)	Jun 99	Oct 01	2381	1169	73	<0.01
Metribuzine (Sencor WG)	Jun 99	Jul 03	4223	2097	85	<0.01
- *metribuzine-diketo*		Jul 10†	11142	5387	85	0.05–0.36
- *metribuzine-desamino*		Jul 03	4223	2097	85	<0.02
- *metribuzine-desamino-diketo*		Apr 08	8689	4192	85	0.14–0.97
Spring barley 2000						
Triasulfuron (Logran 20 WG)	May 00	Apr 03	2740	1283	13	<0.02
- *triazinamin*						<0.02
Propiconazole (Tilt Top)	Jun 00	Jul 03	2948	1341	11	<0.01
Fenpropimorph (Tilt Top)	Jun 00	Jul 03	2948	1341	11	<0.01
- *fenpropimorphic acid*						<0.02
Pirimicarb (Pirimor G)	Jun 00	Apr 03	2622	1263	17	<0.01
- *pirimicarb-desmethyl*						<0.02
- *pirimicarb-desmethyl-formamido*						<0.02
Winter rye 2001						
Pendimethalin (Stomp SC)	Nov 00	Apr 03	2271	1219	109	<0.01
Triazinamin-methyl [2)] (Express)	Nov 00	Apr 03	2271	1219	109	<0.02
Propiconazole (Tilt Top)	May 01	Jul 03	2948	1341	11	<0.01
Fenpropimorph (Tilt Top)	May 01	Jul 03	2948	1341	11	<0.01
- *fenpropimorphic acid*						<0.01
Winter rape 2002						
Clomazone (Command CS)	Sep 01	Jul 04	2534	1194	9	<0.01
- *FMC 65317 (propanamide-clomazone)*						<0.02
Winter wheat 2003						
Bromoxynil (Oxitril CM)	Oct 02	Apr 05	2082	995	53	<0.01
Ioxynil (Oxitril CM)	Oct 02	Apr 05	2082	995	53	<0.01
Fluroxypyr (Starane 180)	May 03	Jul 05	1867	787	50	<0.02
Flamprop-M-isopropyl (Barnon Plus 3)	May 03	Jul 05	2635	1031	42	<0.01
- *Flamprop-M (free acid)*						
Dimethoate (Perfekthion 500 S)	Jul 03	Jul 05	1629	722	14	<0.01
Potatoes 2004						
-*Fluazifop-P (free acid)*[3)] (Fusilade X-tra)	May 04	Jul 06	1754	704	16	<0.01
Rimsulfuron (Titus)	Jun 04	Jul 06	6211	3008	13	<0.02
- *PPU*[4)] (Titus)	Jun 04	Jul 10†	6211	3008	13	<0.01[5)]
- *PPU-desamino*[4)] (Titus)	Jun 04	Jul 10†	6211	3008	13	<0.01[5)]
Maize 2005						
Terbuthylazine (Inter-Terbutylazine)	May 05	Jul 07	2145	933	16	<0.01
-*desethyl-terbuthylazine*						<0.01
-*2-hydroxy-terbuthylazine*						<0.01
-*desisopropyl-atrazine*						<0.01[6)]
-*2-hydroxy-desethyl-terbuthylazine*						<0.01
Bentazone (Laddok TE)	Jun 05	Jul 07	2061	927	33	<0.01
-*AIBA*						<0.01
Spring barley 2006						
-*triazinamin-methyl*[7)] (Express ST)	Jun 06	Jul 08	2349	1184	43	<0.02
Epoxiconazole (Opus)	Jun 06	Jul 08	2233	1148	24	<0.01

Systematic chemical nomenclature for the analysed pesticides is given in Appendix 1.
1) Degradation product of mancozeb. The parent compound degrades too rapidly to be detected by monitoring.
2) Degradation product of tribenuron-methyl. The parent compound degrades too rapidly to be detected by monitoring.
3) Degradation product of fluazifop-P-butyl. The parent compound degrades too rapidly to be detected by monitoring.
4) Degradation product of rimsulfuron. The parent compound degrades too rapidly to be detected by monitoring.
5) Leaching increased the second and third year after application.
6) Leaching increased during the second year after application but measured concentrations did not exceed 0.042µg L^{-1} (see Kjær et al., 2008).
7) Degradation product of tribenuron-methyl. The parent compound degrades too rapidly to be detected by monitoring.

