The Danish Pesticide Leaching Assessment Programme

Monitoring results May 1999–June 2017

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Editor: Annette E. Rosenbom
Front page photo by Henning Carlo Thomsen: Winter wheat growing at a PLAP field
Cover: Henrik Klinge Pedersen
Layout and graphic production: Authors
Printed: February 2019
Price: DKK 200

ISSN (print): 2446-4228
ISSN (online): 2446-4236
ISBN (print) 978-87-7871-492-3
ISBN (online) 978-87-7871-491-6

Available from:
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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. 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), Sachin Karan (GEUS), Carsten B. Nielsen (BIOS), Steen Marcher (Danish EPA) and Anne Louise Gimsing (Danish EPA).

Mette Hyldebrandt-Larsen (Danish EPA) chairs the steering group, and the members are Steen Marcher (Danish EPA), Erik Steen Kristensen (AGRO), Christian Kjær (BIOS), Sachin Karan (GEUS), Claus Kjøller (GEUS) and the project leader Annette E. Rosenbom (GEUS).

This report presents the results for the period May 1999–June 2017. Results including part of the period May 1999–June 2016 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, Rosenbom *et al.*, 2017). 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 2015-2017.

The report was prepared jointly by Annette E. Rosenbom (GEUS), Sachin Karan (GEUS), Nora Badawi (GEUS), Lasse Gudmundsson (GEUS), Carl H. Hansen (GEUS), Jolanta Kazmierczak (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:

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Dansk sammendrag: Der er udarbejdet et dansk sammendrag for perioden maj 1999 til juni 2017 med ISBN (print) 978-87-7871-489-3 og ISBN (online) 978-87-7871-490-9.

Annette E. Rosenbom
February 2019

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 2015–June 2017 comprising 7269 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 6 pesticides and 18 degradation products after applying the maximum allowed dose of 13 specific pesticides in connection with a specific crop except for applying propiconazole in 2016 in only half dose of the maximum allowed. The 24 compounds evaluated have alle been included in PLAP previously (Table 0.1).

Highlights from the monitoring period July 2015–June 2017:

- **The degradation product of many azole 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 terrestrial 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. Given the many detections at especially Estrup and Jyndevad, an evaluation of the leaching of 1,2,4-triazole, as a result of the application of other parent fungicides was conducted. 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 to spring barley undersown with clovergrass in June 2016. 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 were 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 included for testing in PLAP to confirm that 1,2,4-triazole is not formed in major amounts by degradation of prothioconazole. The evaluation revealed 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, though the contribution of 1,2,4-triazole to the groundwater from upstreams fields could not be neglected, when evaluating the detections in the groundwater collected from the downstream wells. Therefore, it is not possible to fully, relate the detections in the groundwater to the specific application of azoles at the fields, since the measurements may be influenced by other sources such as

prior use of other azole fungicides sprayed or applied as seed dressing at the field or upstream fields. The results for the period July 2015–June 2017 show that 1,2,4-triazole was still leaching to the groundwater and at Estrup in concentrations of up to 0.19 µg L^{-1}. 24 groundwater samples out of a total number of 600 samples collected from all the fields had a 1,2,4-triazole concentration exceeding 0.1 µg L^{-1} (Table 0.1). The causes for the many detections of 1,2,4-triazole is under evalution in PLAP.

- **Repeated application of azoxystrobin cause a long-term increase in CyPM detections exceeding 0.1 µg L^{-1} in the groundwater**
  CyPM is a degradation product of azoxystrobin 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 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. CyPM has now been leaching for many years to groundwater at Silstrup and Estrup with exceedences of 0.1µg L^{-1} in 12 and 5 groundwater samples collected within the last four and five years at Silstrup and Estrup, respectively. Possible underlying relationships to these findings are under evaluation in PLAP.

- **Flupyrsulfuron-methyl and three of its degradation products have still 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 was detected in the groundwater. Only IN-KY374 was detected in the variably-saturated zone (suction cups) at Jyndevad in four samples, where three were above 0.1 µg L^{-1}. The total number of samples at Jyndevad in the suction cups was 30.

- **Snowmelt can cause detections of glyphosate exceeding 0.1 µg L^{-1} in the groundwater**
  As was the case in the beginning of 2013, snowmelt at Estrup seems to be the cause for one detection of glyphosate exceeding 0.1 µg L^{-1} in the groundwater in March 2016, i.e. more than two years after application. In addition, 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 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**
  A split application of the herbicide mesotrione was conducted in May-June 2015 and 2016 at Estrup and in June 2015 and 2016 at Silstrup. Both applications triggered more or less immediate detections of high concentrations of mesotrione

and its degradation product MNBA in drainage (1 m depth). The spraying at Estrup in 2015 further resulted in detections of mesotrione and MNBA 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 and one of MNBA in groundwater. The leaching pattern of the split application in 2016 resembled the one in 2015, although mesotrione was detected 10 months later in the young groundwater at 2 m depth at Estrup.

- **Still 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. Detections of 6-hydroxy-bentazone and 8-hydroxy-bentazone in PLAP seem unlikely as these metabolites according to the EFSA conclusion are not found in soil. 6-hydroxy-bentazone is a metabolite found in animals and plants, and 8-hydroxy-bentazone is found in plants, animals and as a photolysis metabolite in surface water.

Throughout the monitoring period (1999-2017) 115 pesticides and/or degradation products (50 pesticides and 65 degradation products) have been analysed in the PLAP, which comprises five fields (1.2 to 2.4 ha) grown with different agricultural crops. The total number of compounds is the same as in the latest PLAP-report (Rosenbom *et al.*, 2017). However, metsulfuron-methyl is now correctly given as a degradation product and not as a pesticide, like in earlier reports. With 12 new compounds included in the hydrological year 2015-2016, no new compounds could, given economical constrains, be added for an evaluation in the hydrological year 2016-2017. The leaching, as a result of the application(s) of 53 pesticides have been evaluated hereamong:

- 16, where only the pesticide was analysed (including epoxiconazole and propiconazole even though their degradation product 1,2,4-triazole is detected, but it is only included as an outcome of tebuconazole in Tables 8.2 and 8.4)
- 34, where the pesticide was analysed together with one or more of its degradation products
- 3 (fludioxonil, mancozeb and tribenuron-methyl), where it was only the degradation products of the pesticide, which were analysed

Of the 53 pesticides (50+3), 17 resulted in detections of the pesticide or its degradation product(s) in groundwater samples in concentrations exceeding 0.1 µg L^{-1}. 15 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}. Four of the 17 pesticides resulted in detections indicating a potential long-term leaching risk through sandy soils (metalaxyl-M, metribuzin, rimsulfuron and tebuconazole), whereas the 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-triazole causing the presented leaching risk for tebuconazole at both sandy soils and fractured clayey tills, can also be the results of degradation of the application of other azole fungicides by spraying or use as seed treatment. This will be evaluted further in PLAP. The PLAP-results on 1,2,4-triazole have led to a 1,2,4-triazole screening in the Danish National Groundwater Monitoring Programme (GRUMO). Based on the results from GRUMO and PLAP, 1,2,4-triazole was included in the Danish Waterworks quality control of the drinking water. The following 10 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, thiacloprid, thiamethoxam and tribenuron-methyl.

Table 0.1 ***(Same as Table 8.5)*** 6 pesticides and 18 *degradation products* have been analysed in PLAP in the period July 2015-June 2017 of which all compounds have been included in PLAP before. 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.** *[μg L^{-1}]*	**Det.**	**>0.1** *[μg L^{-1}]*	**Max conc.** *[μg L^{-1}]*
Azoxystrobin	Azoxystrobin	84	216		0	0	-	1	0	0.01
	CyPM	84	216		74	5	0.16	14	0	0.03
Bentazone	Bentazone	94	340	3 (0.011;-;-)	24	1	4.5	1	0	0.02
	6-hydroxy-bentazone	66	275	3(-)	0	0	-	0	0	-
	8-hydroxy-bentazone	66	275	3(-)	0	0	-	0	0	-
	N-methyl-bentazone	66	275	3(-)	0	0	-	0	0	-
Fludioxonil	*CGA 192155*	44	160	1 (-)	0	0	-	1	0	0.05
	CGA 339833	44	160	1 (-)	0	0	-	1	1	**0.37**
Flupyrsulfuron-methyl	Flupyrsulfuron-methyl	45	255	1 (-)	0	0	-	0	0	-
	IN-JV460	45	255	1 (-)	0	0	-	0	0	-
	IN-KC576	45	255	1 (-)	0	0	-	0	0	-
	IN-KY374	45	255	1 (-)	4	3	0.45	0	0	-
Foramsulfuron	Foramsulfuron	100	249	1 (-)	27	5	0.32	4	0	0.04
	AE-F092944	100	249		1	0	0.01	0	0	-
	AE-F130619	100	249		15	0	0.07	9	0	0.03
Glyphosat	Glyphosate	65	116		12	0	0.05	3	1	**0.13**
	AMPA	65	116		51	2	0.14	2	0	0.02
Mesotrione	Mesotrione	100	249		44	10	1.30	2	0	0.07
	AMBA	100	249		3	0	0.04	0	0	-
	MNBA	100	247		12	0	0.06	0	0	-
Tebuconazole 2014 Epoxiconazole 2015 Prothioconazole 2015 Propiconazole 2016	*1,2,4-triazole*	168	600	4 (-)	114	73	0.45	282	24	**0.19**
Fluroxypyr	*Fluroxypyr-methoxypyridine*	1	88		0	0	-	0	0	-
	Fluroxypyr-pyridinol	1	88		0	0	-	0	0	-
Triasulfuron	*Triazinamin*	47	131		0	0	-	0	0	**-**
Sub total	24 (6 Pesticides; 18 *Degradation products*)	1675	5568	26	**381**	**99**		**320**	**26**	
Percent		23%	77%	0.4%	**23%**	**6%**		**6%**	**0%**	
Total			**7269**							

The results of the PLAP-monitoring in the period May 1999–June 2017 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 dynamically/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 such fields.

- **Long-term leaching of the degradation product CGA 108906 led to further assessment in the Danish National Groundwater Monitoring Programme (GRUMO) and the Danish Waterworks quality control of the groundwater for drinking water purpose (Vandværkernes boringskontrol)**
  CGA 108906 is a degradation product of metalaxyl-M used against fungus (blight) in potatoes in 2010 on the two sandy PLAP-fields. CGA 108906 is still 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-evaluation of metalaxyl-M from 2002 presented results, 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. Recently, it was included in both the revised analysis program of the Danish National Groundwater Monitoring and in the Danish Waterworks quality control of groundwater used for drinking water purposes. In the latter, CGA 108906 was already the fourth-most frequently detected compound in 2016. Further, results from PLAP have been sent to EFSA in connection with the re-evaluation of metalaxyl-M in EU.

- **A degradation product of metribuzin leached 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 into diketo-metribuzin. This compound leaches for a long period of time 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 the sorption, incorporated into the leaching models. However, 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 become available.

- **Pesticide degradates like TFMP, often more water 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 following the application was imperative for the numbers of detections of TFMP. In the assessment of risk of leaching using regulatory models, it is therefore important to make use of updated and relevant climate data. Related to this topic, Denmark is working on improving the EU procedures, as of today data from the period 1961-1990 is applied as standard climatic conditions in the 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. Only once, MCPA was found 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, Rosenbom *et al.*, 2017). 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 2015-June 2017. All reports and associated peer-reviewed articles can be found at: http://pesticidvarsling.dk/om_os_uk/uk-forside.html.

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 concern has initiated monitoring programmes reporting on the quality of the Danish groundwater (the Danish National Groundwater Monitoring Programme; GRUMO; Thorling *et al.*, 2018) and the effect of agricultural practices (Pesticide Leaching Assessment Programme, PLAP). The reported results have and are still continuosly adressed in the regulation of pesticides. GRUMO results seem to indicate that this combined effort may have reduced the detection frequency of certain 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 have been included in PLAP since july 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, 50 pesticides and 65 degradation products have been included in the PLAP. All the compounds analysed since 1999 are listed in Appendix 1.

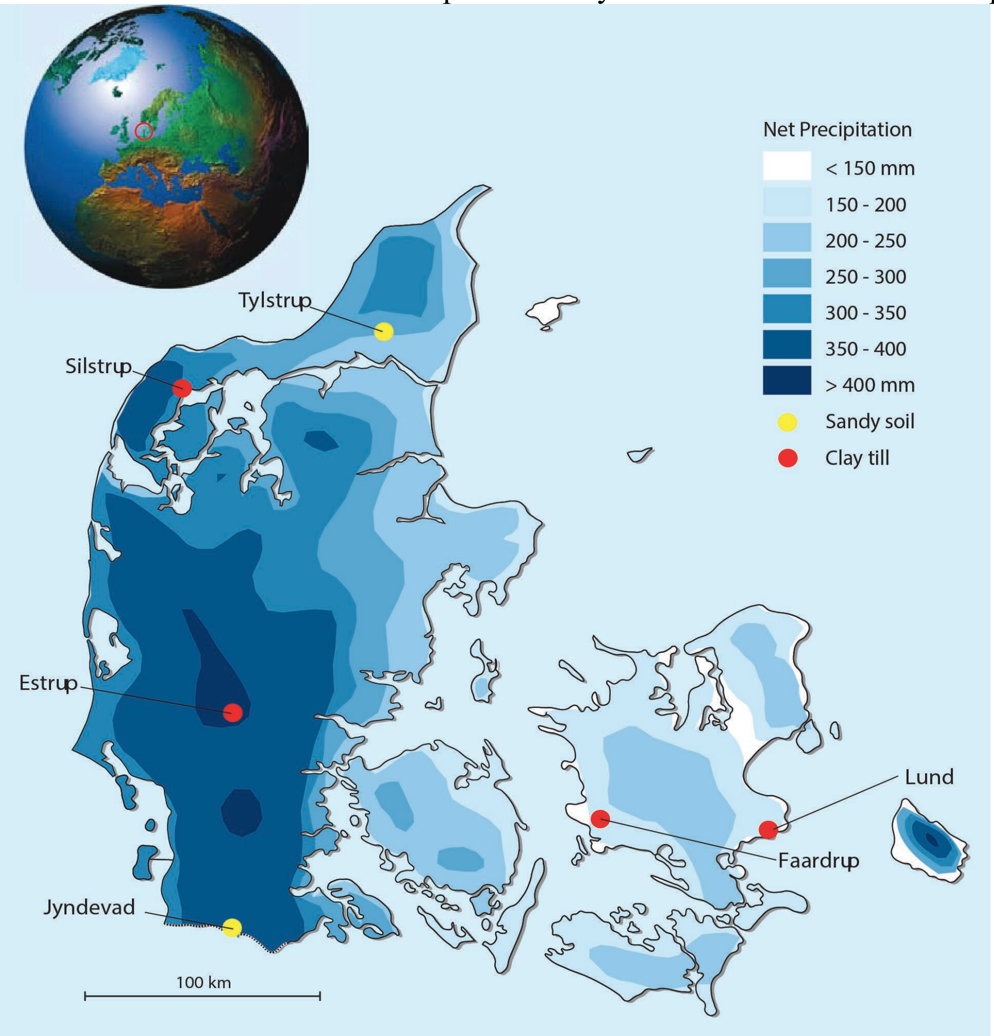


Figure 1.1. Annual net precipitation across Denmark (https://www2.mst.dk/Udgiv/publikationer/1992/87-503-9581-5/pdf/87-503-9581-5.pdf in Danish) and the geographical location of the five PLAP fields: **Tylstrup** (sandy), **Jyndevad** (sandy), **Silstrup** (clayey till), **Estrup** (clayey till) and **Faardrup** (clayey till) included in the monitoring programme of 1999-2017 and the new PLAP field **Lund** (clayey till) to be included in PLAP from July 2018. 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 with a few exceptions 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 1999-2017 (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})	$2.0\cdot10^{-5}$	$1.3\cdot10^{-4}$	$3.4\cdot10^{-6}$	$8.0\cdot10^{-8}$	$7.2\cdot10^{-6}$
Topsoil characteristics					
– DK classification	JB2	JB1	JB7	JB5/6	JB5/6
– Classification	Loamy sand	Sand	Sandy clay loam / sandy loam	Sandy loam	Sandy loam
– Clay content (%)	6	5	18–26	10–20	14–15
– Silt content (%)	13	4	27	20–27	25
– Sand content (%)	78	88	8	50–65	57
– pH	4–4.5	5.6–6.2	6.7–7	6.5–7.8	6.4–6.6
– TOC (%)	2.0	1.8	2.2	1.7–7.3	1.4

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

[2] *Large variation within the field.*

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

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 2017, but the main focus of this report is on the leaching risk of pesticides applied during July 2015 –June 2017. For a detailed description of the earlier part of the monitoring periods (May 1999–June 2016), see previous publications on http://pesticidvarsling.dk/monitor_uk/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 2017. The five field models have been calibrated for the monitoring period May 1999–June 2004 and validated for the monitoring period July 2004–June 2017.

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.

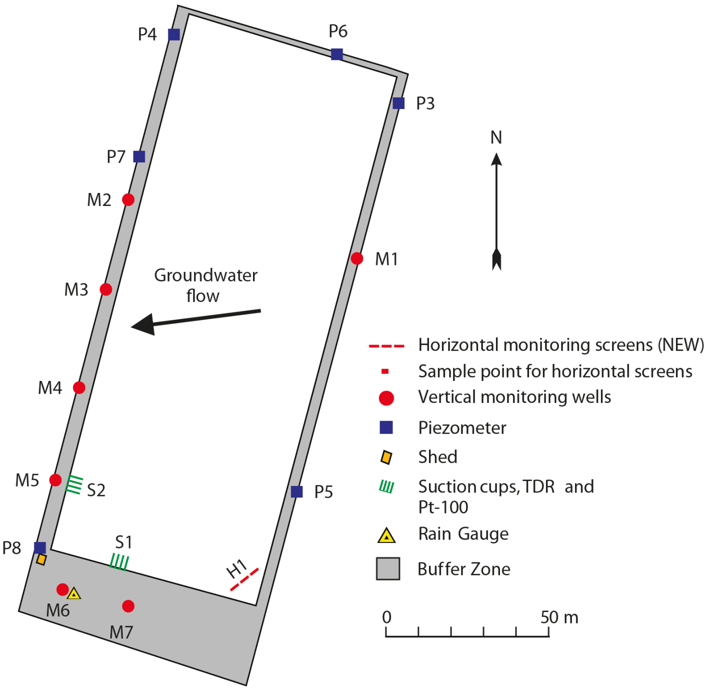


Figure 2.1. Overview of the **Tylstrup** field. The innermost white area indicates the cultivated land, while the grey area indicates the surrounding buffer zone. The positions of the various installations are indicated, as is the direction of groundwater flow (arrow). Pesticide monitoring is conducted 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 2016-17 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.

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. At harvest on 19 August the yield of spring barley was 61.9 hkg ha^{-1} of grain (85 % dry matter). An amount of 27 hkg ha^{-1} of straw (100% dry matter) was remowed 29 August 2016.

The field was rotary cultivated 10 March 2017, promoting the turnover of the grass and clover catchcrop, and then ploughed 22 March. The spring barley crop (cv. Laurikka) was sown 28 March emerged 11 April. Spraying of weeds was done 9 May, using a mixture of iodosulfuron and mesosulfuron. The two degradation products AE F099095 and AE F160459 of mesosulfuron were included in the monitoring. Spraying of fungi was done on 1 June and 14 June using propiconazole. The degradation product 1,2,4-triazole of propiconazole was included in the monitoring.

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 2017 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 2017.

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 indicating a good model description of the overall soil water dynamics in the variably-saturated zone

(Figure 2.2). Overall, the trends in soil water saturation were simulated successfully with only a few outliers as decribed in Rosenbom et al. (2017). For the recent hydraulic year (July 2016-June 2017) the simulated water saturation was overestimated in all depths during the summer period, where the observed decline in water saturation wass not captured (Figure 2.2C-E). This was consistent with overall trends from previous years, where the model was overestimating the water saturation during summers. From November 2016 and onwards, the model was consistent with observed water saturation. Again, this trend of model correspondence with observed data from winter to spring was consistent with overall patterns from previous years, where the observed trends were captured with a slight offset, generally less than 10%.

The simulated dynamics of the groundwater table were generally well captured for the recent hydraulic year (Figure 2.2B). The decline in water table during the summer 2016 was slightly underestimated compared to the observed water table. The observations for the subsequent period was well captured by the model.

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 2016-June 2017, precipitation and the actual evapotranspiration were comparable to average values, since the monitoring began at the field. This results in the groundwater recharge also being in the medium range compared to the other hydraulic years (Figure 2.2A-B). The monthly precipitation pattern for the hydraulic year 2016-2017 was generally comparable to the mean value of earlier years (Appendix 4) although the precipitation in September 2016 was the lowest recorded.