Table A7.1B. Pesticides analysed at **Tylstrup**. For each pesticide (P) and degradation product (M) the application date (appl. date) as well as end of monitoring period (End mon.) is listed. Precipitation and percolation 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 [µg L^{-1}] at 1 m b.g.s. the first year after application. See Appendix 2 for calculation method and Appendix 8 (Table A8.1) for previous applications of pesticides.

Crop	Applied product	Analysed pesticide	Appl. date	End mon.	Y 1st precip.	Y 1st percol.	M 1st precip.	M 1st percol.	C_{mean}
Winter Rape 2007	CruiserRAPS	Thiamethoxam(P)	Aug 06	Apr 08	1250	700	87	57	<0.01
		CGA 322704(M)	Aug 06	Apr 08	1250	700	87	57	<0.02
	Kerb 500 SC	Propyzamide(P)	Feb 07	Apr 09	1052	472	48	40	<0.01
		RH-24580(M)	Feb 07	Apr 09	1052	472	48	40	<0.01
		RH-24644(M)	Feb 07	Apr 09	1052	472	48	40	<0.01
		RH-24655(M)	Feb 07	Apr 09	1052	472	48	40	<0.01
	Matrigon	Clopyralid(P)	Mar 07	Apr 09	1055	488	30	24	<0.02
Winter wheat 2008	Amistar	Azoxystrobin(P)	Jun 08	Jun 11	1316	662	141	0	<0.01
		CyPM(M)	Jun 08	Jun 11	1316	662	141	0	<0.01
	Folicur EC 250	Tebuconazole(P)	Nov 07	Mar 10	1133	461	69	43	<0.01
	Stomp	Pendimethalin(P)	Oct 07	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

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

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

Systematic chemical nomenclature for the analysed pesticides is given in Appendix 1.
[1)] Degradation product of tribenuron-methyl. The parent compound degrades too rapidly to be detected by monitoring.
[2)] Degradation product of pyridate. The parent compound degrades too rapidly to be detected by monitoring.
[3)] Degradation product of rimsulfuron. The parent compound degrades too rapidly to be detected by monitoring.
[4)] Leaching increased the second year after application.
[5)] Degradation product of fluazifop-P-butyl. The parent compound degrades too rapidly to be detected by monitoring.

Table A7.2B. Pesticides analysed at **Jyndevad**. For each compound it is listed whether it is a pesticide (P) or degradation product (M), as well as the application date (Appl. date) and end of monitoring period (End. mon.). Precipitation (precip. in mm) and percolation (percol. in mm) 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 [µg L^{-1}] at 1 m b.g.s. the first year after application. See Appendix 2 for calculation method and Appendix 8 (Table A8.2) for previous applications of pesticides.

Crop	Applied product	Analysed pesticide	Appl. date	End mon.	Y 1st precip.	Y 1st percol.	M 1st precip.	M 1st percol.	C_{mean}
Triticale 2007	Atlantis WG	Mesosulfuron-methyl(P)	Oct 06	Dec 09	1346	809	95	73	<0.01
		Mesosulfuron(M)	Oct 06	Dec 09	1346	809	95	73	<0.02
	Cycocel 750	Chlormequat(P)	Apr 07	Jun 08	1223	638	79	1	<0.01
	Opus	Epoxiconazole(P)	May 07	Dec 09	1193	644	123	6	<0.01
Winter wheat 2008	Folicur EC 250	Tebuconazole(P)	Dec 07	Mar 10	1396	827	60	97	<0.01
	Pico 750 WG	Picolinafen(P)	Oct 07	Mar 10	1418	777	77	55	<0.01
	Pico 750 WG	CL 153815(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

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

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

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

Crop and analysed pesticides	Application date	End of monitoring	Prec. (mm)	Perc. (mm)	1st month perc.	C_{mean} (µg L^{-1})
Winter rape 2006						
Propyzamide (Kerb 500 SC)	Nov 05	Apr 08	2345	1115	75	0.22[4)]
- *RH-24644*						0.01[4)]
- *RH-24580*						<0.01[4)]
- *RH-24655*						<0.01[4)]
Clopyralid (Matrigon)	Apr 06	Apr 08	2009	859	8	<0.01
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						
- *Fluazifop-P* (Fusilade Max)	Jul 08	Jun 12	985	494	21	<0.01
- *TFMP* (Fusilade Max)	Jul 08	Jun 12	985	494	21	0.24
Metamitron (Goliath)	May 08	Dec 10	969	498	4	0.01
- *Desamino-metamitron*	May 08	Dec 10	969	498	4	0.02
Triflusulfuron-methyl (Safari)	May 08	Jun 10	969	498	4	<0.01
- *IN-D8526*	May 08	Jun 10	969	498	4	<0.01
- *IN-E7710*	May 08	Jun 10	969	498	4	<0.01
- *IN-M7222*	May 08	Jun 10	969	498	4	<0.02
Ethofumesate (Tramat 500 SC)	May 08	May 10	969	497	3	<0.01

1) Degradation product of tribenuron-methyl. The parent compound degrades too rapidly to be detected by monitoring.
2) Degradation product of pyridate. The parent compound degrades too rapidly to be detected by monitoring.
3) Average leachate concentration within the first drainage season after application could not be calculated, as monitoring started January 2003 (7 months after application). See Kjær et al. (2007) for further information.
4) Drainage runoff commenced two weeks prior to the application of propyzamide, and the weighted concentrations refer to the period from the date of application until 1 July 2007.

Table A7.4B. Pesticides analysed at **Silstrup**. For each compound it is listed whether it is a pesticide (P) or degradation product (M), as well as the application date (Appl. date) and end of monitoring period (End. mon.). Precipitation (precip. in mm) and percolation (percol. in mm) 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 [µg L^{-1}**]** at 1 m b.g.s. the first year after application. See Appendix 2 for calculation method and Appendix 8 (Table A8.3) for previous applications of pesticides.

Crop	Applied product	Analysed pesticide	Appl. date	End mon.	Y 1st Precip.	Y 1st Percol	M 1st Precip	M 1st 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