Table 2.1. Annual water balance for **Tylstrup** (mm yr^{-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
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	1096	53	514	635
01.07.16–30.06.17	773	860	0	483	377

$^{1)}$ Accumulated for a two-month period. $^{2)}$ Normal values based on time series for 1961–1990.

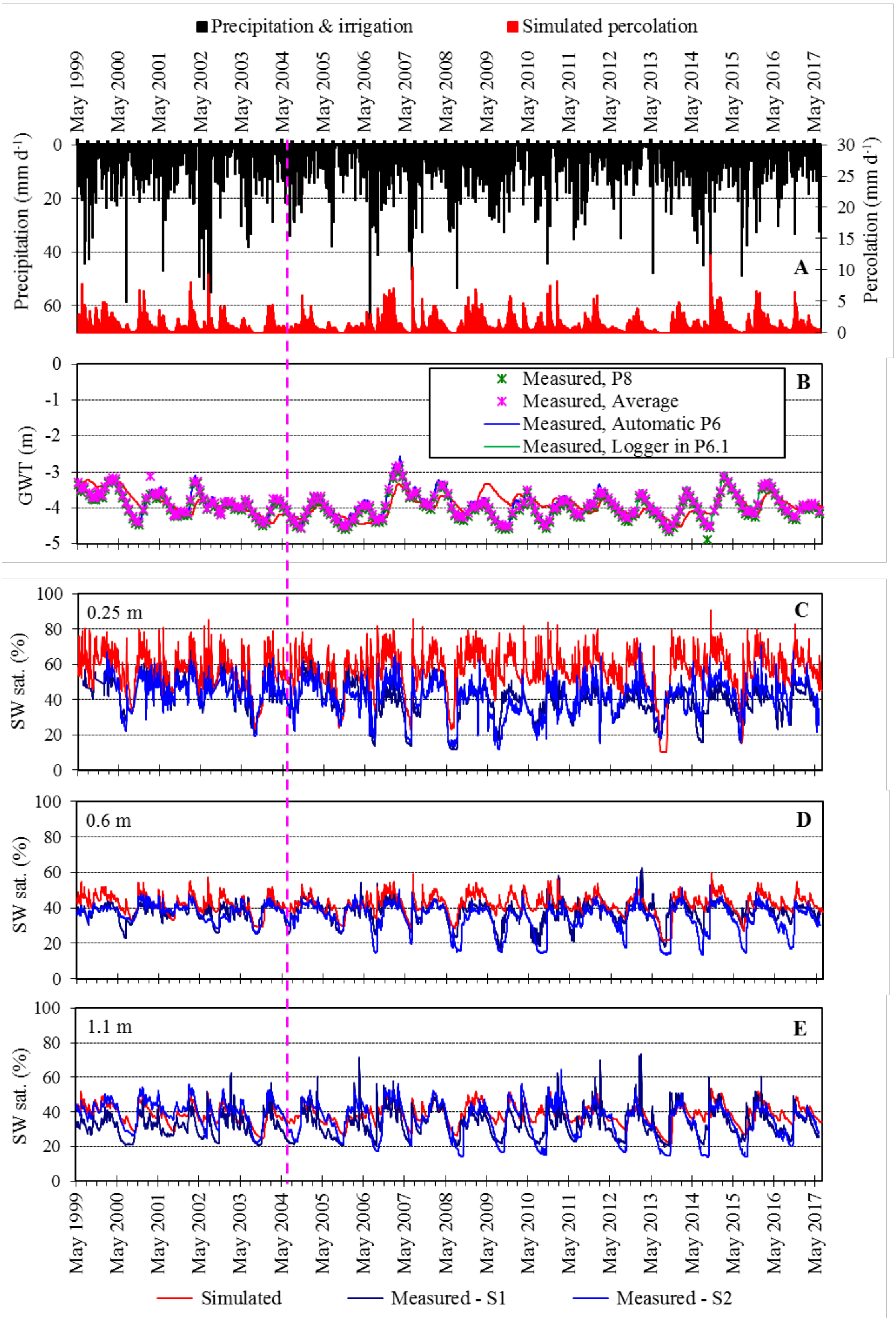


Figure 2.2. Soil water dynamics at **Tylstrup**: Measured precipitation, irrigation and simulated percolation 1 m b.g.s. (A), simulated and measured groundwater table GWT (B), and simulated and measured soil water saturation (SW sat.) at three different soil depths (C, D and E). The measured data in 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 2017).

2.2.2 Bromide leaching

Bromide has 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.

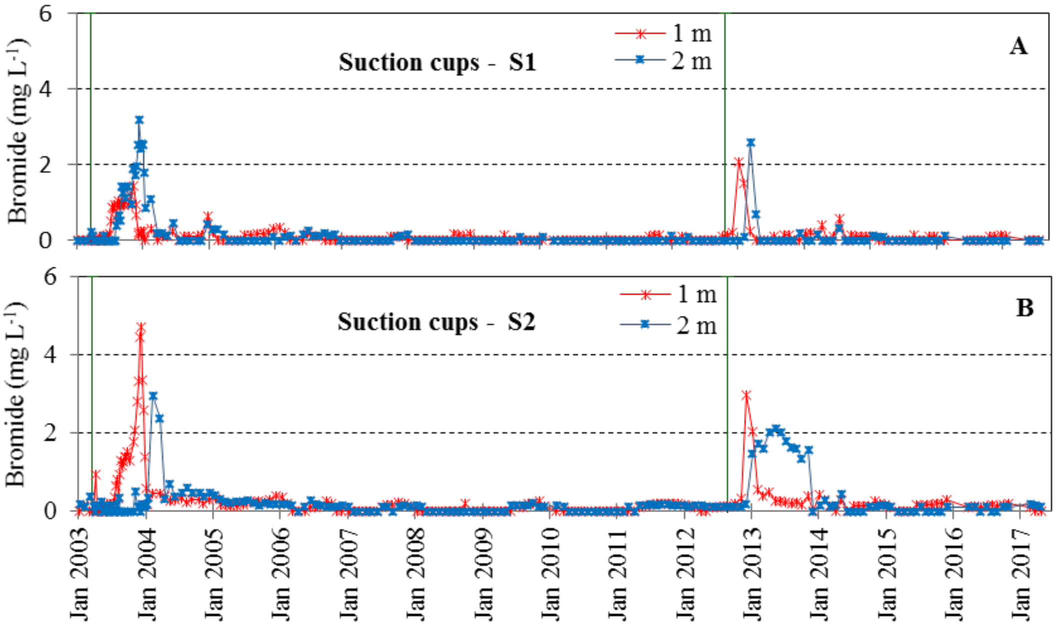


Figure 2.3. Measured bromide concentration in the variably-saturated zone at **Tylstrup**. The measured data derive from suction cups installed 1 m b.g.s. and 2 m b.g.s. at locations S1 (A) and S2 (B) indicated in Figure 2.1. The green vertical lines indicate the dates of bromide applications.

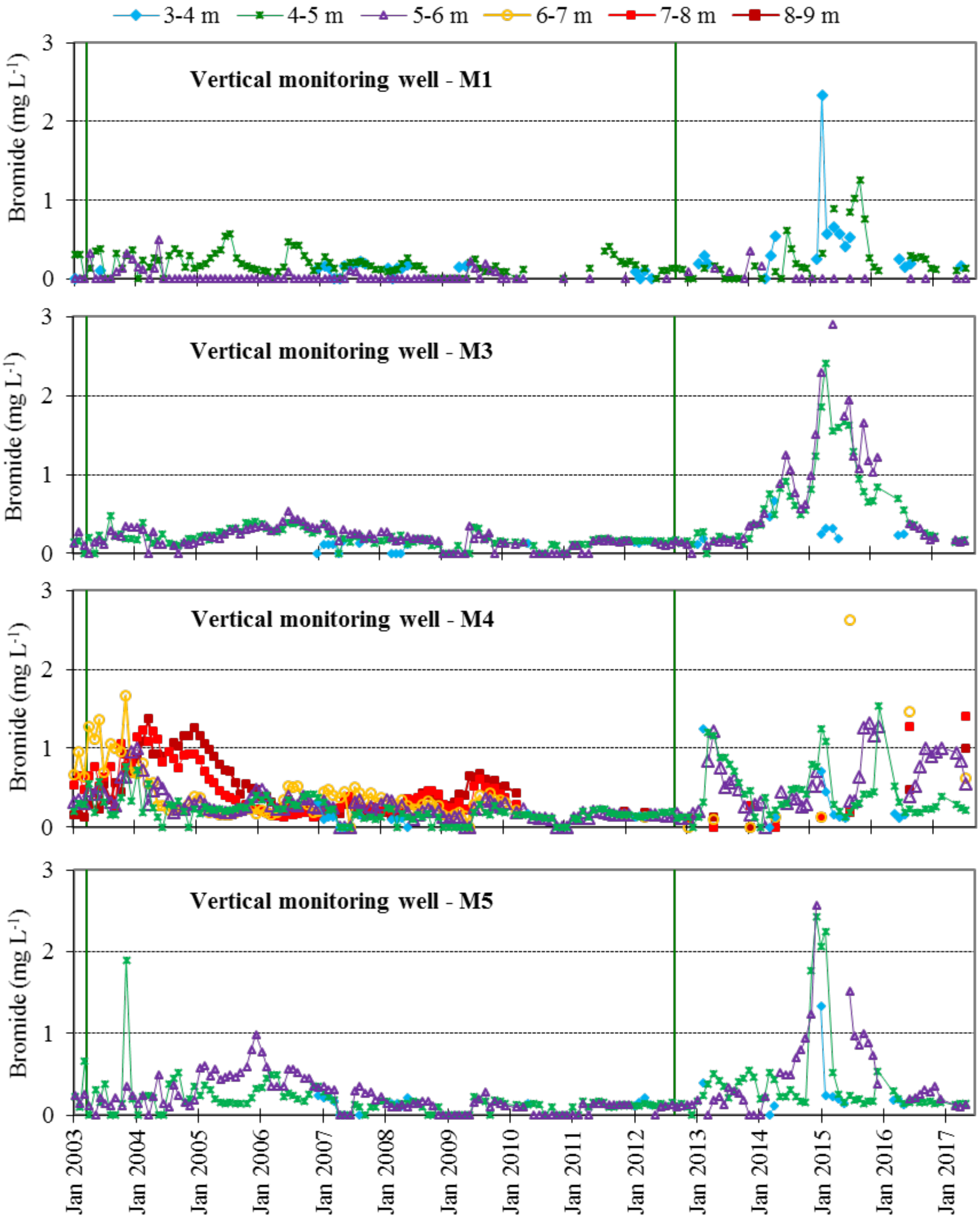


Figure 2.4. Bromide concentration in the groundwater at **Tylstrup.** The data derive from monitoring wells M1 and M3–M5. Screen depth is indicated in m b.g.s. The green vertical lines indicate the dates of bromide application.

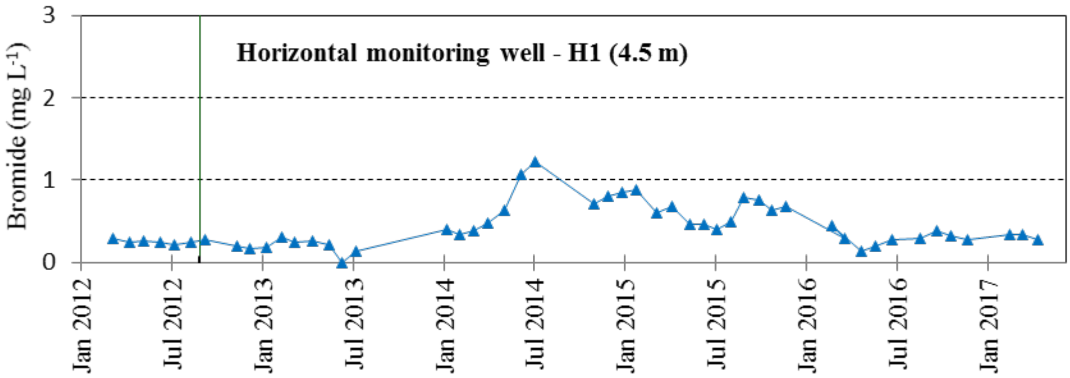


Figure 2.5. Bromide concentration in the groundwater at **Tylstrup.** Data derives from the horizontal monitoring well H1. The green vertical line indicates the date of bromide application.

2.2.3 Pesticide leaching

Monitoring at Tylstrup began in May 1999 and encompasses the pesticides and degradation products until 2009/2010 as shown in Appendix 7. Pesticide applications from 2010/2011 until the latest growing seasons are listed in Table 2.2 and are shown together with precipitation and simulated percolation from 2015/2016 and 2016/2017, 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 May 2017 are not evaluated in this report, and they are not included in Figure 2.6 and hence not listed in Table 2.2.

The present report primarily focuses on the pesticides applied from 2015 and onwards, while the leaching risk of pesticides applied before 2015 has been evaluated in previous monitoring reports (see http://pesticidvarsling.dk/monitor_uk/index.html).

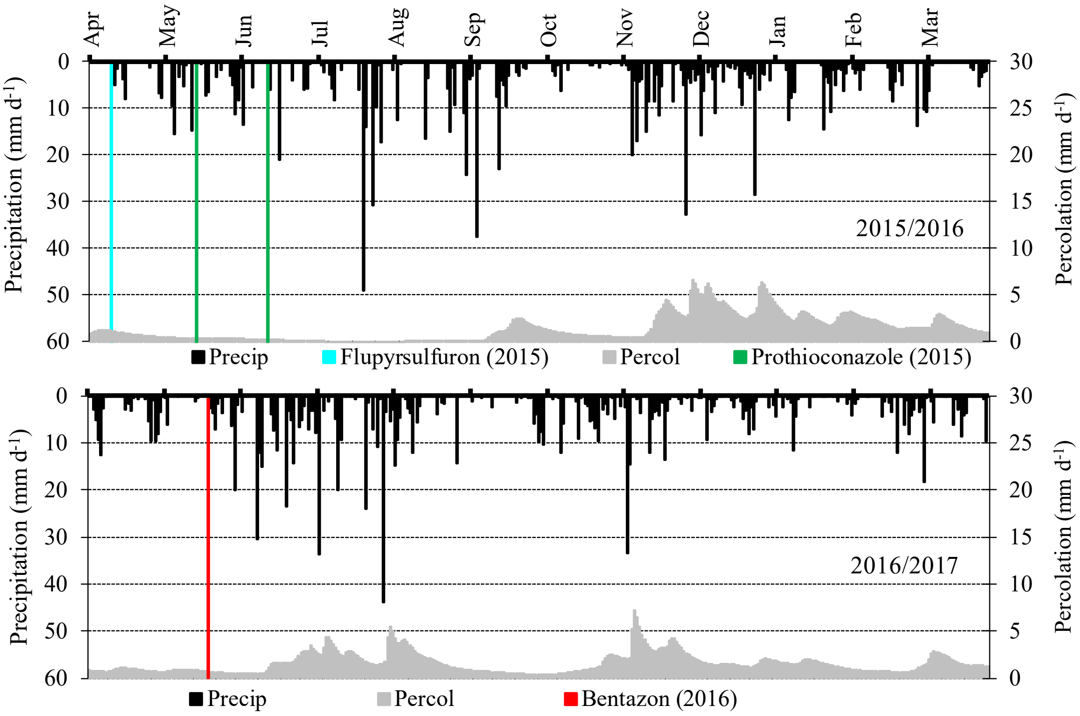


Figure 2.6. Application of pesticides included in the monitoring programme, precipitation and irrigation (primary axis; Precip) together with simulated percolation 1 m b.g.s. (secondary axis; Percol) at **Tylstrup** in 2015/2016 (upper) and 2016/2017 (lower).

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 7 (Table A7.1) 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 17*	1045	467	105	80	<0.01
	Proline EC 250 Prothioconazole (P)	1,2,4-triazole(M)	May 15	Jun 17*	1060	504	76	9	<0.01
Spring barley 2016	Fighter 480 Bentazone(P)	Bentazone(P)	May 16	Jun 17*	935	464	132	23	<0.01
		6-hydroxy-bentazone(M)	May 16	Jun 17*	935	464	132	23	<0.01
		8-hydroxy-bentazone(M)	May 16	Jun 17*	935	464	132	23	<0.01
		N-methyl-bentazone(M)	May 16	Jun 17*	935	464	132	23	<0.01
Spring barley 2017	Hussar Plus OD Mesosulfuron-methyl(P)	AE F099095	May 17	Jun 17*	-	-	110	16	-
		AE F160459	May 17	Jun 17*	-	-	110	16	-
	Bumper 25 BC*** Propiconazole(P)	1,2,4-triazole(M)	Jun 17	Jun 17*	-	-	-	-	-

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

**Monitoring continues the following year.*

***If difference between S1 and S2.*

**** Application both 1st June and 14th June.*

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.

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-triazole in minor amounts in soil 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 wasconducted. 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. This indicates that prothioconazole degrades to 1,2,4-triazole in amounts which cause detactable leaching, but due to detections of 1,2,4-triazole before the application of prothioconazole it is difficult to directly link the findings to the use of prothioconazole. 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. Nearly a year after in April 2017, 1,2,4-triazole was still detected in S1 at 2 m depth (Figure 2.7B) where no detections were observed in the upstream monitoring wells (Figure 2.7C). The monitoring period from November 2014 – June 20117 does not reveal the cause for this late appearance of 1,2,4-triazole in samples collected from the variably saturated zone (17%; 12/72) nor the high proportion of groundwater samples having detections (41%; 80/196), where 18% (15/80) of the groundwater samples with detections (max. 0.03 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).

Bentazone was applied in May 2016. None of the three degradation products 6-hydroxy-bentazone, 8-hydroxy-bentazone and N-methyl-bentazoneare were detected. The quality of the 8-hydroxy-bentazone analyses are however subject to uncertainty as described in paragraph 7. Bentazone was only detected twice (max 0.02 µg L^{-1}) in the spring of 2017 in water samples from suction cups situated in 1 m depth at S1.

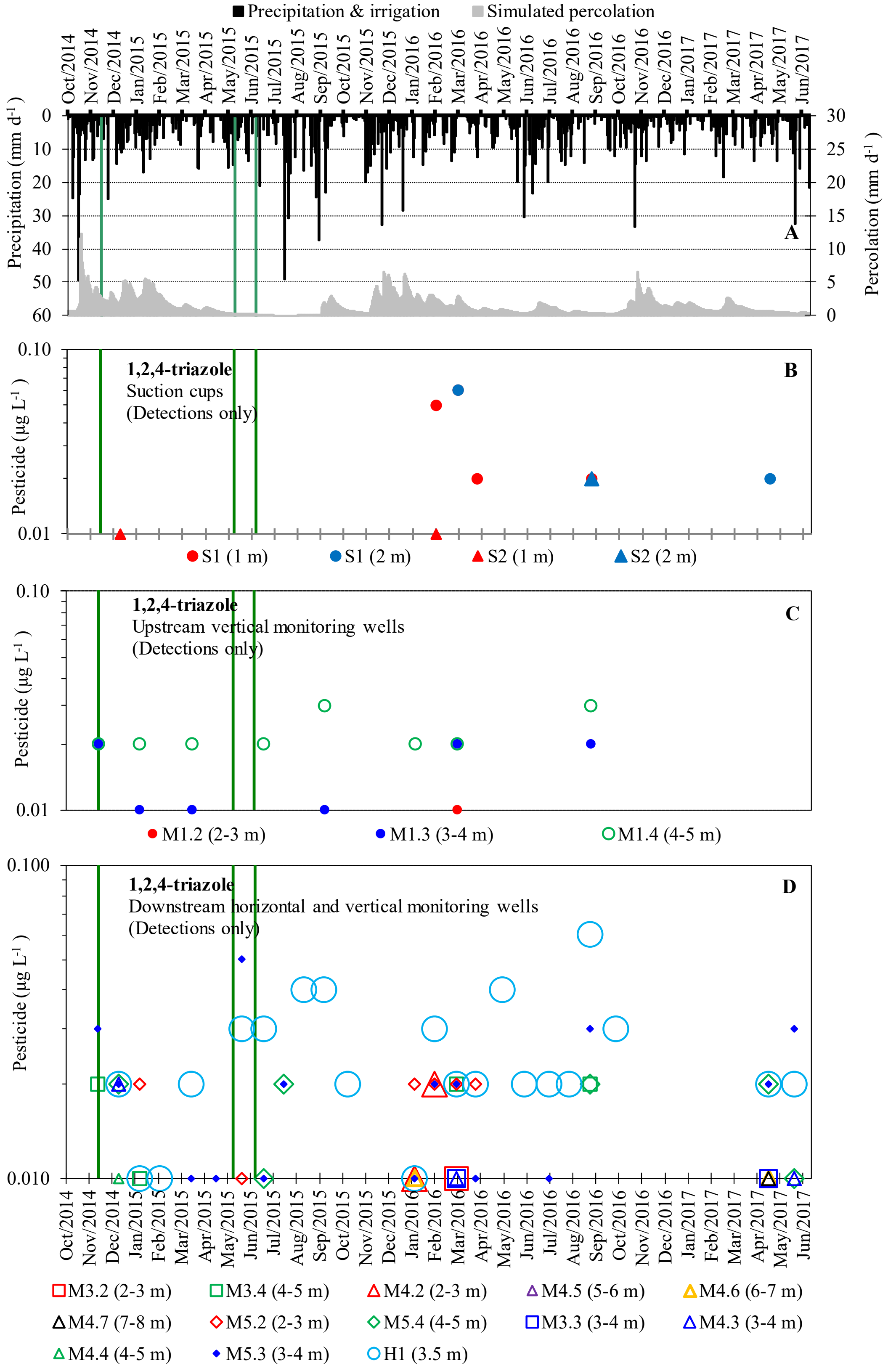


Figure 2.7. 1,2,4-triazole detections at **Tylstrup**: Precipitation, irrigation and simulated percolation 1 m b.g.s. (A) together with measured concentration of 1,2,4-triazole detections in the variably-saturated zone (B; water collected from suction cups at S1 and S2 in 1 and 2 m depth) and saturated 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. The first pesticide was tebuconazole and the two following were prothioconazole.

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 2016-17 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/monitor_uk/index.html.

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. Its 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. The yield of spring barley at harvest 17 August was 48.3 hkg ha^{-1} (85% dry matter). At 30 August 27.4 hkg ha^{-1} of straw had been removed from the field.

The field, with the remains of the catch crop, was ploughed 3 February 2017. Having been rolled with a concrete roller 20 February, a crop of peas (cv. Mascara) was sown 23 March. Spraying of weeds was done 9 May, using a mixture of pendimethalin and bentazon. Only the bentazone itself and its three degradation products N-methyl bentazone, bentazone-8-hydroxy, bentazone-6-hydroxy were included in the monitoring. On 19 May cycloxydim was used against weeds and two of its degradation products; BH 517-T2SO2 and E/Z BH 517-TSO, were included in the monitoring. On 27 May and 22 June the field was irrigated 30 mm ha^{-1}.

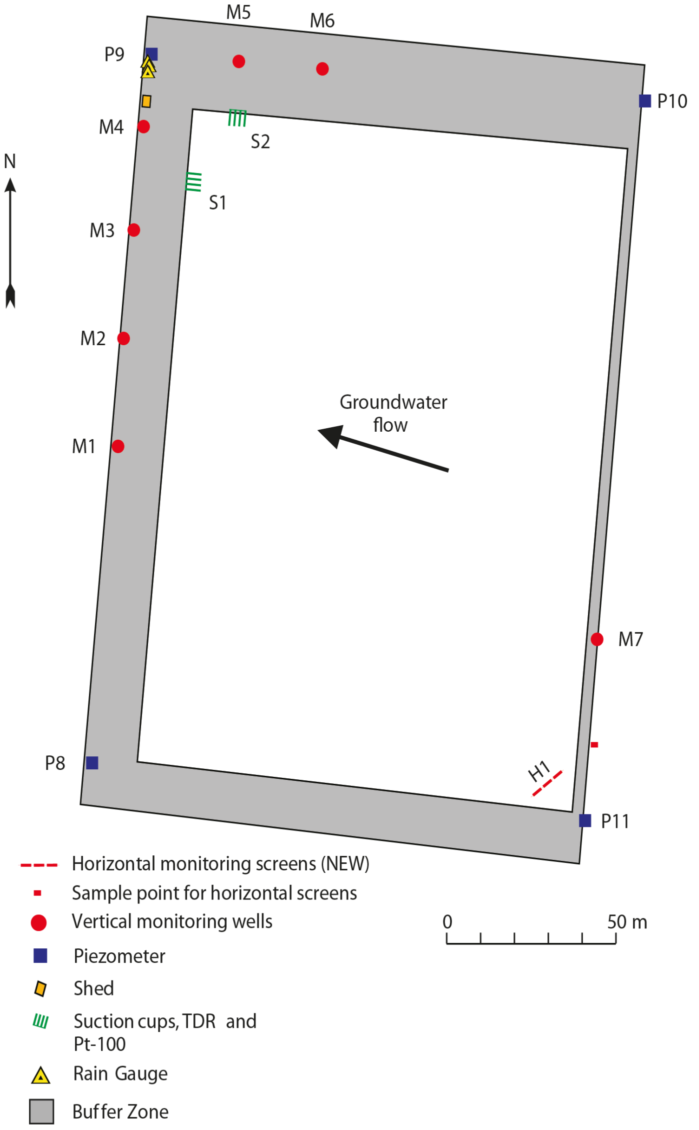


Figure 3.1. Overview of the **Jyndevad** field. The innermost white area indicates the cultivated field, while the grey area indicates the surrounding buffer zone. The positions of the various installations are indicated, as is the direction of groundwater flow (by an arrow). Pesticide monitoring is 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 entire monitoring period July 1999–June 2017 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 2017. 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 indicating a good model description of the overall soil water dynamics in the variably-saturated zone at Jyndevad (Figure 3.2). Generally, 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.

Dynamics of the groundwater table were overall well captured by the model. Although the simulated levels of groundwater table for the recent hydraulic year, 2016-2017, are slightly overestimated during the observed minimum of 2016. The resulting water balance for Jyndevad for all the monitoring periods is shown in Table 3.1. Compared to the previous seventeen years, the recent hydraulic year was characterised by having medium precipitation as well as irrigation and simulated actual evapotranspiration. Thus, the groundwater recharge value was also in the medium range. Continuous percolation at 1m depth was simulated for the current hydraulic year.

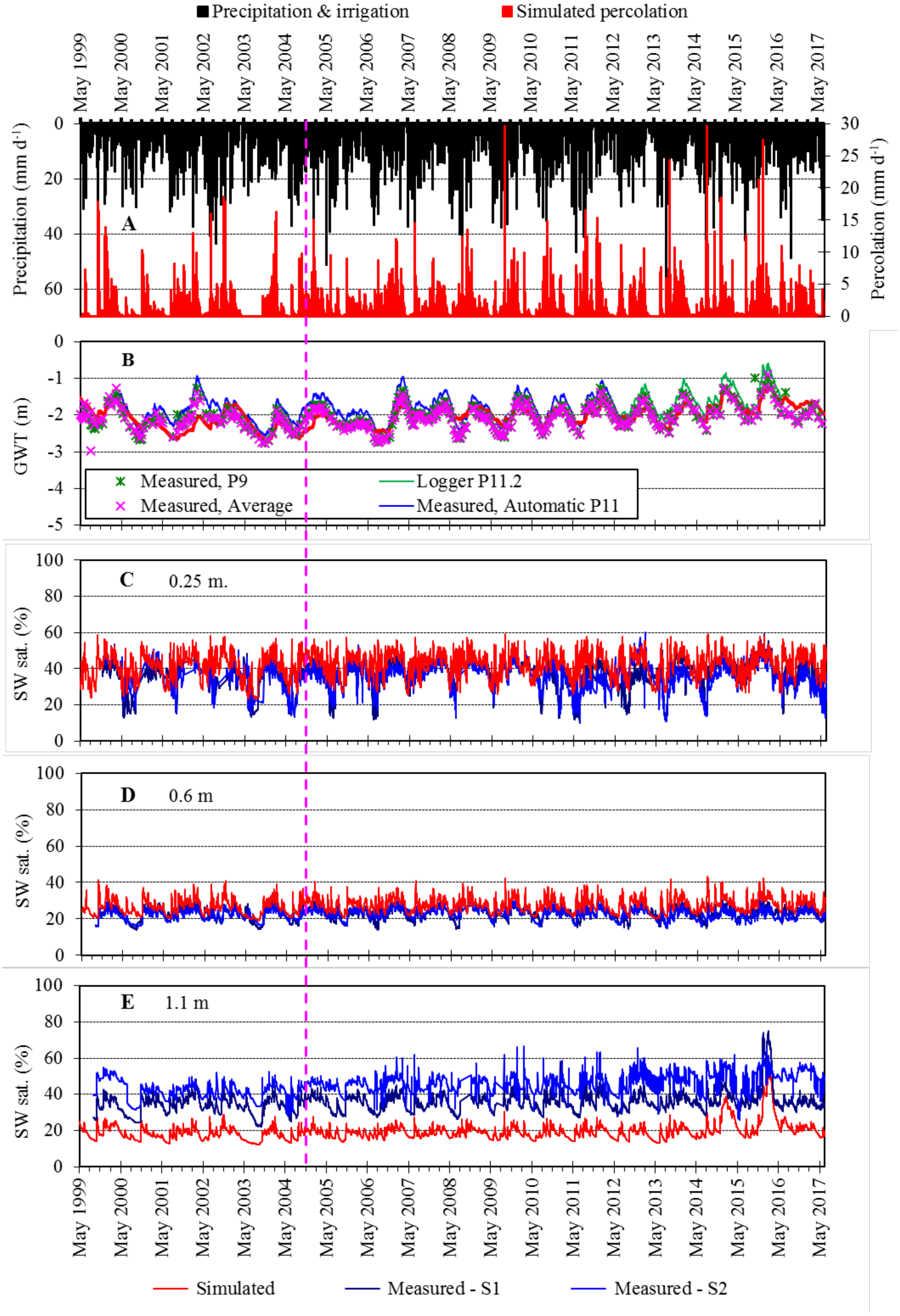


Figure 3.2. Soil water dynamics at **Jyndevad**: Measured precipitation, irrigation and simulated percolation 1 m b.g.s. (A), simulated and measured groundwater table, GWT (B), and simulated and measured soil water saturation (SW sat.) at three different soil depths (C, D and E). The measured data in 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 2017).

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 precipitation1)	Precipitation	Irrigation	Actual evapotranspiration	Groundwater recharge2)
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	1365	105	581	888
01.07.16–30.06.17	995	1031	60	531	559

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^{-1} in October 2012 to approx. 0.1 mg L^{-1} in June 2014 (Figure 3.5).

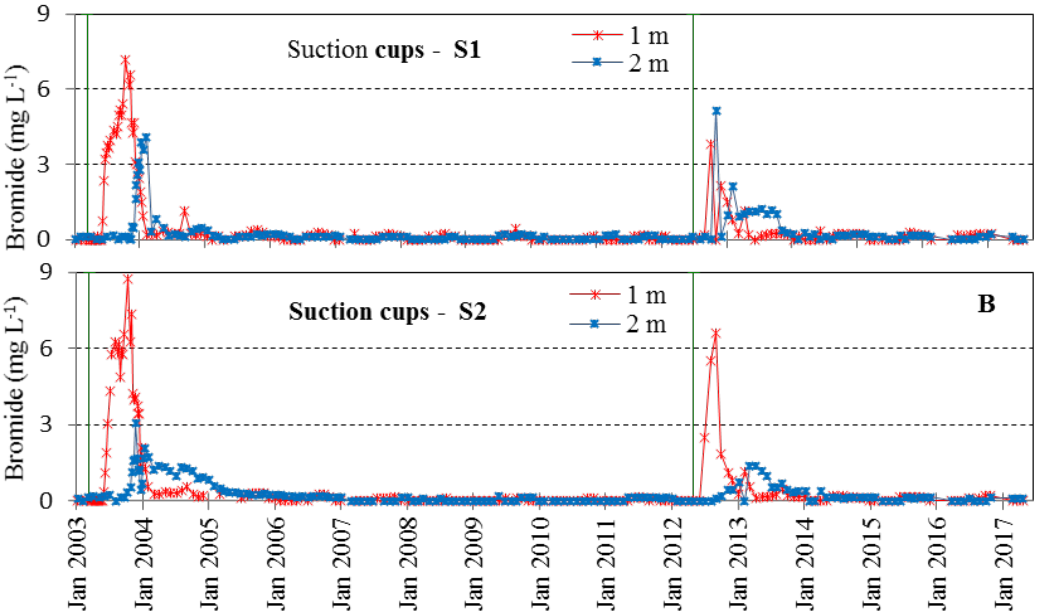


Figure 3.3. Bromide concentration in the variably-saturated zone at Jyndevad. The measured data derive from suction cups installed 1 m b.g.s. (A) and 2 m b.g.s. (B) at locations S1 and S2 (Figure 3.1). The green vertical lines indicate the dates of bromide applications.

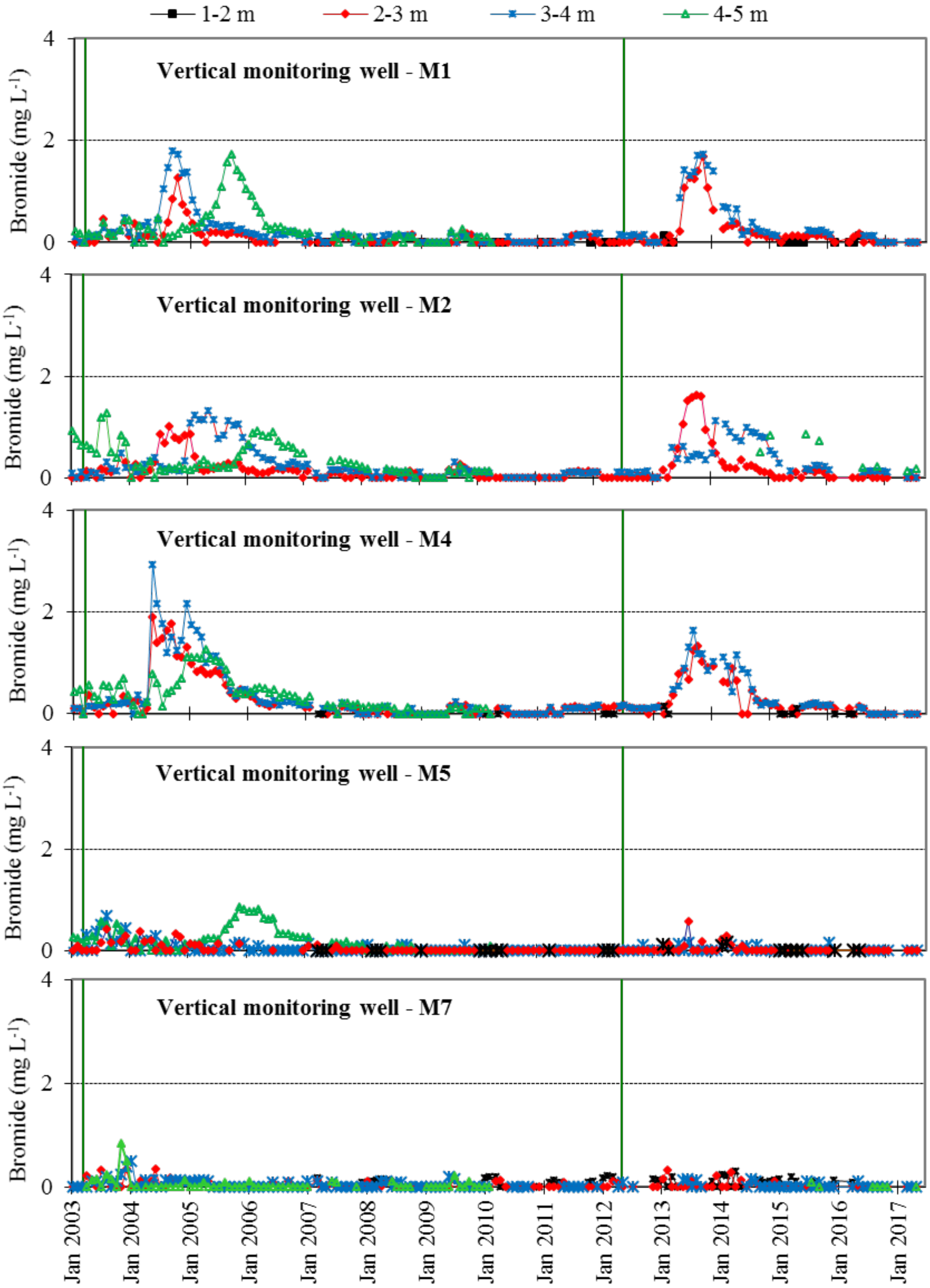


Figure 3.4. Bromide concentration in the groundwater at **Jyndevad**. The data derive from monitoring wells M1, M2, M4, M5 and M7. Screen depth is indicated in m b.g.s. The green vertical lines indicate the dates of bromide applications.

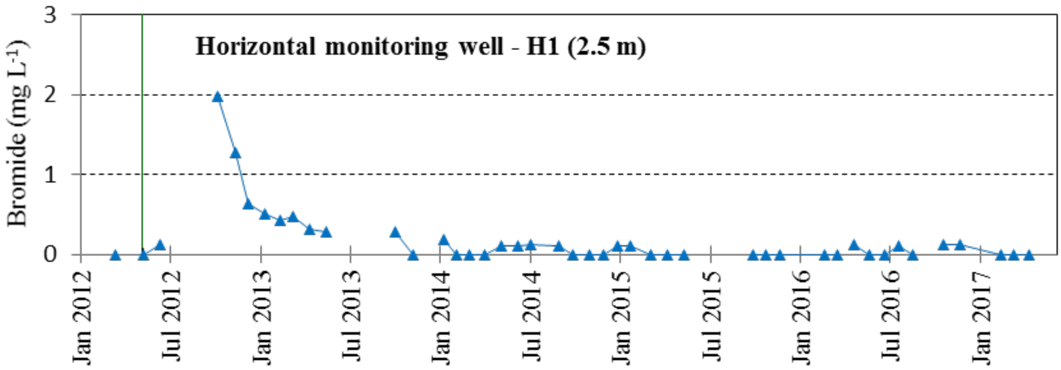


Figure 3.5. Bromide concentration in the groundwater at **Jyndevad.** The data derive from the horizontal monitoring well H1. The green vertical line indicates the date of bromide application.

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 percolation from 2015/2016 and 2016/2017 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 2017 are not evaluated in this report and hence not listed in Table 3.2.

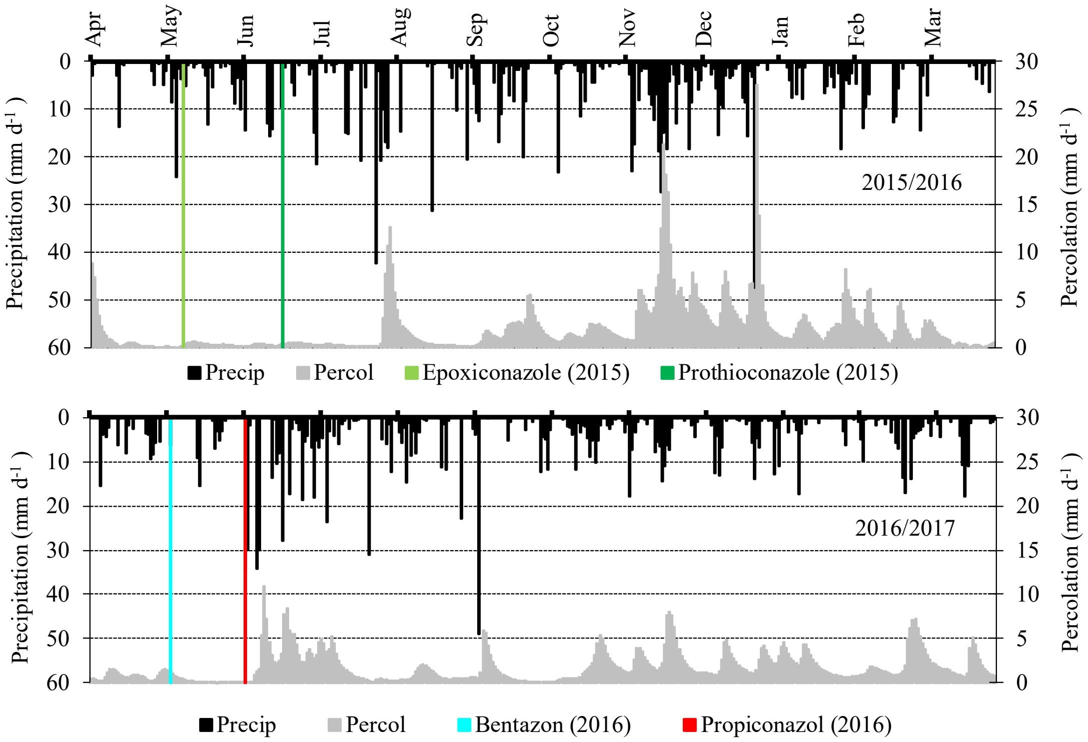


Figure 3.6. Application of pesticides included in the monitoring programme, precipitation and irrigation (primary axis; Prec) together with simulated percolation (Percol) 1 m b.g.s. (secondary axis) at **Jyndevad** in 2015/2016 (upper) and 2016/2017 (lower).