Table A7.4A. 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. 1^{st} 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} ($\mu g\ L^{-1}$)
Spring barley 2000						
Metsulfuron-methyl (Ally)	May 00	Apr 03	2990	1456	29	<0.01
- *triazinamin*						<0.02
Flamprop-M-isopropyl (Barnon Plus 3)	May 00	Apr 03	2914	1434	2	0.02
- *flamprop (free acid)*						0.01
Propiconazole (Tilt Top)	Jun 00	Apr 05	4938	2294	0	0.01
Fenpropimorph (Tilt Top)	Jun 00	Jul 02	2211	1048	0	<0.01
- *fenpropimorphic acid*						<0.02
Dimethoate (Perfekthion 500 S)	Jun 00	Jul 02	2211	1048	0	<0.01
Pea 2001						
Glyphosate (Roundup Bio)	Oct 00	Jul 14†	10484	4977	123	0.54
- *AMPA*						0.17
Bentazone (Basagran 480)	May 01	Jul 08	7629	3621	9	0.03
- *AIBA*						<0.01
Pendimethalin (Stomp SC)	May 01	Jul 03	2208	1096	9	<0.01
Pirimicarb (Pirimor G)	Jun 01	Jul 05	4251	1995	10	0.01
- *pirimicarb-desmethyl*						<0.02
- *pirimicarb-desmethyl-formamido*						<0.02
Winter wheat 2002						
Ioxynil (Oxitril CM)	Nov 01	Jul 03	1580	860	52	0.04[1)]
Bromoxynil (Oxitril CM)	Nov 01	Jul 03	1580	860	52	0.01[1)]
Amidosulfuron (Gratil 75 WG)	Apr 02	Jul 04	2148	928	8	<0.01
MCPA (Metaxon)	May 02	Jul 04	2091	928	0	<0.01
- *4-chlor,2-methylphenol*						<0.01
Propiconazole (Tilt 250 EC)	May 02	Apr 05	2920	1336	39	0.02
Pirimicarb (Pirimor G)	Jun 02	Jul 05	2982	1403	58	0.01
- *pirimicarb-desmethyl*						<0.02
- *pirimicarb-desmethyl-formamido*		Apr 06				<0.02
Fodder beet 2003						
Glyphosate (Roundup Bio)	Sep 02	Jul 14	8289	3900	0	0.43
- *AMPA*						0.19
Ethofumesate (Betanal Optima)	May 03	Apr 06	2901	1371	50	0.11
Metamitron (Goltix WG)	May 03	Apr 06	2901	1371	50	1.1
- *metamitron-desamino*						0.21
Pirimicarb (Pirimor G)	Jul 03	Jul 05	2071	939	0	<0.01
- *pirimicarb-desmethyl*		Jul 05				<0.01
- *pirimicarb-desmethyl-formamido*		Apr 06				0.12
Spring barley 2004						
Fluroxypyr (Starane 180)	May 04	Jul 06	2073	1030	0	<0.02
Azoxystrobin (Amistar)	Jun 04	Jul 08	4452	2209	38	0.12
- *CyPM*						0.23
Maize 2005						
Terbuthylazine (Inter-Terbuthylazin)	May 05	Apr 09	4247	2042	32	0.48
- *desethyl-terbuthylazine*		Jul 09	4406	2051	32	0.31
- *2-hydroxy-terbuthylazine*		Jul 08	3338	1628	32	0.11
- *desisopropyl-atrazine*		Apr 09	4247	2042	32	0.02
- *2-hydroxy-desethyl-terbuthylazine*		Jul 08	3338	1628	32	0.24
Bentazone (Laddok TE)	Jun 05	Jul 08	3338	1628	10	0.18
- *AIBA*						<0.01
Glyphosate (Roundup Bio)	Nov 05	Jul 14	5191	2460	68	4.04[1)]
- *AMPA*						0.42[1)]
Spring barley 2006						
Florasulam (Primus)	Jun 06	Jul 08	2442	1163	0	<0.01
- *florasulam-desmethyl*						<0.03
Azoxystrobin (Amistar)	Jun 06	Jul 08	2414	1170	0	0.03
- *CyPM*						0.13

Table A7.4A 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)	1st month perc. (mm)	C_{mean} (µg L^{-1})
Winter wheat 2007						
Mesosulfuron-methyl (Atlantis WG)	Oct 06	Jul 08	1420	305	29	0.01
- *Mesosulfuron*	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 A7.5B. Pesticides analysed at **Estrup**. For each compound it is listed, whether it is a pesticide (P) or degradation product (M), as well as the application date (Appl. date) and end of monitoring period (End. mon.). Precipitation (precip. in mm) and percolation (percol. in mm) 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 [µg L^{-1}**]** at 1 m b.g.s. the first year after application. See Appendix 2 for calculation method and Appendix 8 (Table A8.4) for previous applications of pesticides.