The current report focuses primarily on the pesticides applied from 2015 and onwards, while leaching risk of pesticides applied before 2015 has been evaluated in previous monitoring reports (see http://pesticidvarsling.dk/monitor_uk/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 7 (Table A7.2) 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$_{mean}$
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	Oct 16	1221	670	45	76	<0.01
		IN-KC576(M)	Oct 14 +Mar 15	Oct 16	1221	670	45	76	<0.01
		IN-KY374(M)	Oct 14 +Mar 15	Oct 16	1221	670	45	76	<0.01
		IN-JV460(M)	Oct 14 +Mar 15	Oct 16	1221	670	45	76	<0.01
	Orius 200 EW Tebuconazole (P)	1,2,4-triazole(M)	Nov 14	Jun 17*	1253	645	86	35	<0.01
	Opus Epoxiconazole(P)	1,2,4-triazole(M)	May 15	Jun 17*	1323	754	81	10	0.08
	Proline EC 250 Prothioconazole(P)	1,2,4-triazole(M)	Jun 15	Jun17*	1435	789	103	10	0.08
Spring barley 2016	Fighter 480	Bentazone(P)	May 16	Jun 17*	1174	633	85	6	0.01
		6-hydroxy-bentazone(M)	May 16	Jun 17*	1174	633	85	6	<0.01
		8-hydroxy-bentazone(M)	May 16	Jun 17*	1174	633	85	6	<0.01
		N-methyl-bentazone(M)	May 16	Jun 17*	1174	633	85	6	<0.01
	Bumper 25 EC Propiconazole(P)^{2}	1,2,4-triazol(M)	Jun 16	Jun 17*	1171	631	247	112	0.05
Pea 2017	Fighter 480	Bentazone(P)	May 17	Jun 17*	-	-	148	6	-
		6-hydroxy-bentazone(M)	May 17	Jun 17*	-	-	148	6	-
		8-hydroxy-bentazone(M)	May 17	Jun 17*	-	-	148	6	-
		N-methyl-bentazone(M)	May 17	Jun 17*	-	-	148	6	-

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 **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). 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 except for one detection of 0.01 µg L^{-1} in a groundwater sampled from the horizontal well, no traces are found in 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. After the application of bentazone in May 2016, detections of bentazone are again monitored in the suction cups starting from August 2016. Generally, the bentazone concentration seems to level off after February 2017. However, an overall maximum concentration of 4.6 µg L^{-1} is detected in S2 in June 2017 after the bentazone application in May 2017 (Figure 3.7). Hence, the bentazone concentrations after the application in May 2017 seem to differ from the previous year, where bentazone concentrations appeared after approximately three months. Although the data from the latest application is still sparse (one detection), there could be a trend similar to what was observed after two annually applications as seen in 2012/2013. Here, the peak concentrations were observed within a relative short time after the second application (Figure 3.7). Bentazone has, however, not been detected in the groundwater since February 2013.

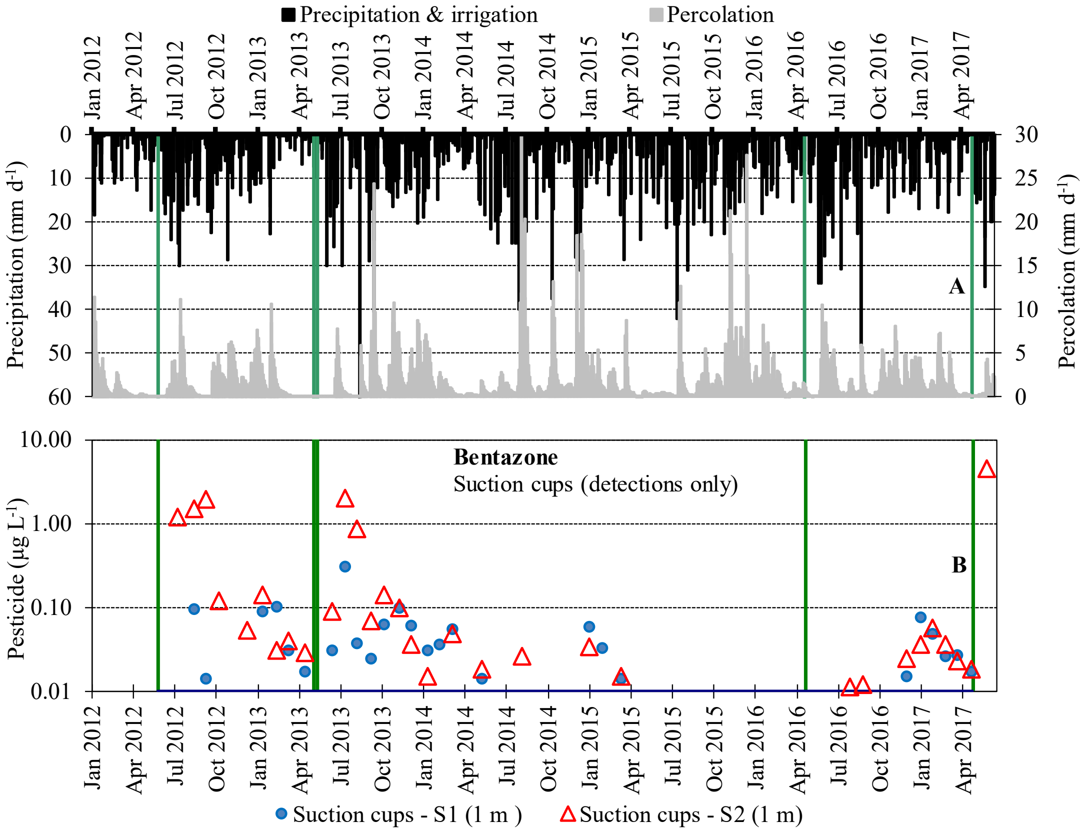


Figure 3.7. Precipitation, irrigation and simulated percolation 1 m b.g.s. (A) together with measured concentrations of **bentazone** in water samples collected from suction cups at 1 m depth at S1 and S2 (B) in **Jyndevad**. The green vertical lines indicate the dates of bentazone application.

Tebuconazole, **epoxiconazole** and **prothioconazole** were applied to the winter wheat on 11 November 2014, 8 May 2015 and 17 June 2015 respectively. On 16 June 2016 propiconazole was applied to the spring barley (Table 3.2). Their degradation product 1,2,4-triazole was monitored from the 13 November 2014 and onwards. As there had not been taken a background sample prior to the first application of tebuconazole it is difficult to evaluate, whether the detections following the first application 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 (Figure 3.8D). Additionally, that day water collected from the upstream screen of M7 in 3-4 m depth contained 0.1 µg L^{-1} (Figure 3.8C). Posterior to these two initial detections, general detections of 1,2,4-triazole in groundwater were less than 0.1 µg L^{-1}. Although, the application within the current hydrological year showed 1,2,4-triazole detections equal to 0.1 µg L^{-1} in May and June 2017 (Figure 3.8.C). Following each application, an increase in the concentration level was detected in water from certain sampling points. In the downstream well intakes of M1, M2 and M3 detections of 1,2,4-triazole until June 2016 were only observed within the first half year of application (Figure 3.8D). After June 2016, however, 1,2,4-triazole concentrations were detected throughout the year. Furthermore, based on the two previous hydrological years, where monitoring for the entire hydrological year were attained, there was an increase of 1,2,4-triazole concentration detections in the vertical monitoring wells. Thus, from the hydrological year 2015-2016 (with 46 detetions in vertical wells, M, and 5 detections in horizontal wells, H) to 2016-2017 (with 72 detections in M-wells and 4 detections in H-wells), there was a 49% increase in detections. For the upstream M-wells and downstream M-wells, the increase between the two hydrological years is equivalent to 31% and 90%, respectively. This could indicate that the application of azols, which form 1,2,4-triazole, has an accumulative effect in the number of detections of 1,2,4-triazole. Though, detections hitherto have been below 0.1 µg L^{-1} within the two previous hydrological years disregarding the two 0.1 µg L^{-1} detections, which were found in the upstream wells (Figure 3.8C and D). Based on all groundwater samples (255 from M-wells and 34 from H-wells) analysed for 1,2,4-triazole, 58% of these revealed detections, while none had concentrations larger than 0.1 µg L^{-1}. In the suction cups, a similar trend of increased detections between the previous two hydrological years was observed. Of the 32 detections there was a 45% increase between 2015-2016 (with 11 detections) and 2016-2017 (with 16 detections). From the 32 detections 25% showed concentrations larger than 0.1 µg L^{-1}. By including 0.1 µg L^{-1} the procent increase to 81%. The highest concentration of 0.27 µg L^{-1} was measured in S2 in June 2017. Further, from the entire monitoring period of 1,2,4-triazole, the compound is detected in all S2 samples except one from June 2016. The concentrations in the variably-saturated zone at S2 and the saturated zone did not vary much throughout the years. The detections following the application of epoxiconazole and prothioconazole did reveal an increase in concentration of 1,2,4-triazole, indicating degradation of the applied pesticides and a 1,2,4-triazole leaching through the variably-saturated zone to groundwater. Although no detections were observed in S1 until February 2016, there is a pattern of increased detections hereafter (Figure 3.8B). In the 36 water samples collected from the horizontal well H1, there were 20 detections with no detections larger than 0.1 µg L^{-1}. Whether the concentration level is caused by the four applications alone or in combination with other sources cannot be concluded from this monitoring. Though, as noted above with for instance an increase in total detections of 49% hereamong an increase of 90% in downstream vertical wells, there is a clear pattern of increased detections within the latest hydrological year. Still, 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.

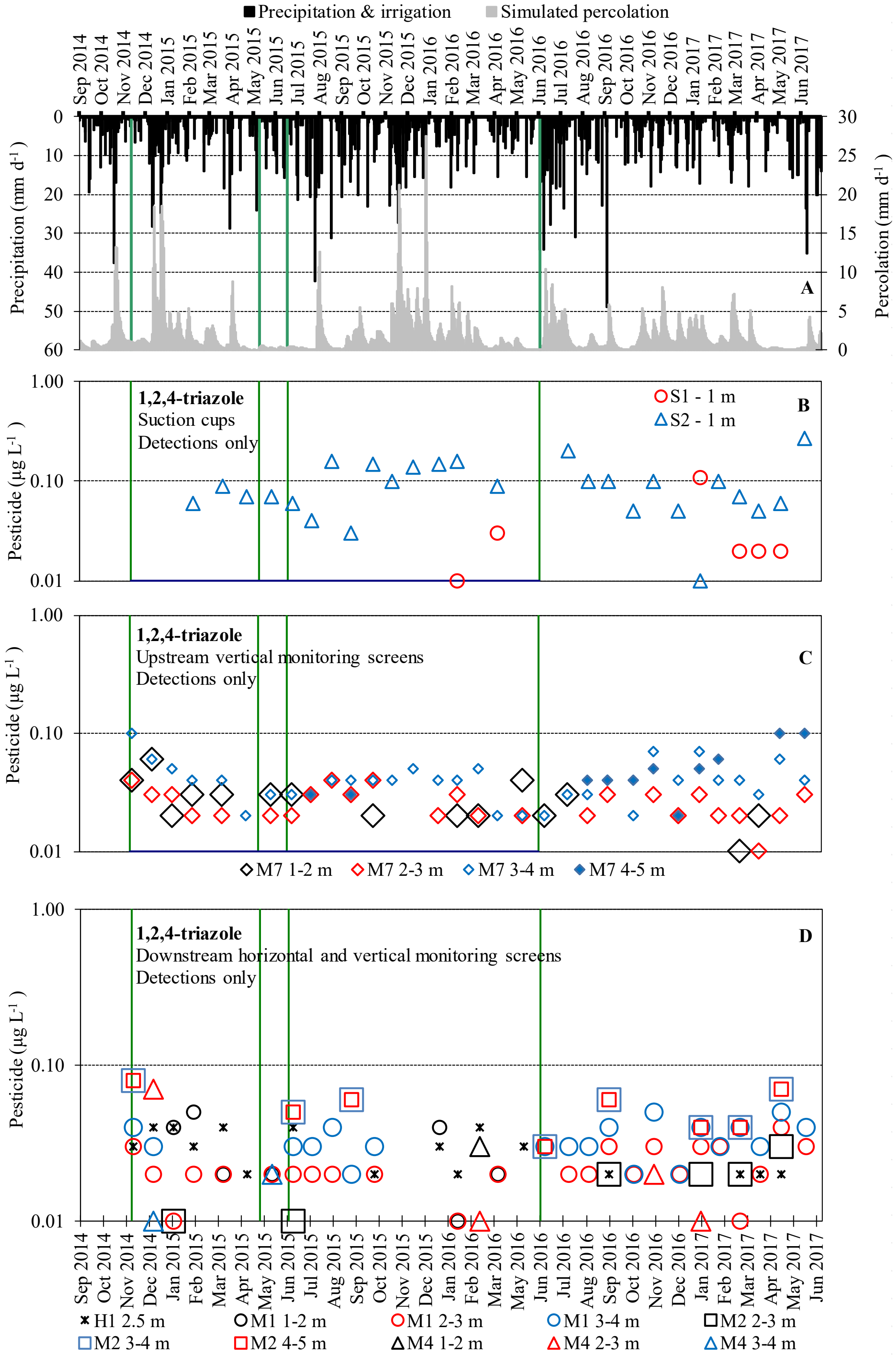


Figure 3.8. 1,2,4-triazole detections at **Jyndevad**: Precipitation, irrigation and simulated percolation 1 m b.g.s. (A) together with measured concentration of 1,2,4-triazole detections in the variably-saturated zone (B; water collected from suction cups at S1 and S2 in 1 and 2 m depth) and saturated 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: tebuconazole on 11 November 2014, epoxiconazole on 8 May 2015, prothioconazole on 17 June 2015, and propiconazole on 16 June 2016.

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.

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 not detected in the groundwater, but four times in the variably-saturated zone that was sampled via suction cups (both from S1 and S2) five to eight months after the March 2015 application. The highest concentration was 0.45 µg L^{-1}, Figure 3.9B. Monitoring ended 11 October 2016.

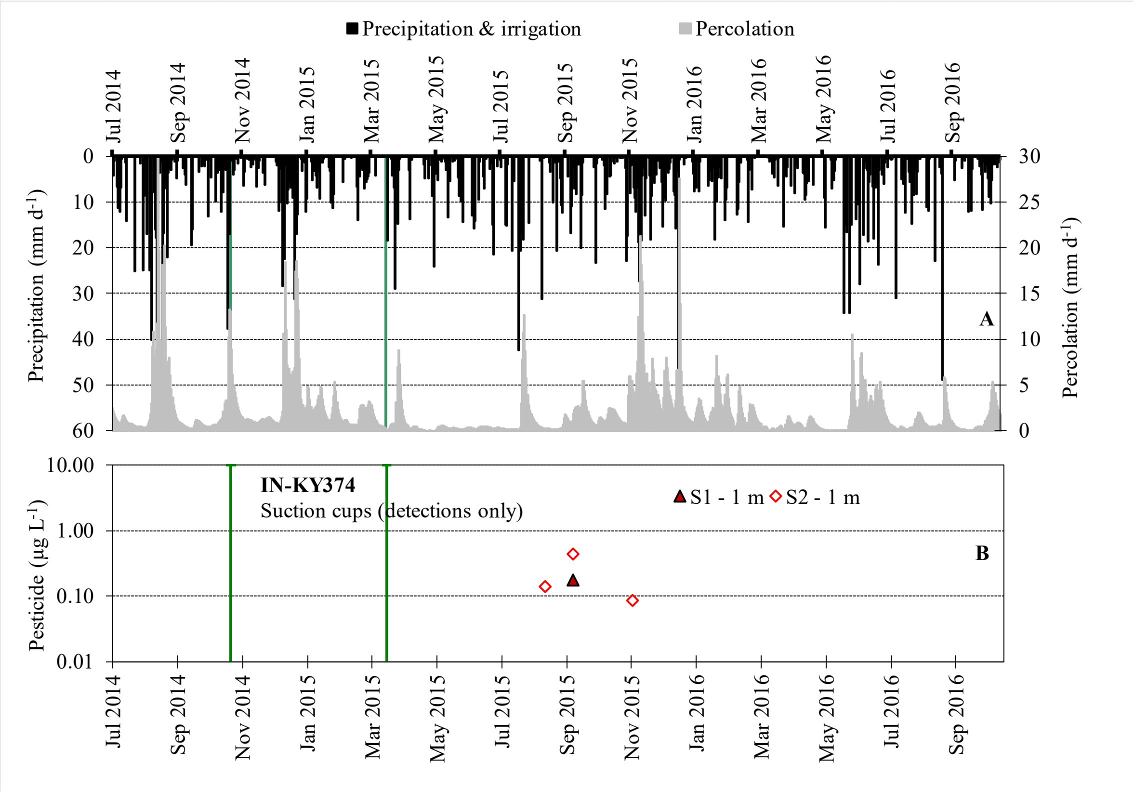


Figure 3.9. Precipitation, irrigation and simulated percolation at 1 m depth (A) together with measured concentrations of IN-KY374 in water samples from the variably-saturated zone at 1 m depth (suction cups S1 and S2) (B) at **Jyndevad**. The green vertical lines indicate the dates of application of 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 2016-17 growing seasons is briefly summarized below and detailed in Appendix 3 (Table A3.3). For information about management practice during the past monitoring periods, see previous reports available on http://pesticidvarsling.dk/monitor_uk/index.html.

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.

The maize was harvested for silage on 11 October yielding 120.9 hkg ha^{-1}. Stubble from the maize was crushed with a cutter 13 October, and the fields was then ploughed 12 November 2016.

After a seedbed preparation on 28 April 2017 the field was sown with spring barley (cv. KWS Irina) which emerged 11 May. On 29 May 30 t ha^{-1} of pig slurry was trail hose applied.

The spring barley was sprayed with halauxifen-methyl and florasulam against weeds on 15 June 2017. The degradation product X-757 of halauxifen-methyl and TSA of florasulam were included in the monitoring. The fungicide propiconazol was applied twice - 27 June and 10 July - and the degradation product 1,2,4-triazol included in the monitoring.

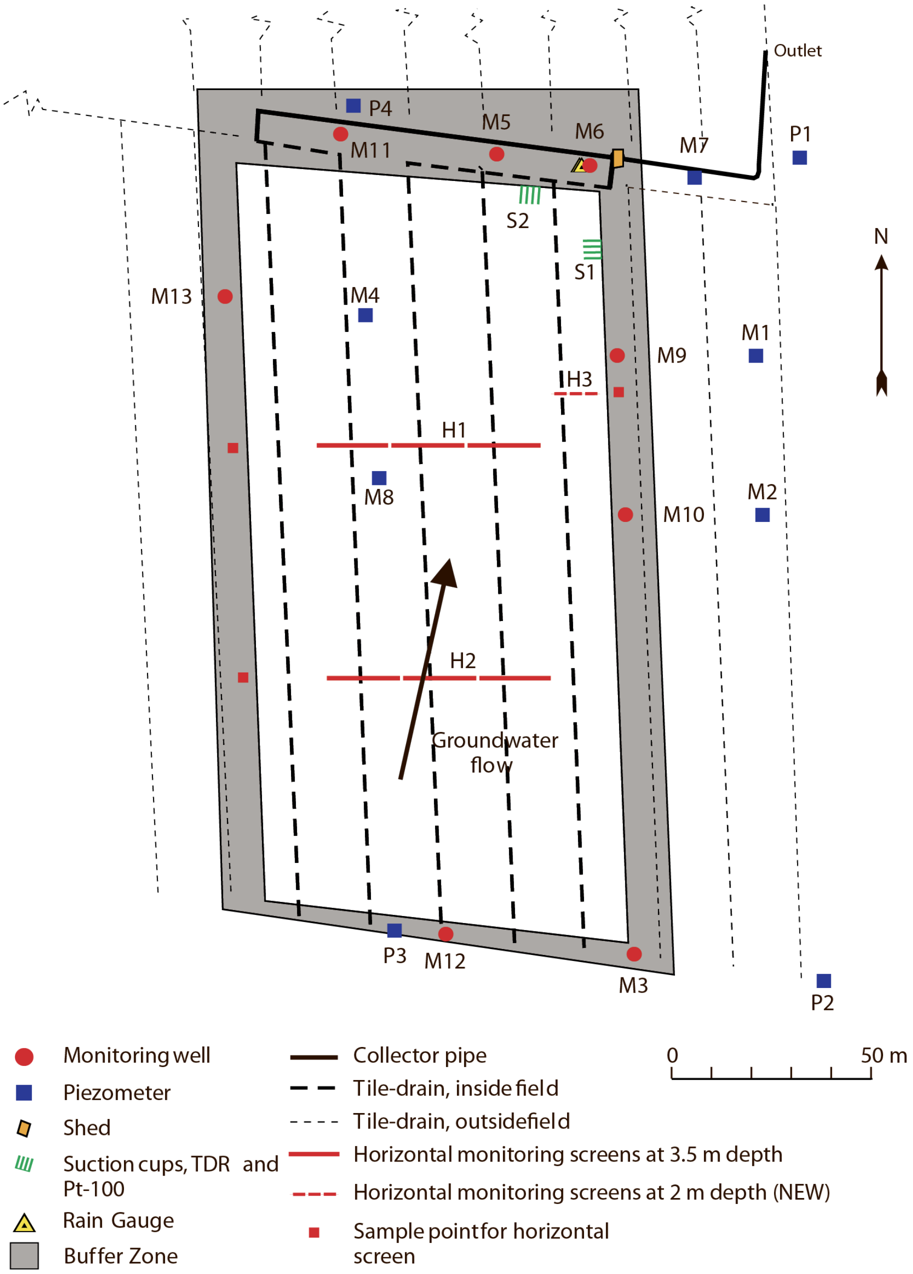


Figure 4.1. Overview of the **Silstrup** field. The innermost white area indicates the cultivated land, while the grey area indicates the surrounding buffer zone. The positions of the various installations are indicated, as is the direction of groundwater flow (by an arrow). Pesticide monitoring is conducted weekly from the drainage system (during 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 2017. 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). In the observed groundwater table dynamics, there is generally an offset between the observations during summer periods in filters of piezometers located the furthest apart, P3.1 and P4.1, while the seasonal patterns as well as winter observations are comparable (Figure 4.2B). Further, the observation levels in piezometers within close proximity, P1.2 and P4.1, are comparable during the seasons. The simulated groundwater table dynamics during summers are generally in correspondence with the measured watertable at P3.1 although the recent two years showed model correspondence with observations in P4.1. Thus, the greater decline in watertable observed in P3.1 during summer 2016 is not captured by the model. This is contradictionary to measurements from earlier year's where the simulated groundwater table was validated against the much more fluctuating groundwater table measured in piezometer P3.1, which for these years until 2015 yielded the best description of measured drainage (Figure 4.2B and 4.2C). The drainage during 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 caused by TDR measurements primarily representing the soil matrix conditions and not in the same extent as the model the conditions surrounding the preferential transport pathways in the soil like wormholes and fractures.

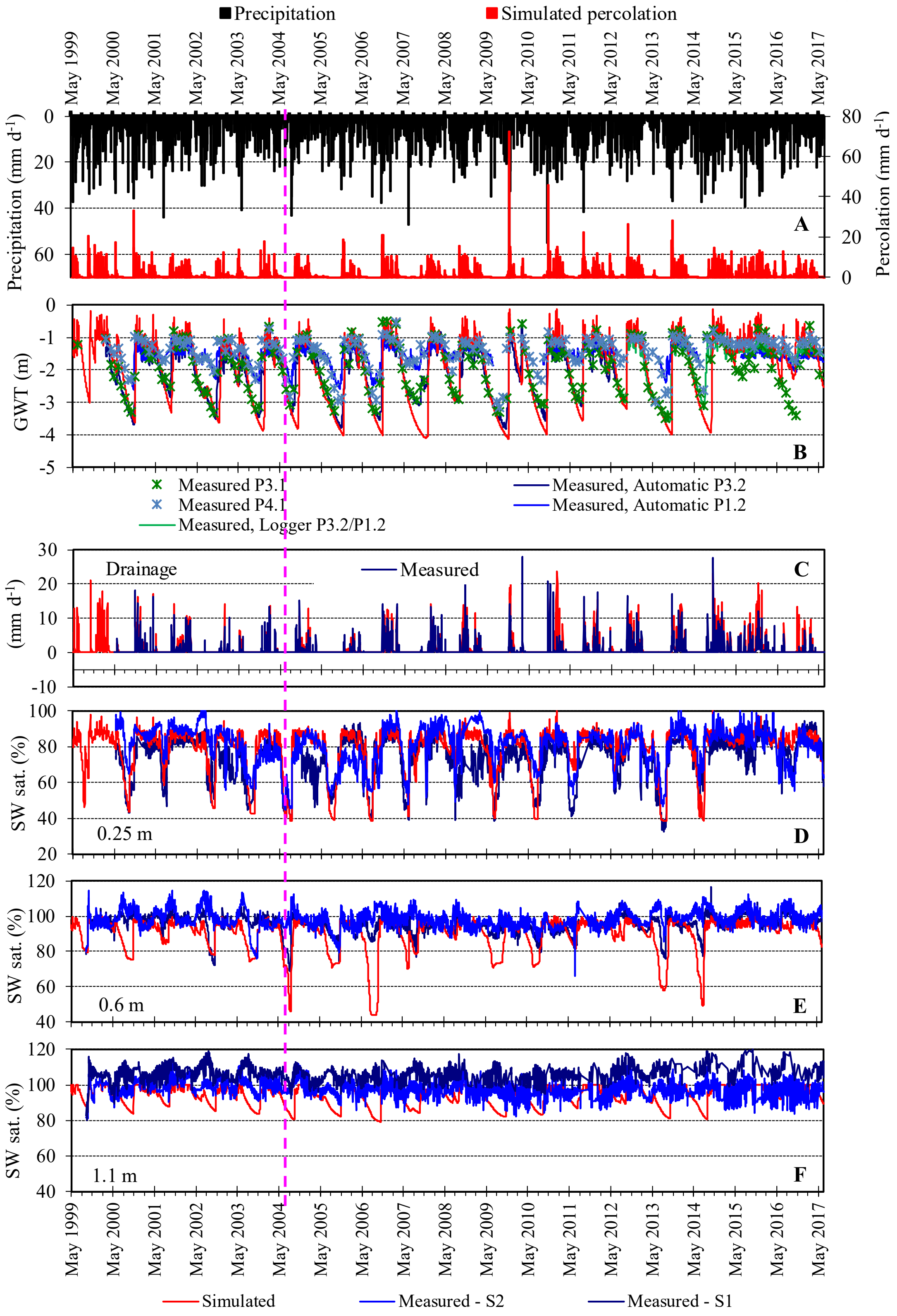


Figure 4.2. Soil water dynamics at **Silstrup**: Measured precipitation and simulated percolation 1 m b.g.s. (A), simulated and measured groundwater table, GWT (B), simulated and measured drainage (C), and simulated and measured soil water saturation (SW sat.) at three different soil depths (D, E and 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 2017)**.**

Table 4.1. Annual water balance for **Silstrup** (mm yr^{-1}). Precipitation is corrected to the soil surface according to the method of Allerup and Madsen (1979).

	Normal precipitation2)	Precipitation	Actual evapotranspiration	Measured drainage	Simulated drainage	Groundwater recharge3)
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	462	329	412	523
01.07.15–30.06.16	976	1200	352	293	517	551
01.07.16–30.06.17	976	869	415	95	228	359

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 to the previous 17 years, the recent hydraulic year July 2016-June 2017 was characterised by having a low precipitation, low actual evapotranspiration, and low drainage. In fact, the measured drainage was second lowest in the past seventeen years. From September 2016 to February 2017, the precipitation was generally >40% lower than the average from the previous years (Appendix 4).

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.

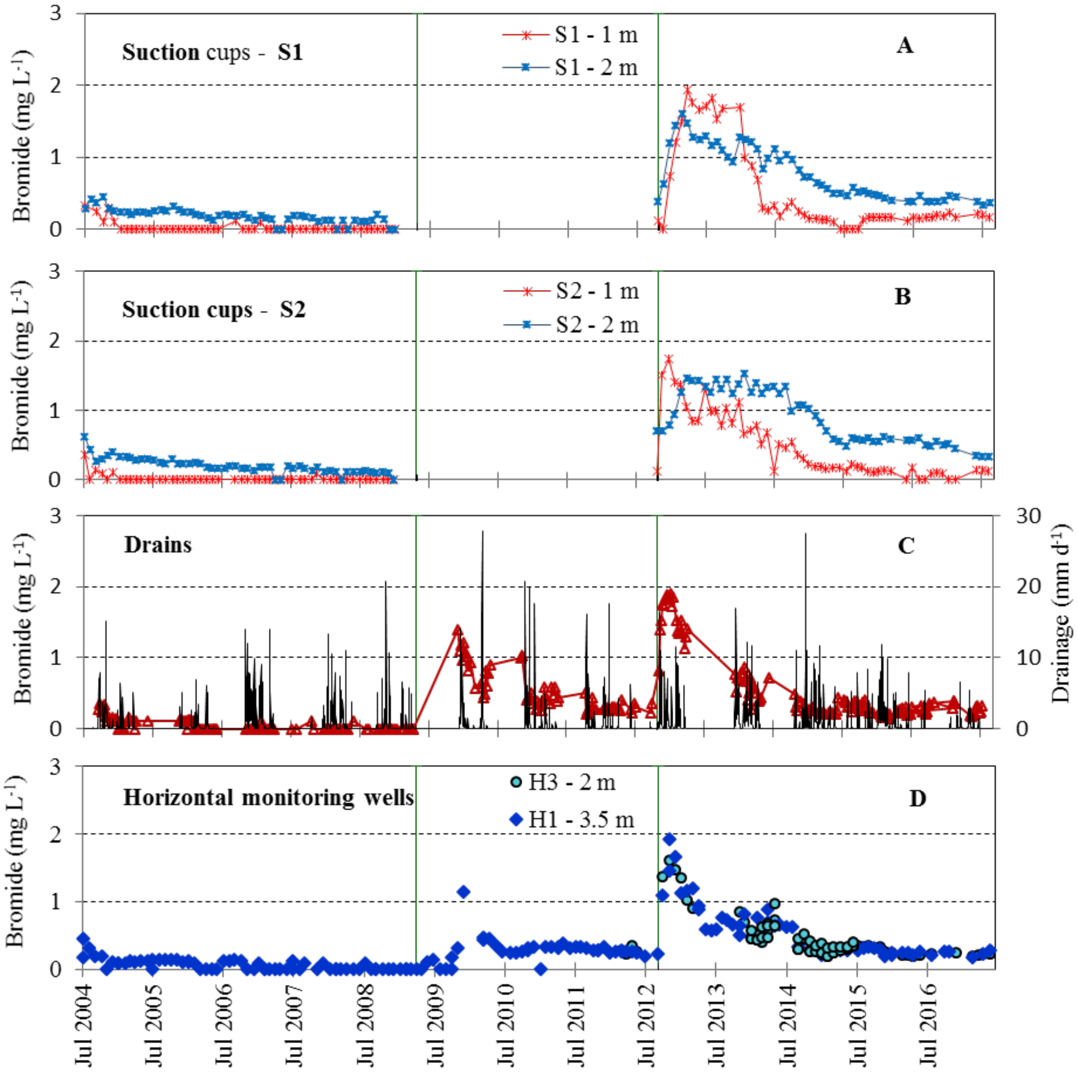


Figure 4.3. Bromide concentration at **Silstrup**. A and B refer to suction cups located at S1 and S2 (see Figure 4.1). The bromide concentration is also shown for drainage runoff (C) and the horizontal monitoring wells H1 and H3 (D). From January 2009 to September 2012, bromide measurements in the suction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

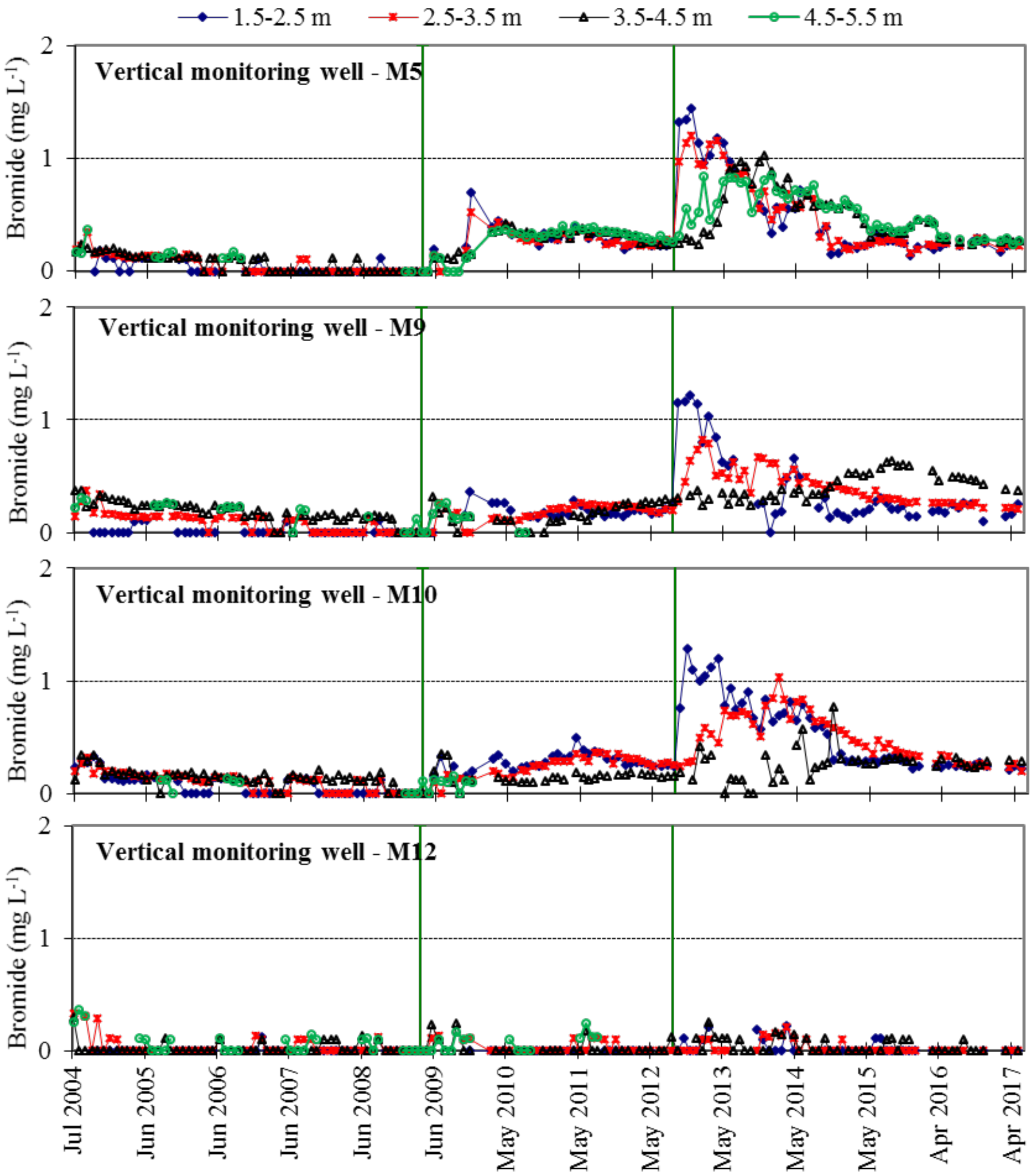


Figure 4.4. Bromide concentration at **Silstrup**. The data derive from the vertical monitoring wells (M5, M9, M10 and M12). In September 2008, monitoring wells M6 and M11 were suspended (Appendix 2). Screen depth is indicated in m b.g.s. The green vertical lines indicate the dates of bromide applications.

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 2011 to 2017 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 from 2015/2016 to 2016/2017 as simulated with the MACRO model. Moreover, pesticides applied later than May 2017 are not evaluated in this report and not included in Table 4.2.

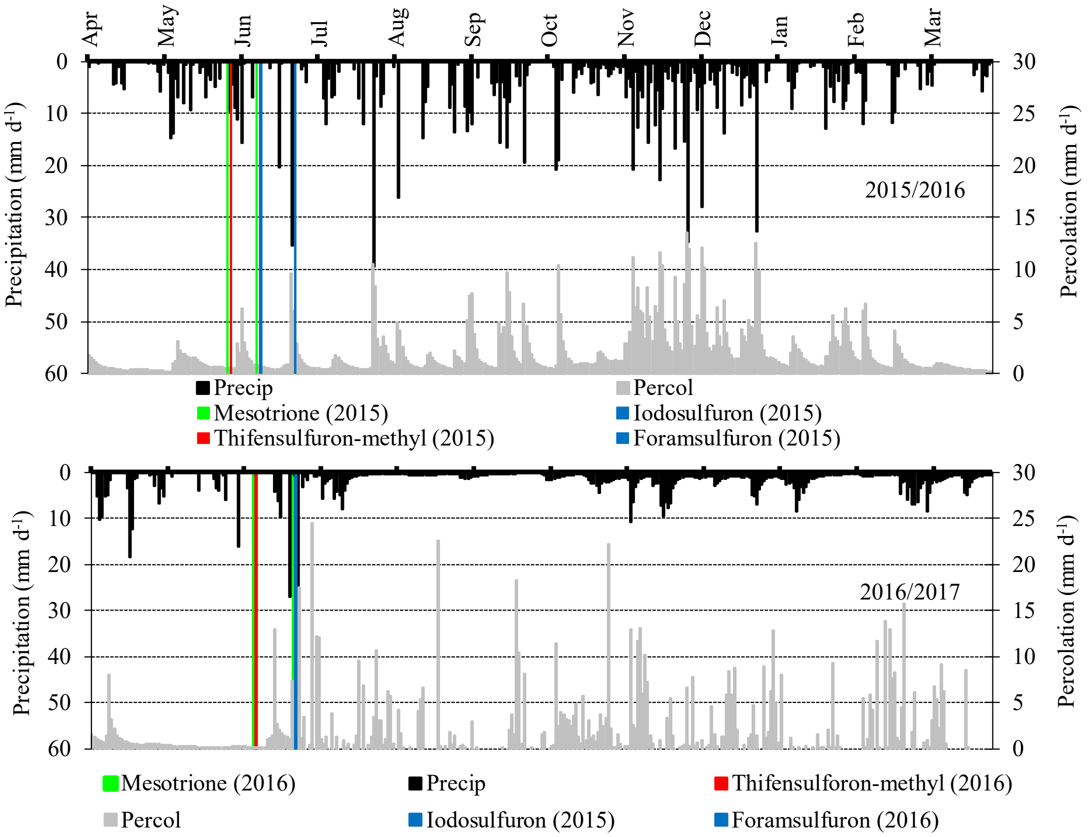


Figure 4.5. Application of pesticides included in the monitoring programme, precipitation (primary axis; Precip) together with simulated percolation 1 m b.g.s. (secondary axis; Percol) at **Silstrup** in 2015/2016 (upper) and 2016/2017 (lower).

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 [$\mu g\ L^{-1}$] at 1 m depth the first year after application. See Appendix 2 for calculation method and Appendix 7 (Table A7.3) 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	Oct16	1059	534	15	0	0.132
	Glyfonova 450 Plus	Glyphosate(P)	Aug 13	Apr 16	1008	538	125	0	0.01
		AMPA(M)	Aug 13	Apr 16	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	Apr 16	1309	691	187	0	<0.01
		AMPA(M)	Jul 14	Apr 16	1309	691	187	0	<0.01
Maize 2015	Callisto	Mesotrione (P)	May 15***	Jun 17*	1219	783	117	52	0.05
		AMBA(M)	May 15***	Jun 17*	1219	783	117	52	<0.01
		MNBA(M)	May 15***	Jun 17*	1219	783	117	52	<0.01
	MaisTer	Foramsulfuron (P)	Jun 15****	Jun 17*	1257	791	100	37	<0.01
		AE-F130619(M)	Jun 15****	Jun 17*	1257	791	100	37	<0.01
		AE-F092944(M)	Jun 15****	Jun 17*	1257	791	100	37	<0.01
Maize 2016	Callisto	Mesotrione (P)	Jun 16*****	Jun 17*	562	826	77	26	0.1
		AMBA(M)	Jun 16*****	Jun 17*	562	826	77	26	<0.01
		MNBA(M)	Jun 16*****	Jun 17*	562	826	77	26	0.01
	MaisTer	Foramsulfuron (P)	Jun 16	Jun 17*	514	881	82	121	0.03
		AE-F130619(M)	Jun 16	Jun 17*	514	881	82	121	<0.01
		AE-F092944(M)	Jun 16	Jun 17*	514	881	82	121	<0.01
	Iodosulfuron (P)	Triazinamine(M)	Jun 16	Jun 17*	514	881	82	121	<0.01
	Harmony SX Thifensulfuron-methyl (P)	Triazinamine(M)	Jun 16	Jun 17*	562	826	77	26	<0.01
Spring barley 2017	Bumper 25 EC Propiconazole(P)	1,2,4-triazol (M)	Jun 17**	Jun 17*	-	-	-	-	-
	Zypar Florasulam(P)	TSA (M)	Jun 17	Jun 17*	-	-	-	-	-
	Halauxifen-methyl(P)	X-757 (M)	Jun 17	Jun 17*	-	-	-	-	-

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

**Monitoring continues the following year.*

** *Propiconazole was applied twice as Bumper 25 EC 27 June 2017 and 10 July 2017.*

*** *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 2015 and onwards, while the leaching risk of pesticides applied in 2014 and before, has been evaluated in previous monitoring reports (see http://pesticidvarsling.dk/monitor_uk/index.html).