Crop	Applied product	Analysed pesticide	Appl. date	End mon.	Y 1st precip	Y 1st percol	M 1st precip	M 1st 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
		CL 153815(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

Table A7.5A. 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)	1st month perc. (mm)	C_{mean} (µg L^{-1})
Winter wheat 1999						
Glyphosate (Roundup 2000)	Aug 99	Apr 03	2526	947	0	<0.01
- *AMPA*						<0.01
Bromoxynil (Briotril)	Oct 99	Apr 02	1738	751	35	<0.01
Ioxynil (Briotril)	Oct 99	Apr 02	1738	751	35	<0.01
Fluroxypyr (Starane 180)	Apr 00	Apr 02	1408	494	7	<0.01
Propiconazole (Tilt Top)	May 00	Jul 03	2151	669	0	<0.01
Fenpropimorph (Tilt Top)	May 00	Jul 02	1518	491	0	<0.01
- *fenpropimorphic acid*						<0.01
Pirimicarb (Pirimor G)	Jun 00	Jul 03	2066	684	0	<0.01
- *pirimicarb-desmethyl*						<0.01
- *pirimicarb-desmethyl-formamido*						<0.02
Sugar beet 2001						
Glyphosate (Roundup 2000)	Oct 00	Jul 03	1747	709	0	<0.01
- *AMPA*						0.01
Metamitron (Goltix WG)	May 01	Jul 03	1512	507	4	0.01
- *metamitron-desamino*						0.01
Ethofumesate (Betanal Optima)	May 01	Jul 03	1512	507	4	0.06
Desmedipham (Betanal Optima)	May 01	Jul 03	1512	507	4	<0.01
- *EHPC*						<0.02
Phenmedipham (Betanal Optima)	May 01	Jul 03	1512	507	4	<0.01
- *MHPC*						<0.02
Fluazifop-P-butyl (Fusilade X-tra)	Jun 01	Jul 03	1460	503	0	<0.01
- *fluazifop-P (free acid)*						0.02
Pirimicarb (Pirimor G)	Jul 01	Jul 03	1460	503	1	<0.01
- *pirimicarb-desmethyl*						<0.01
- *pirimicarb-desmethyl-formamido*						<0.02
Spring barley 2002						
Flamprop-M-isopropyl (Barnon Plus 3)	May 02	Jul 04	1337	333	0	<0.01
- *flamprop-M (free acid)*						<0.01
MCPA (Metaxon)	May 02	Jul 04	1358	337	4	<0.01
- *4-chlor-2-methylphenol*						<0.02
- *triazinamin-methyl*[1)] (Express)	May 02	Jul 04	1358	337	4	<0.02
Dimethoate (Perfekthion 500 S)	Jun 02	Jul 04	1328	333	0	<0.01
Propiconazole (Tilt 250 EC)	Jun 02	Jul 04	1328	333	0	<0.01
Winter rape 2003						
Clomazone (Command CS)	Aug 02	Apr 05	1761	509	4	<0.02
- *FMC 65317 (propanamide-clomazon)*						<0.02
Winter wheat 2004						
Prosulfocarb (Boxer EC)	Oct 03	Apr 06	1542	454	0	<0.01
MCPA (Metaxon)	Jun 04	Jul 06	1307	331	0	<0.01
- *4-chlor,2-methylphenol*						<0.01
Azoxystrobin (Amistar)	Jun 04	Jul 07	2098	636	0	<0.01
- *CyPM*						<0.01
Maize 2005						
Terbuthylazine (Inter-Terbutylazin)	May 05	Jul 08	2078	666	4	0.67
- *desethyl-terbuthylazine*	May 05	Jul 08	2078	666		0.59
- *2-hydroxy-terbuthylazine*	May 05	Jul 08	2078	666		0.04
- *desisopropyl-atrazine*	May 05	Jul 08	2078	666		0.03
- *2- hydroxy-desethyl-terbuthylazine*	May 05	Jul 07	1428	465	4	0.07
Bentazone (Laddok TE)	May 05	Jul 07	1408	464	6	2.82
- *AIBA*						<0.01
Spring barley 2006						
Fluroxypyr (Starane 180 S)	May 06	Jul 08	1496	524	17	<0.02
Epoxiconazole (Opus)	Jun 06	Jul 08	1441	507	3	<0.01

Systematic chemical nomenclature for the analysed pesticides is given in Appendix 1.
[1)] *Degradation product of tribenuron-methyl. The parent compound degrades too rapidly to be detected by monitoring.*
† Monitoring will continue during the following year. The values for prec. and perc. are accumulated up to July 2009.