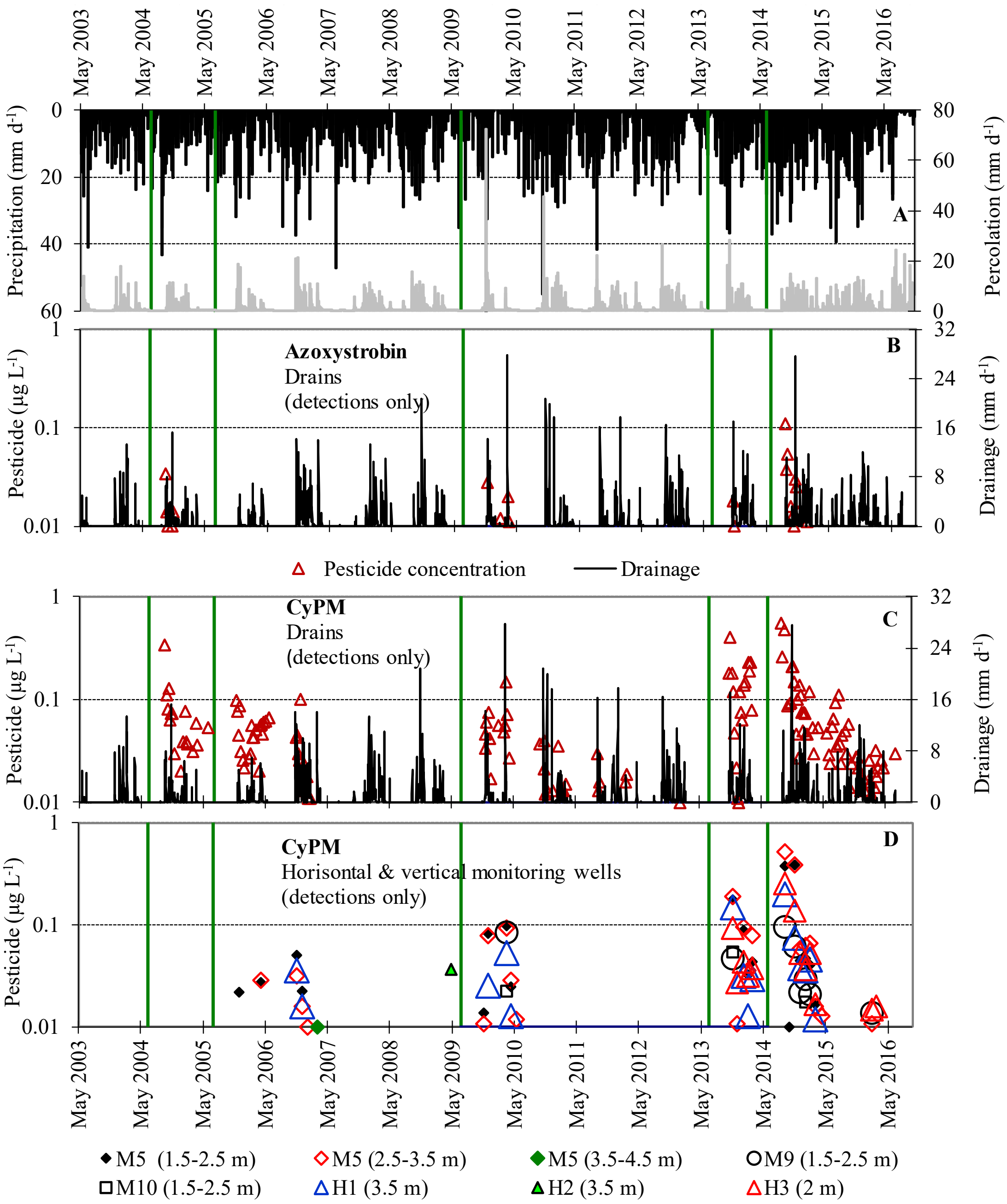


Figure 4.6. Azoxystrobin and **CyPM** detections at **Silstrup**: Precipitation and simulated percolation 1 m b.g.s. (A) together with the concentration of azoxystrobin (B) and CyPM (C) in the drainage runoff, and the concentration of CyPM (D) in water samples collected from the groundwater monitoring 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 overall highest concentration at Silstrup. Throughout the period 2004 until October 2016 azoxystrobin was detected in only eight of 644 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 188 samples, with 0.11 µg L^{-1} on 27 August 2014 as the sole above 0.1 µg L^{-1}. From a total of 211 drainage samples merely 59 did not contain CyPM, a degradation product of azoxystrobin, whereas 24 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 756 groundwater samples taken over the years at Silstrup, 100 samples contained CyPM, whereof 12 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, while it was detected in: 57 out of 66 water samples from drainage (86 %) with 9 exceeding 0.1 µg L^{-1} (This is one exceedance less than given in the PLAP-report of 2017 – here an erroneous detection of 0.1 µg L^{-1} was included), 21 water samples out of 111 (19%) collected from the downgradient wells with four detections exceeding 0.1 µg L^{-1}, 8 out of 34 water samples (24%) collected from H1 (3.5 m depth) with one detection exceeding 0.1 µg L^{-1} and 20 out of 44 water samples (45%) collected at H3 (2 m depth) with 4 exceeding 0.1 µg L^{-1}. This reveals that the distance from the surface reduces the number of detections and that the source is coming from the surface and not upgradient fields. Monitoring ended October 2016.

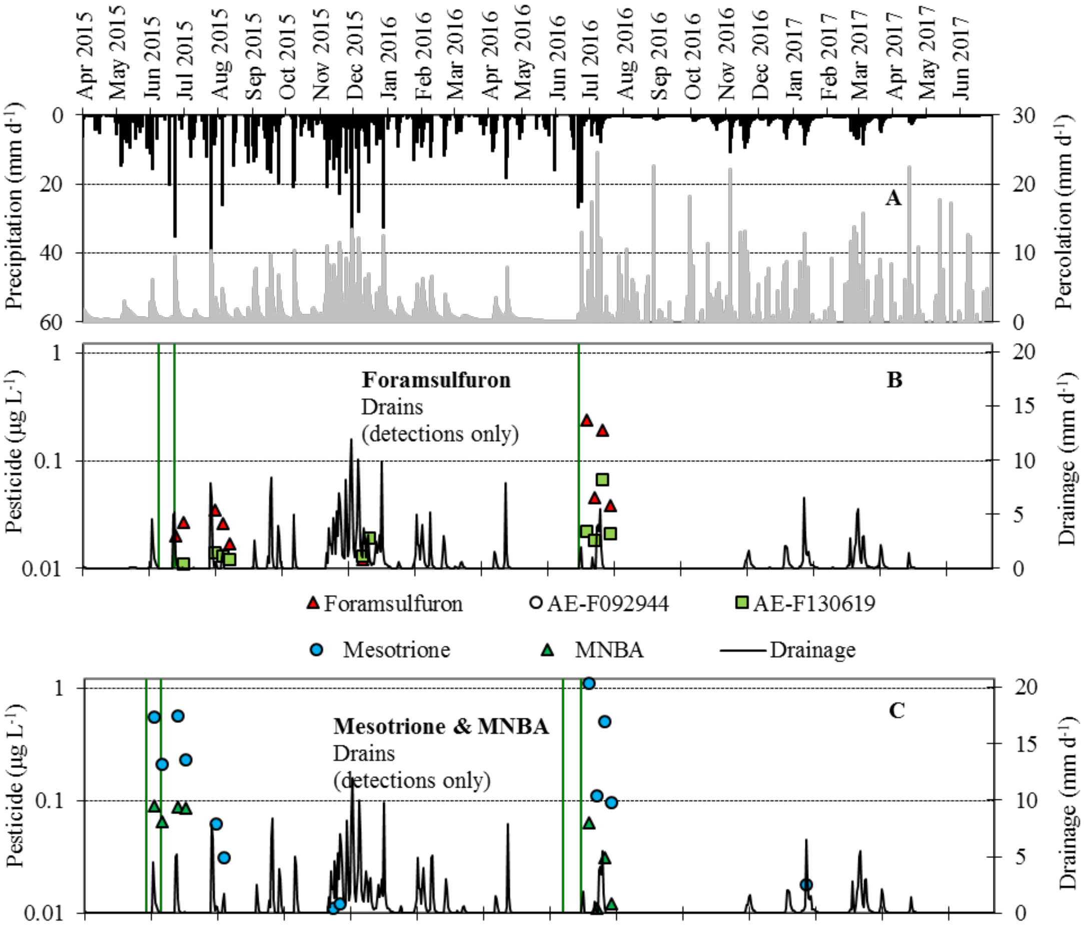


Figure 4.7. Foramsulfuron, AE-F092944, AE-F130619, and **Mesotrione** and **MNBA** detections in samples of drainage at **Silstrup**: Precipitation and simulated percolation 1 m b.g.s. (A) together with the concentration of mesotrione and MNBA (B); and foramsulfuron (C) in the drainage runoff. The green 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 was applied on three occassions: 9 and 23 June 2015 and 22 June 2016 (Figure 4.7B). Both oramsulfuron and two of its degradation products, AE-F092944 and AE-F120619, have been included in PLAP since May 2015. Following all three applications, foramsulfuron was found in samples of drainage water. Of the 48 drainage samples taken between the first application of foramsulfuron on 9 June 2015 and the last drainage sample taken 19 April 2017, foramsulfuron was found in 10 water samples. All detections were observed within 3-4 weeks following the three applications, except one detected December 2015. In 2015, where the maximum alloved dosage of 45 g a.i. ha^{-1} of foramsulfuron was applied as 30 g a.i. ha^{-1} on 9 June and 15 g a.i. ha^{-1} on 23 June, there were no exceedances of 0.1 µg L^{-1}. However, when all of the 45 g a.i. ha^{-1} was applied 22 June, detections of 0.24 µg L^{-1} and 0.038 µg L^{-1} were apparent in the drains one and four weeks after spraying, respectively, Figure 4.7B. Whereas the degradation product AE-F092944 was found in neither drainage nor groundwater samples, the degradation product AE-F130619 was found in both (Figure 4.7B). From the total 169 samples of groundwater collected during the monitoring period, AE-F130619 was detected in 9 samples and none of these were above 0.1 µg L^{-1}. AE-F130619 was detected in 5 of 57 samples collected from the horizontal wells with highest concentration being 0.032 µg L^{-1}. In 112 groundwater samples from the vertical wells 3 contained AE-F130619 with highest concentration being 0.012 µg L^{-1} (data not shown). The highest concentration, 0.067 µg L^{-1} of AE-F130619 was detected in drainage water three weeks after the June 2016 application. From a total of 48 samples of drainage 9 contained AE-F130619, although all detections were below 0.1 µg L^{-1}.

Mesotrione was applied to a crop of maize in late May and early June 2015, and twice in June 2016 (Figure 4.7C). Mesotrione was not detected in any of the water samples collected prior the initial application 27 May 2015. A mesotrione concentration of 0.55 and 0.21 µg L^{-1} was detected in the drainage following the May 2015 application and the June 2015 spraying, respectively. Highest overall concentration related to the 2015 applications was 0.56 µg L^{-1} on 24 June. When mesotrione was applied 6 June there were no drainage, and the most recent detection was 0.012 µg L^{-1} on 18 November 2015. At the day of the second mesotrione spraying, 22 June, a drainage sample was collected containing no mesotrione. On 29 June drainage contained mesotrione concentration of 1.1 µg L^{-1}. Out of the total of 49 drainage samples collected between 3 June 2015 and 19 April 2017, 7 contained more than 0.1 µg L^{-1} mesotrione and 6 less than 0.1 µg L^{-1}. Before the May 2015 application mesotrione could not be detected in neither horizontal nor vertical groundwater wells. Out of a total 177 groundwater samples taken between April 2015 and May 2017 none contained mesotrione. Also, two degradation products of mesotrione, AMBA and MNBA were monitored. Neither of the two were detected in groundwater samples. Only MNBA was found in 8 out of 49 drainage samples, four times following both the 2015 and 2016 applications. Maximum detection in 2015 was 0.09 µg L^{-1} one week after the first application in 2015 and 0.064 µg L^{-1} three weeks after the first application in 2016. Monitoring continues until 30 April 2018.

Thifensulfuron-methyl was sprayed to the field on 2 June 2016 and its metabolite IN-A4098 (triazinamine) was included in the monitoring. Hitherto, IN-A4098 has not been detected in neither 20 samples of drainage nor 77 samples of groundwater. Results are preliminary and monitoring continues.

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 2016-17 growing seasons is briefly summarized below and detailed in Appendix 3 (Table A3.4). For information about management practice during the past monitoring periods, see previous monitoring reports available on http://pesticidvarsling.dk/monitor_uk/index.html.

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 2015 program was continued and complemented with triazinamine (IN-A4098), a degradation product of both thifensulfuron-methyl and iodosulfuron. Maize for silage harvested 30 September 2016 yielded 184.8 hkg ha^{-1} (100% dry matter).

On 8 April 2017 peas (cv. Mascara) were sown in the maize stuble using a combination of a rotary harrow and a seed drill. The peas emerged 14 April. Weeds were sprayed with a mixture of pendimethaline and bentazone; neither of them were monitored.

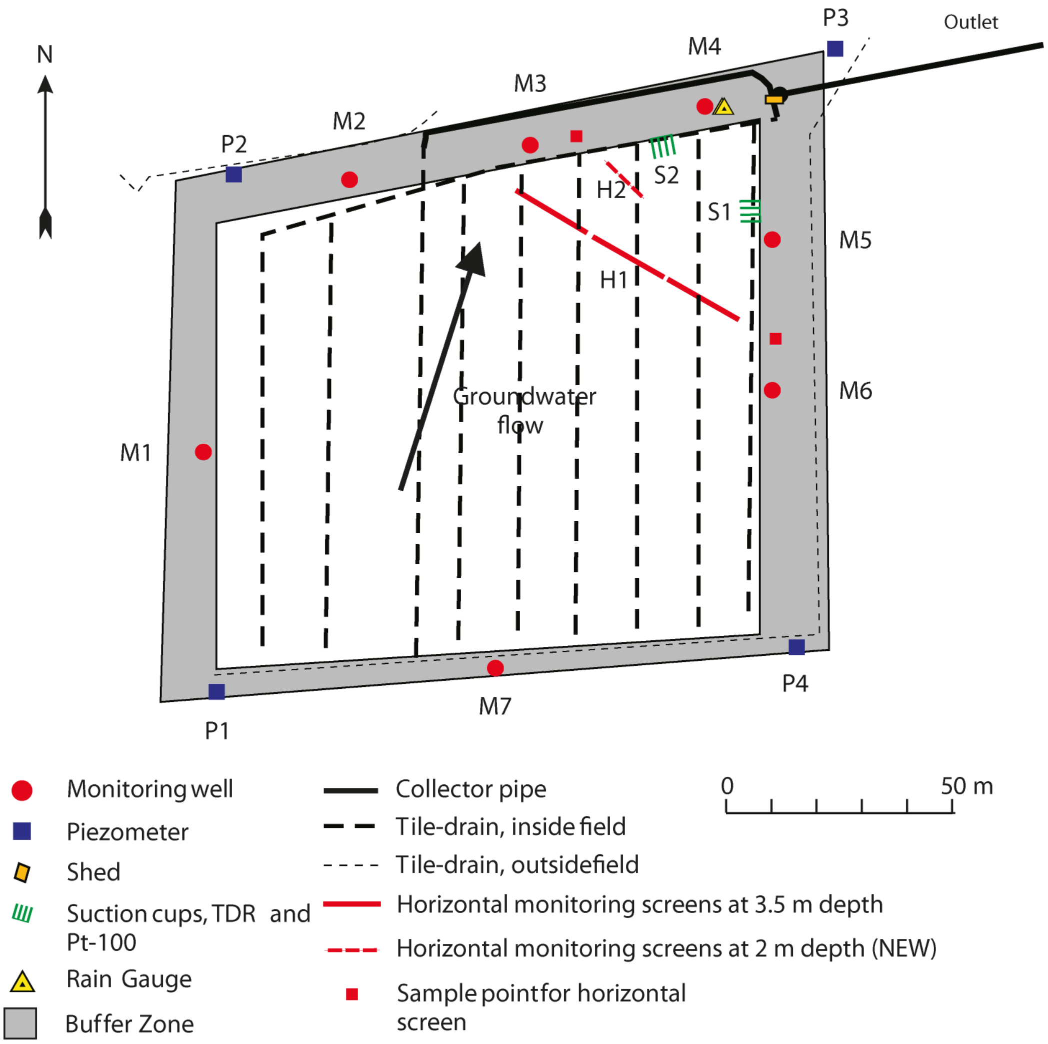


Figure 5.1. Overview of the **Estrup** field. The innermost white area indicates the cultivated area, while the grey area indicates the surrounding buffer zone. The positions of the various installations are indicated, as is the direction of groundwater flow. Pesticide monitoring is conducted weekly 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 2017 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 2017. 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 Compared to the summer of 2015 and the early summer of 2016, where the watertable decline was not well captured, the model again captured the pattern during the late summer of 2016 and early summer of 2017 (Figure 5.2B). Also, the decrease in water saturation at 0.25 m depth was better captured during the late summer of 2016 and early summer of 2017 (Figure 5.2D).. As noted in Rosenbom et al. (2016), TDR probes do not always have a sufficient contact to the surrounding soil, which could be the case at 0.25 m depth where the TDR are reinstalled after ploughing. The simulated pattern in drainage during the recent hydraulic year, July 2016-June 2017, is comparable to the measured drainage. Though, the simulated absolute values were somewhat underestimated.

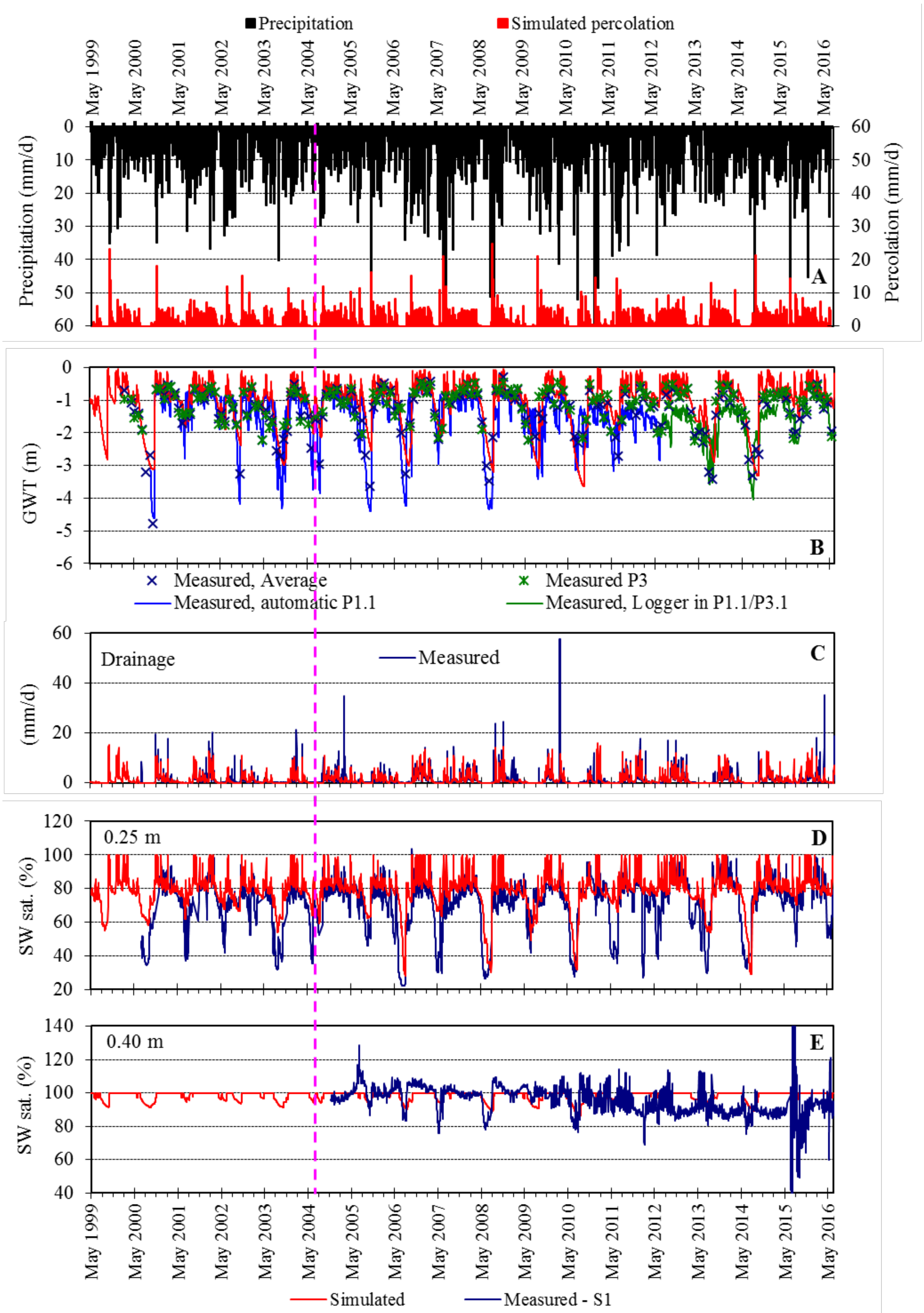


Figure 5.2. Soil water dynamics at **Estrup**: Measured precipitation and simulated percolation 0.6 m b.g.s. (A), simulated and measured groundwater table, GWT (B), simulated and measured drainage (C), and simulated and measured soil saturation (SW sat.) at two different soil depths (D and E). The measured 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 2017).

Table 5.1. Annual water balance for **Estrup** (mm yr^{-1}). 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	1230	390	491	624	350
01.07.16–30.06.17	968	840	522	274	266	44

[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.*

Drainage measured in connection with snowmelt was generally well captured in regard to the dynamics for this hydrological year (Figure 5.2C), but the amount is underestimated. 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 to the previous seventeen years, the recent hydrological year July 2016-June 2017 yielded the lowest measured precipitation and the second highest simulated actual evapotranspiration leading to the lowest simulated groundwater recharge and drainage. The measured drainage was also among the lowest measured in the previous seventeen years. Precipitation of especially January, May and September, where comparable to the lowest measured values since the initiation of the PLAP-monitoring (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.

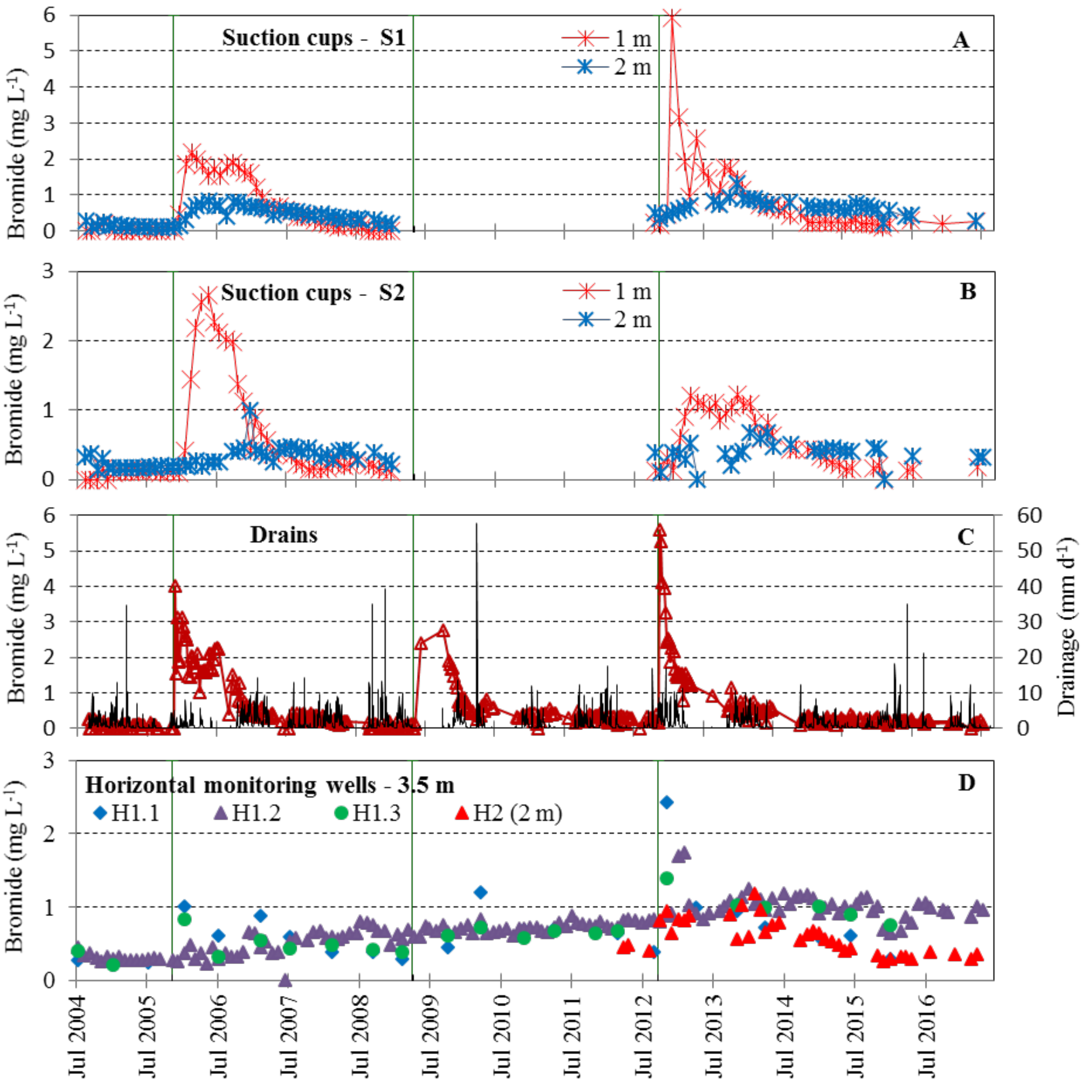


Figure 5.3. Bromide concentration at **Estrup**. A and B refer to suction cups located at S1 and S2, respectively. The bromide concentration is also shown for drainage runoff (C) and the horizontal monitoring well H1 and H3 (D). From September 2008 to August 2012, bromide measurements in the suction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

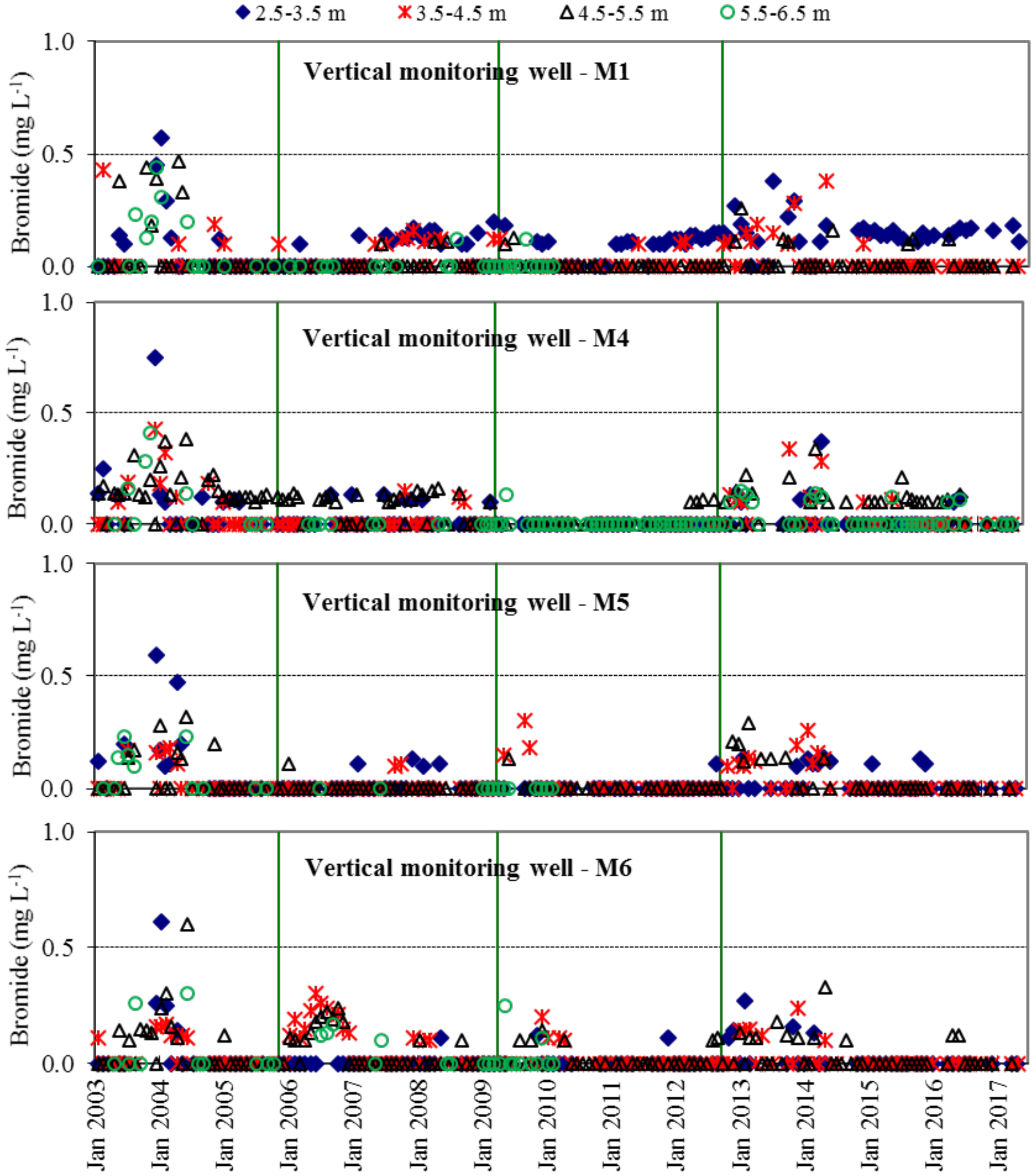


Figure 5.4. Bromide concentration at **Estrup**. The data derive from the vertical monitoring wells (M1, M4, M5 and M6). Screen depth is indicated in m b.g.s. In September 2008, monitoring wells M3 and M7 were suspended. The green vertical lines indicate the dates of the three most recent bromide applications.

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 (20010-2016) and Table A7.4 in Appendix 7 (2000-2009). Pesticide application during the most recent growing season (2015-2017) 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 May 2017 are not evaluated in this report although included in Table 5.2.

The current report focuses on pesticides applied from 2015 and onwards, while leaching risk of pesticides applied in 2014 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 7 (Table A7.4) 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	Apr 16	1083	281	151	29	0.04
		CyPM(M)	Jun 12	Apr 16	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	Apr 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	Apr 16	928	237	131	13	0.10
		AMPA(M)	Aug 13	Apr 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 17*	1152	249	51	0.4	0.01
	Amistar	Azoxystrobin(P)	Jun 14	Apr 16	1176	257	49	0	0.02
		CyPM(M)	Jun 14	Apr 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 17*	1196	299	91	23	0.11
		AMBA(M)	May 15	Jun 17*	1196	299	91	23	<0.01
		MNBA(M)	May 15	Jun 17*	1196	299	91	23	<0.01
	MaisTer****	Foramsulfuron(P)	May 15	Jun 17*	1196	299	91	23	<0.01
		AE-F130619(M)	May 15	Jun 17*	1196	299	91	23	<0.01
		AE-F092944(M)	May 15	Jun 17*	1196	299	91	23	<0.01
Maize 2016	Callisto	Mesotrione(P)	Jun 16	Jun 17*	870	209	148	19	<0.01
		AMBA(M)	Jun 16	Jun 17*	870	209	148	19	<0.01
		MNBA(M)	Jun 16	Jun 17*	870	209	148	19	<0.01
	Harmony SX Thifensulfuron-methyl (P)	Triazinamine(M)	Jun 16	Jun 17*	870	209	148	19	<0.01
	MaisTer	Foramsulfuron(P)	Jun 16	Jun 17*	936	204	201	28	<0.01
		AE-F130619(M)	Jun 16	Jun 17*	936	204	201	28	<0.01
		AE-F092944(M)	Jun 16	Jun 17*	936	204	201	28	<0.01
Pea 2017									

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.*

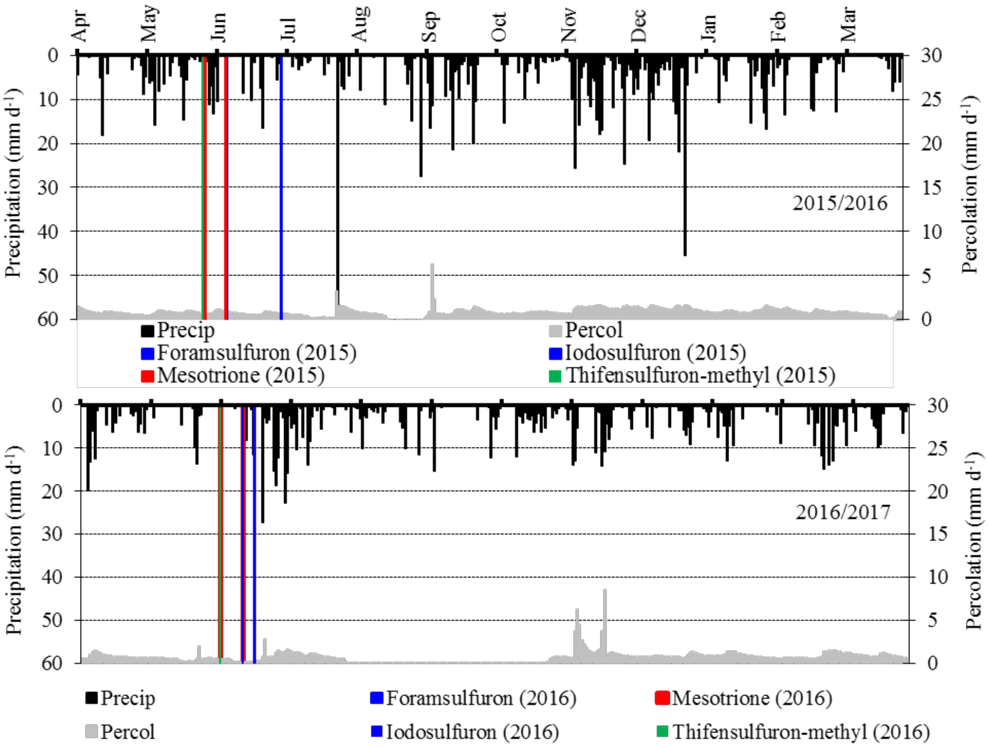


Figure 5.5. Application of pesticides included in the monitoring programme and precipitation (primary axis; Precip) together with simulated percolation 1 m b.g.s. (secondary axis; Percol) at **Estrup** in 2015/2016 (upper) and 2016/2017 (lower).

Azoxystrobin has 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 415 drainage samples were taken from August 2004 to April 2017. Azoxystrobin was detected in 141 of the samples and in 16 samples concentrations were above 0.1 µg L^{-1}. In only 40 of the 415 drainage samples CyPM was absent, and in 150 samples, concentrations were above 0.1 µg L^{-1}. During the same period 765 groundwater samples were collected and only two had detections of azoxystrobin with the highest reading being 0.04 µg L^{-1}. In the 765 groundwater samples CyPM was detected in 41, of which five were above the limit. The first one above the limit 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. None of the samples from the vertical wells exceeded 0.1 µg L^{-1}. Monitoring of azoxystrobin is terminated, whereas that of CyPM continues until April 2018.

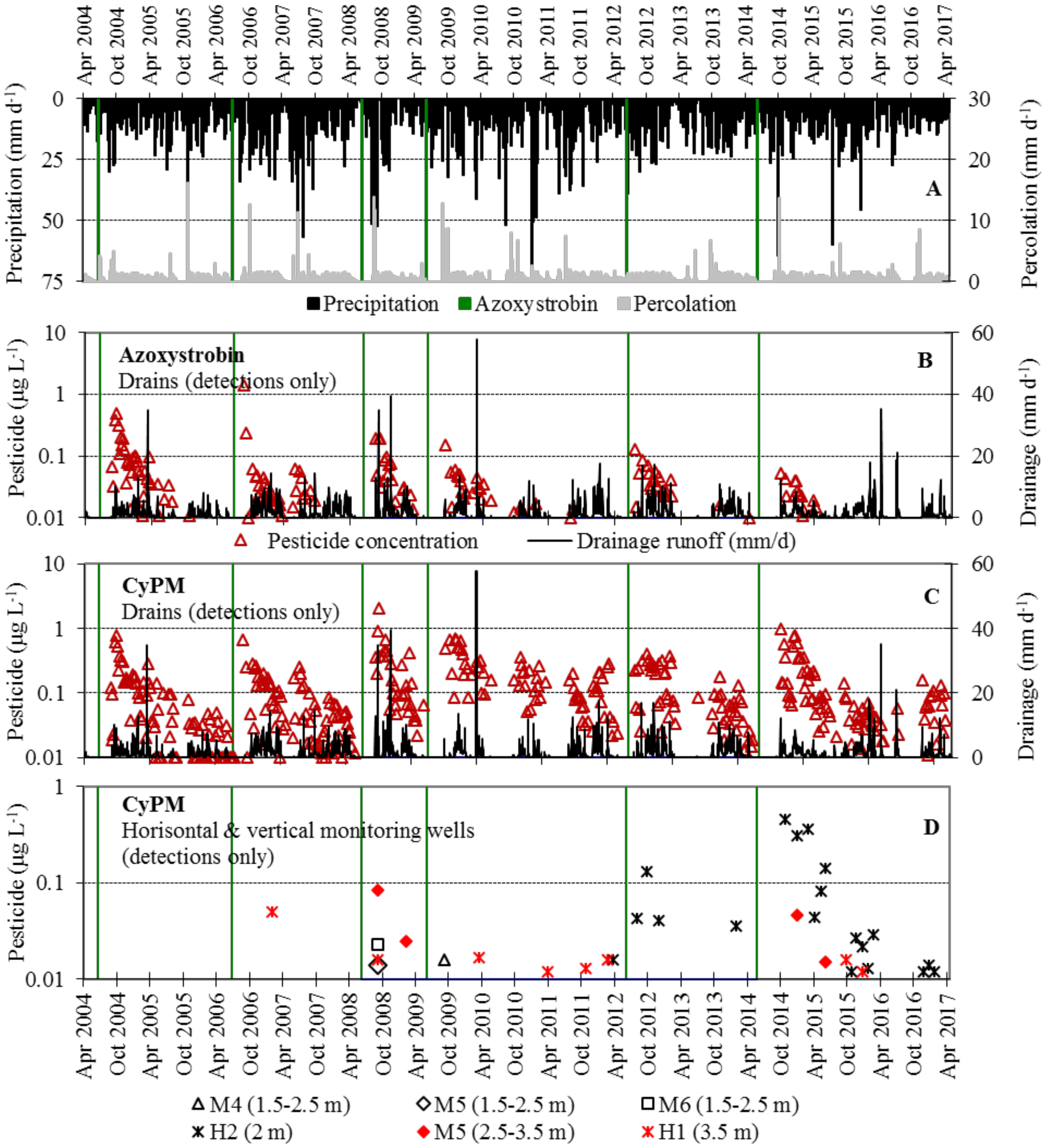


Figure 5.6. Azoxystrobin and CyPM detections at **Estrup**: Precipitation and simulated percolation 0.6 m b.g.s. (A) together with concentration of azoxystrobin (B) and CyPM (C) in water samples from drainage (DR on the secondary axis)**.** Detections of CyPM in water samples collected from groundwater 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).

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. A total of 47 drainage samples were collected between the first spraying 6 June 2015 until 30 June 2016. Foramsulfuron was present in 19 samples of which 3 were above 0.1 µg L^{-1} with highest detections being 0.32 µg L^{-1} on 29 July 2015. Neither foramsulfuron nor its two degradation products were detected in any of the 85 groundwater samples. Drainage was sampled 47 times during the period. The AE-F092944 was detected once, 13 January 2016, with the concentration being 0.012 µg L^{-1}. In the drainage, AE-F130619 was detected 6 times with highest concentration being 0.055 µg L^{-1} on 6 July 2016 and lowest being 0.011 µg L^{-1} 16 September 2015. Neither AE-F130619 nor AE-F092944 were detected in any of the 85 groundwater samples. Monitoring was ended on 30 June 2017.

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, were included in the monitoring (as was also the case at Silstrup). None of the three compounds were detected in the background samples collected before application (Figure 5.7). Mesotrione, AMBA and MNBA were detected in 29, 4 and 10 samples of a total of 48 drainage samples, respectively.