Table A7.5B. Pesticides analysed at **Faardrup**. For each compound it is listed whether it is a pesticide (P) or degradation product (M), as well as the application date (Appl. date) and end of monitoring period (End. mon.). Precipitation (precip. in mm) and percolation (percol. in mm) 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 [µg L^{-1}] at 1 m b.g.s. the first year after application. See Appendix 2 for calculation method and Appendix 8 (Table A8.5) for previous applications of pesticides.

Crop	Applied product	Analysed pesticide	Appl. date	End mon.	Y 1st Precip.	Y 1st Percol.	M 1st Precip.	M 1st Percol	C_{mean}
Spring barley 2006	Opus	Epoxiconazole(P)	Jun 06	Jun 08	790	306	17	3	<0.01
	Starane 180 S	Fluroxypyr(P)	May 06	Jun 08	708	333	37	17	<0.02
Winter rape 2007	CruiserRAPS	Thiamethoxam(P)	Aug 06	Jun 08	806	294	57	23	<0.01
		CGA 322704(M)		Jun 08	806	294	57	23	<0.02
	Kerb 500 SC	Propyzamide(P)	Feb 07	Mar 09	735	199	64	46	0.01
		RH-24580(M)		Mar 09	735	199	64	46	<0.01
		RH-24644(M)		Mar 09	735	199	64	46	<0.01
		RH-24655(M)		Mar 09	735	199	64	46	<0.01
Winter wheat 2008	Folicur 250	Tebuconazole(P)	Nov 07	Dec 09	693	158	64	56	<0.01
	Stomp SC	Pendimethalin(P)	Oct 07	Dec 09	673	180	51	24	<0.01
Sugar beet 2009	Ethosan	Ethofumesate(P)	Apr 09	Jun 11	609	146	50	2	0.01
	Goliath	Metamitron(P)	Apr 09	Jun 11	609	146	42	2	0.02
		Desamino-metamitron(M)	Apr 09	Jun 11	609	146	42	2	0.06
	Safari	Triflusulfuron-methyl(P)	Apr 09	Jun 11	609	146	50	2	<0.01
		IN-D8526(M)	Apr 09	Jun 11	609	146	50	2	<0.01
		IN-E7710(M)	Apr 09	Jun 11	609	146	50	2	<0.01
		IN-M7222(M)	Apr 09	Jun 11	609	146	50	2	<0.02

Appendix 8

New horizontal wells

New horizontal wells at each PLAP-field, with three new horizontal screens were established at each PLAP-field 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-fields to optimize monitoring of the fields both in time and space.

The aim of the optimization was:

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

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

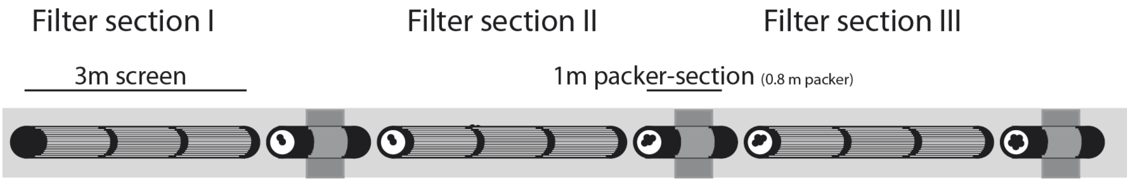

Figure A8.1. Design of horizontal well with three filter sections of 3 m (inner diameter 25 mm; outer diameter 32 mm) each separated by 1m packer-section attached 0.8 m bentonite (thickness at installation 1 cm; expand to a thickness of 3.5 cm). Water can be sampled through two PE-tubes (inner diameter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

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

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

- **Clayey till fields** 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 field investigations carried out at the various PLAP fields offer good opportunity to model the groundwater age from soil porosity and netprecipitation assuming simple piston flow for groundwater.

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

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

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

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

The other fields were discounted becauce of:

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

Age from recharge modelling

Recharge data obtained by the MACRO model for the 2000-2009 (Rosenbom *et al.*, 2010) were used to estimate water velocity and groundwater age from the deepest screens at the Jyndevad and Tylstrup fields, 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 per year for Jyndevad and 1.35–1.38 m per year for Tylstrup. A water velocity of 1.4 m per year appears reasonable for estimating groundwater age at both fields based on recharge data. Groundwater age estimates using a water velocity of 1.4 m per year for all filters, except for the deep one at Tylstrup (1.1 m per year) 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.

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

Age from tritium-helium analysis

Samples for tritium and helium collected in one liter plastic bottles and clamped copper tubes respectively were shipped to the University of Bremen and analysed according to Sültenfuß et al. (2009). The age of water was determined from the ratio between tritium (^3H), half-life 12.5 years, 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 fields are shown with increasing depth from left to right in Figure A9.1. The depths are meters below water table to the mid-screen. The length of each screen is 1 m, meaning that the water table was 10 cm below top-screen for the shallowest depth indicated in the figure. Depth of water table checked during pumping did not indicate problems with intake of air, and no bubbles were observed during sampling.

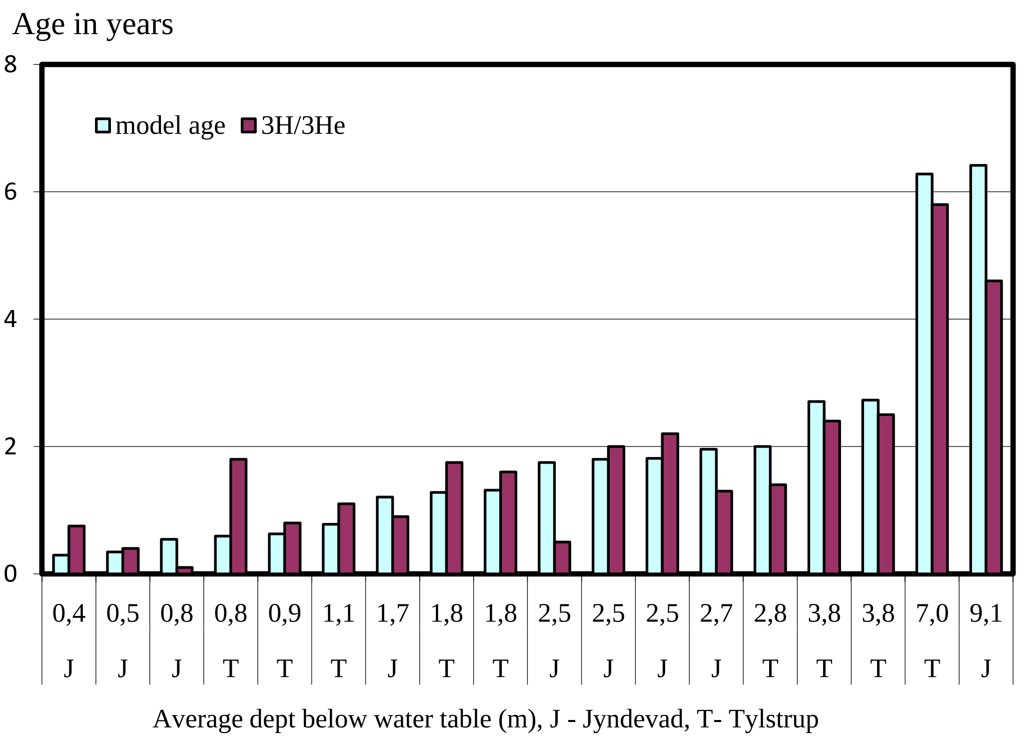

Figure A9.1. Groundwater age at Jyndevad and Tylstrup. Recharge model age assumes water velocity of 1.4 m per year, except for the deep filter at Tylstrup (1.1 m per year).

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