A week after the first application in 2015, 3.3 µg L^{-1} of mesotrione was detected in the drainage. In groundwater sampled from the horizontal wells mesotrione was detected in 3 of the 39 samples and the highest concentration measured was 0.13 µg L^{-1} on 17 June 2015. Two of 50 samples from the vertical groundwater wells contained mesotrione and the highest concentration was 0.067 µg L^{-1} on 6 June 2015. AMBA was detected four times in drainage and the highest concentration was 0.039 µg L^{-1} on 24 February 2016. None of the 89 groundwater samples contained AMBA. MNBA was found in 10 of 48 drainage samples, 2 were above 0.1 µg L^{-1}, the highest being 0.46 µg L^{-1} one week after application. MNBA was only detected once in the groundwater at a concentration of 0.017 µg L^{-1}. Monitoring is ongoing until 30 April 2018.

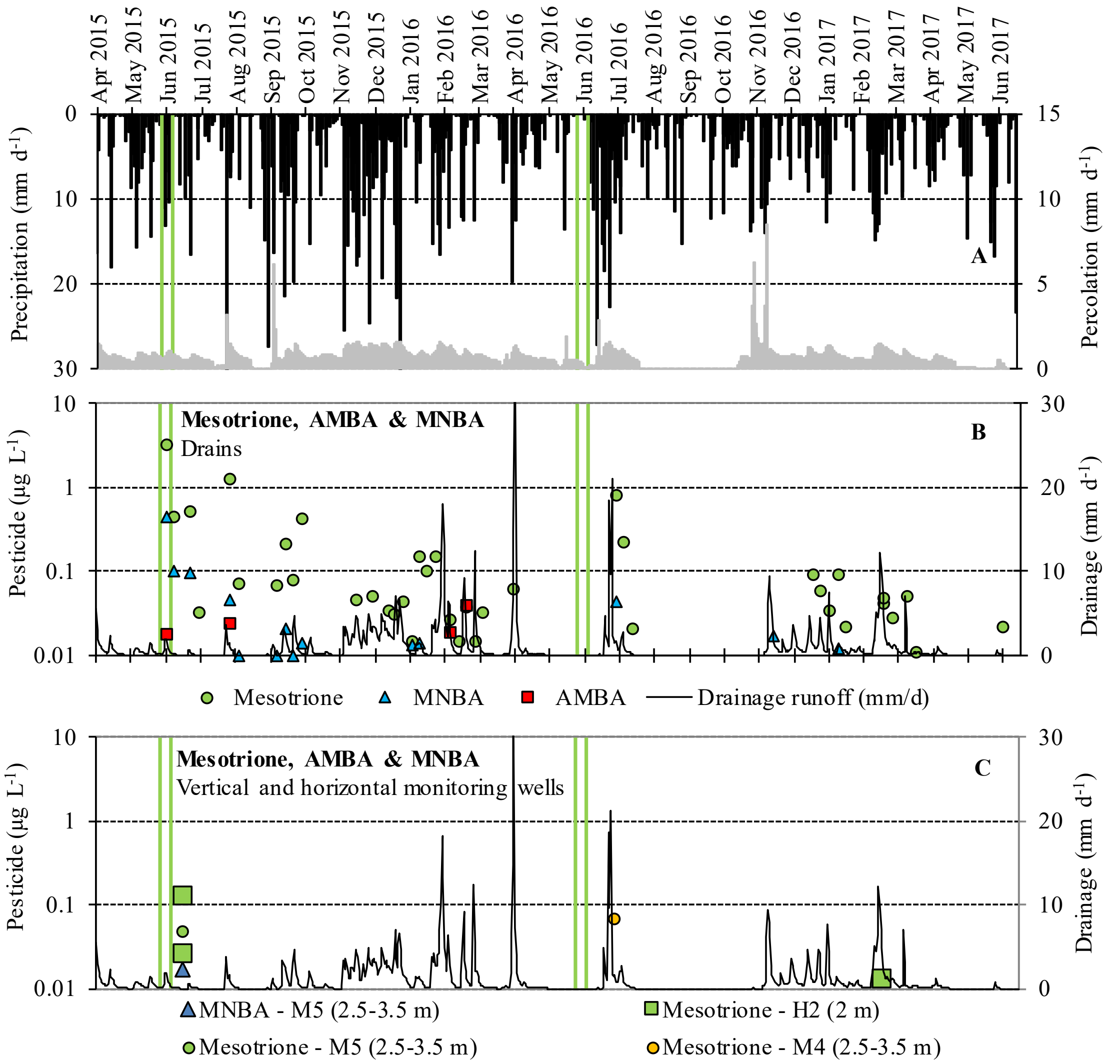


Figure 5.7. Mesotrione, AMBA and MNBA detections at **Estrup**: Precipitation and simulated percolation 1 m b.g.s. (A) together with the concentration of Mesotrione, AMBA and MNBA in water samples collected from drainage (B) and groundwater samples (C). The green vertical line indicates the date of mesotrione 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 5.8). As seen from Figure 5.8B, drainage did not start until 1 October 2014, where 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 116 drainage samples collected from 1 October 2014 to 14 June 2017 contained 1,2,4-triazole and only four of these contained less than 0.1 µg L^{-1}. The highest concentrations found were 0.45 µg L^{-1} detected on both 29 July 2015 and 6 July 2016. Figure 5.8C 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. In 2016 and 2017 the first detections in 3.5 to 5.5 m depth was done, with the highest being 0.09 µg L^{-1} in M4.4. 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 (Figure 5.8). 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. 73 groundwater samples have been collected from the horizontal wells and all contained 1,2,4-triazole, 9 thereof above 0.1 µg L^{-1}. From the vertical wells 100 samples has been collected and only 18 did not contain 1,2,4-triazole and 39 contained concentrations more than 0.1 µg L^{-1}. Monitoring is ongoing.

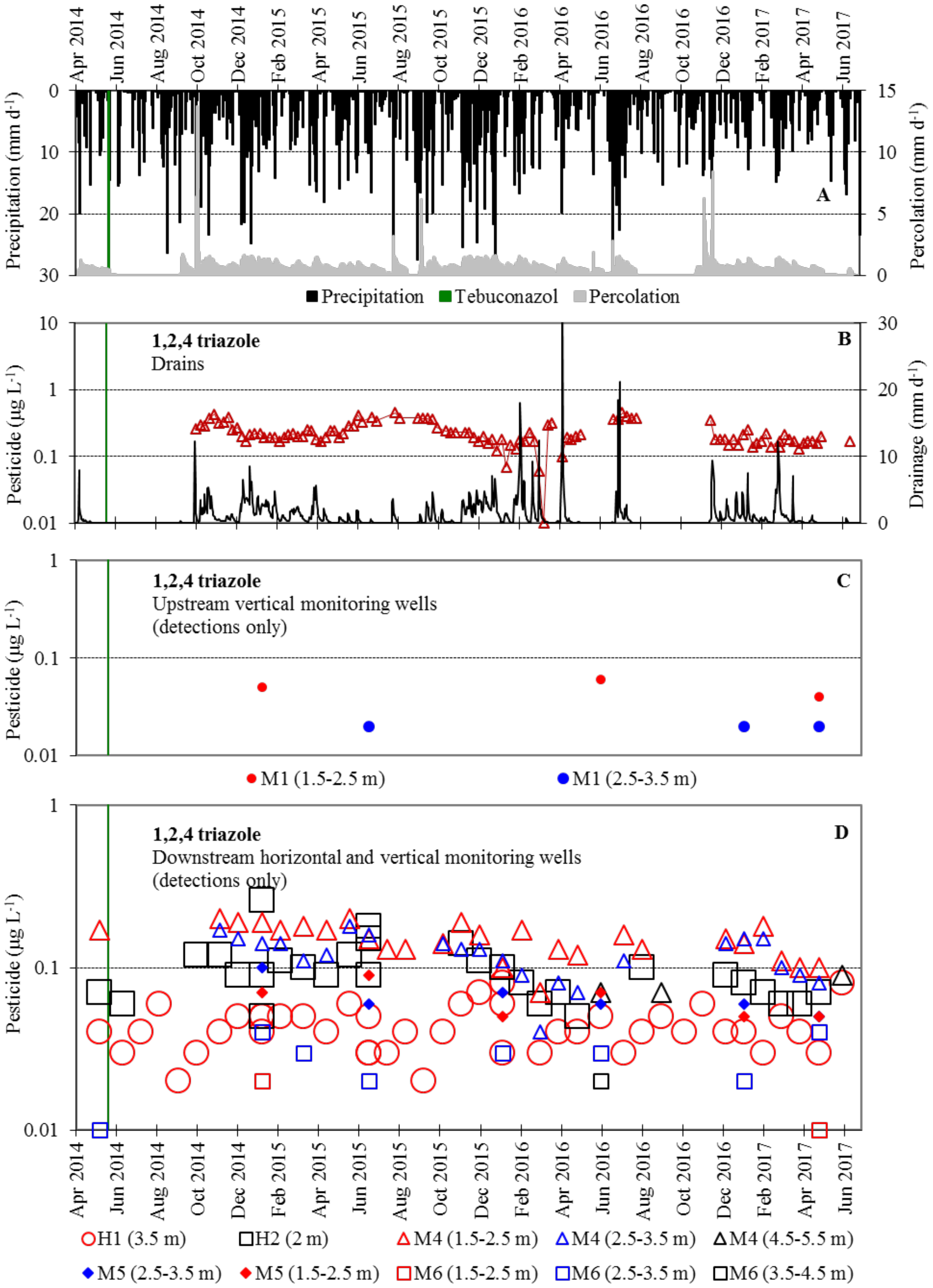


Figure 5.8. 1,2,4-triazole detections at **Estrup**: Precipitation and simulated percolation 1 m b.g.s. (A) together with measured concentration of 1,2,4-triazole detections in drainage water and groundwater (C-D; Water collected from upstream and downstream horizontal (H) and vertical screens (M)). The green vertical lines indicate the date of pesticide application.

Thifensulfuron-methyl was applied in both May 2015 and June 2016. However, its degradation product, IN-A4098 (triazinamine), was not monitored before June 2016. As of now none of 27 drainage samples and 53 groundwater samples contained IN-A4098. Monitoring continues until May 2018.

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.

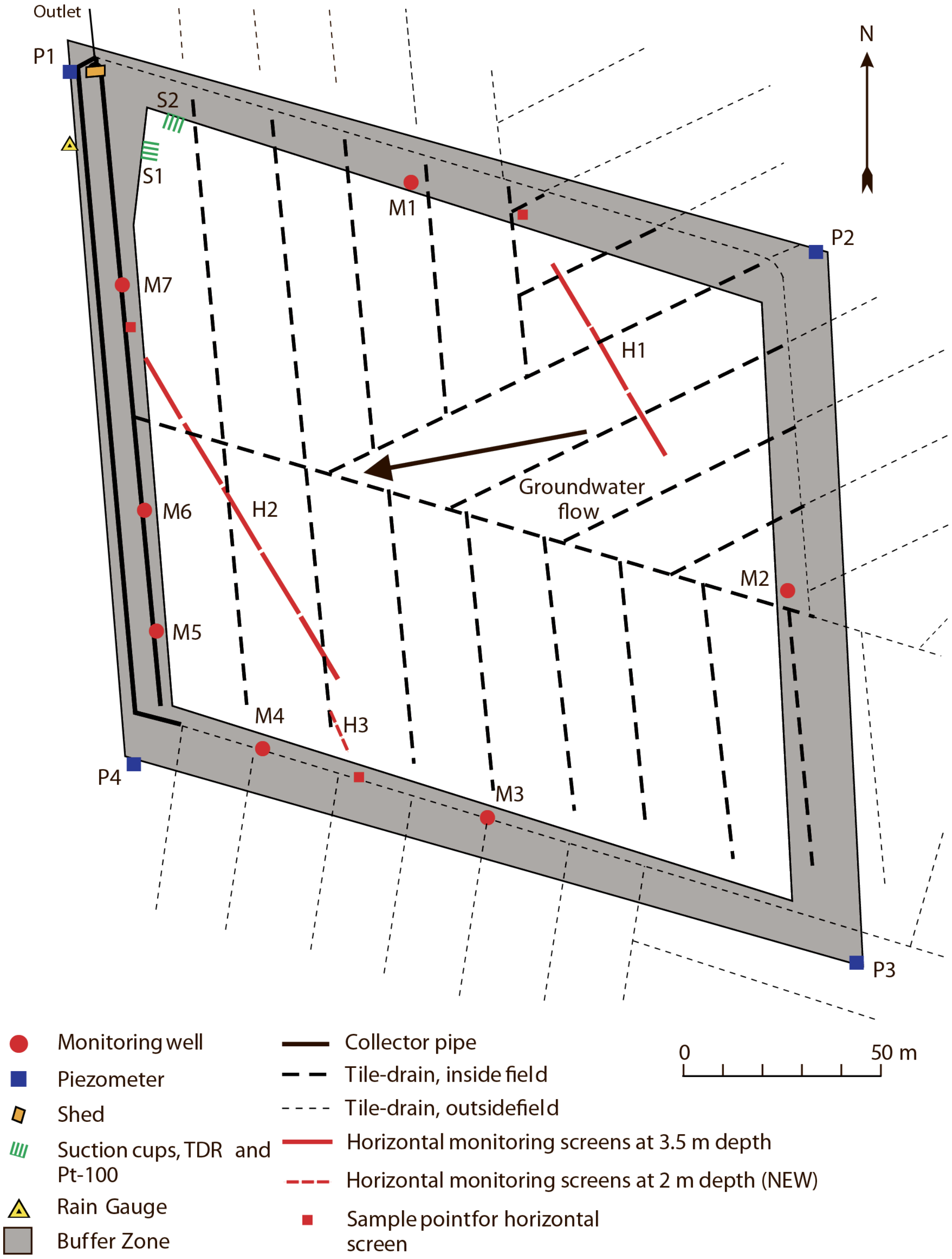


Figure 6.1. Overview of the **Faardrup** field. The innermost white area indicates the cultivated land, while the grey area indicates the surrounding buffer zone. The positions of the various installations are indicated, as is the direction of groundwater flow (arrow). Pesticide monitoring is conducted 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 2016-17 growing seasons is briefly summarized below and detailed in Appendix 3 (Table A3.5). For information about management practice during the past monitoring periods, see previous monitoring reports available on http://pesticidvarsling.dk/monitor_uk/index.html.

On 11 April 2016, a mixture of spring barley varieties was sown using a combined rotary harrow and a seed drill. 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}. On the 11 August, the spring barley was sprayed with the herbicide glyphosate (not included in the monitoring). Grain yield harvested 26 August was 57.7 hkg ha^{-1} (85% dry matter) and 54.0 hkg ha^{-1} (fresh weight) taken off the field the following day. The field was ploughed 20 December 2016.

Spring barley (cv. Quench) was sown 2 May 2017, using a combined rotary harrow and a seed drill, emerged 10 May. The spring barley was sprayed with the herbicides iodosulfuron-methyl and mesulfuron-methyl on 2 June. Neither of the substances were monitored. On 19 June the fungicide propiconazol was sprayed together with the herbicides haluxifen-methyl and florasulam. The degradation product X-757 of haluxifen-methyl and TSA of florasulam were included in the monitoring. 1,2,4-triazole, a degradation product of propiconazol, were already included in the monitoring.

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 2017 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 2017. 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 yr^{-1}). 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	493	123	167	202
01.07.15–30.06.16	626	800	405	124	167	271
01.07.16–30.06.17	626	594	409	0	43	184

[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 2016-June 2017 were generally well described by the model (Figure 6.2D, 6.2E and 6.2F). As generally observed, the water saturation patterns are captured with an offset in all three depths (Figure 6.2D, 6.2E and 6.2F) during both summer and winter. Still, in 0.25 and 0.6 m depth, the decline in water saturation during summer were not well captured. 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 model yields a simulated drainage although no drainage was recorded (Figure 6.2C and Table 6.1).

The resulting water balance of all monitoring periods is shown in Table 6.1. Compared to the previous seventeen years, the recent hydraulic year (July 2016-June 2017) was characterised by low precipitation, an intermediate actual evapotranspiration, no measured drainage, and low simulated drainage. Due to the simulated low drainage, the deduced recharge yielded a value above the average from the previous seventeen years.

Precipitation values during this year were overall characterised by being lower than the average of the previous years (Appendix 4). Together with the groundwater table being substantially lower than the previous year, this may be the reason that an all-time low water saturation is measured at 0.25 m depth during the summer of 2016. Further, the generally low precipitation during the year could explain the lack in measured drainage.

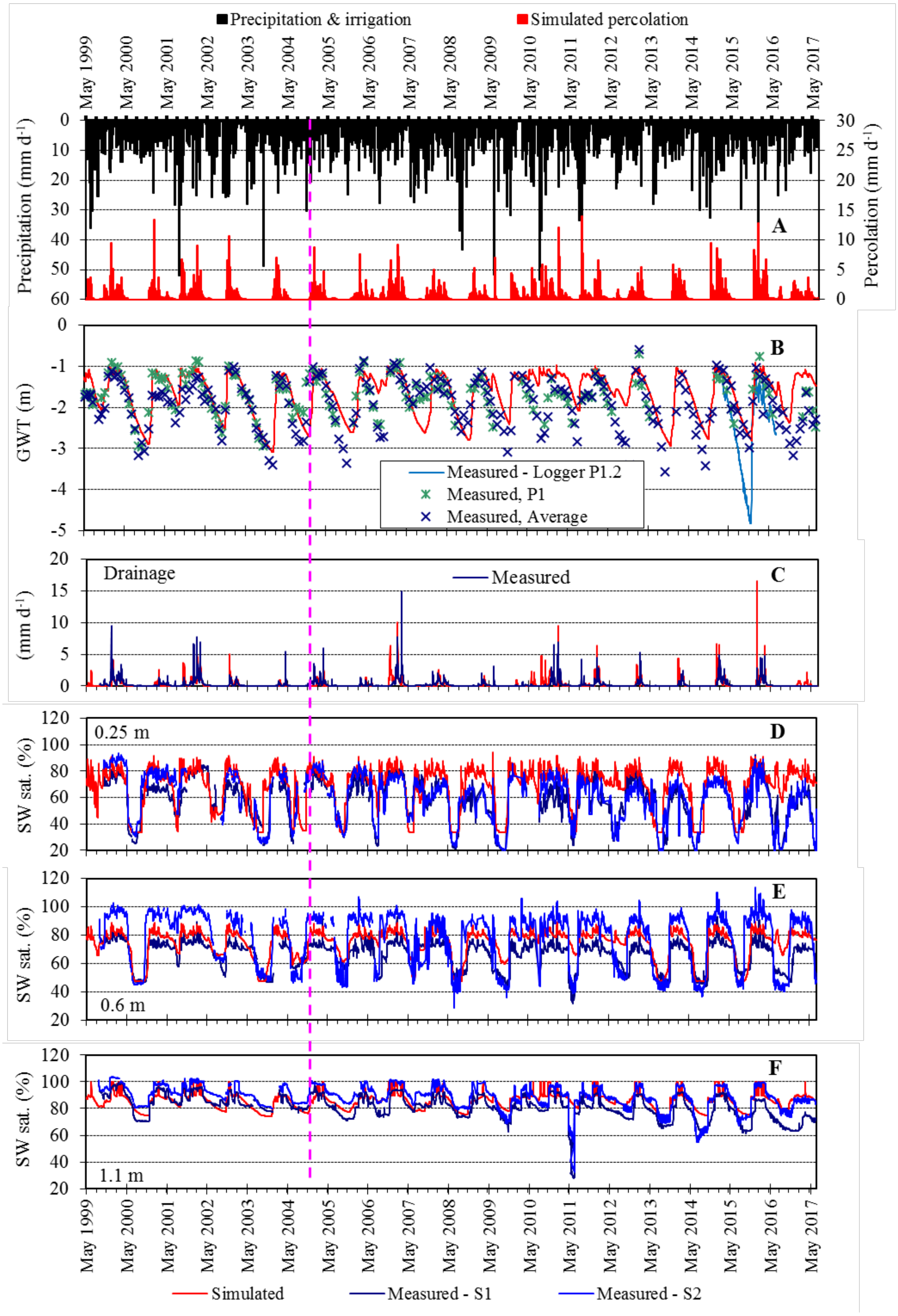


Figure 6.2. Soil water dynamics at **Faardrup.** Measured precipitation and simulated percolation 1 m b.g.s. (A), simulated and measured groundwater table, GWT (B), simulated and measured drainage (C), and simulated and measured soil water saturation (SW sat.) at three different soil depths (D, E and 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 2017).

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; (i) a very local and uncertain picture of the overall bromide leaching as well as (ii) an indication of the local variability in leaching of bromide. Supporting this is that the bromide concentration level in 2 m depth at S2 is approximately comparable to the one measured in the drainage (not present during the hydrological year 2016/2017) collected from 1 m depth, such that the concentration measured in water from 2 m depth at S2 could be caused by focused preferential bromide transport.

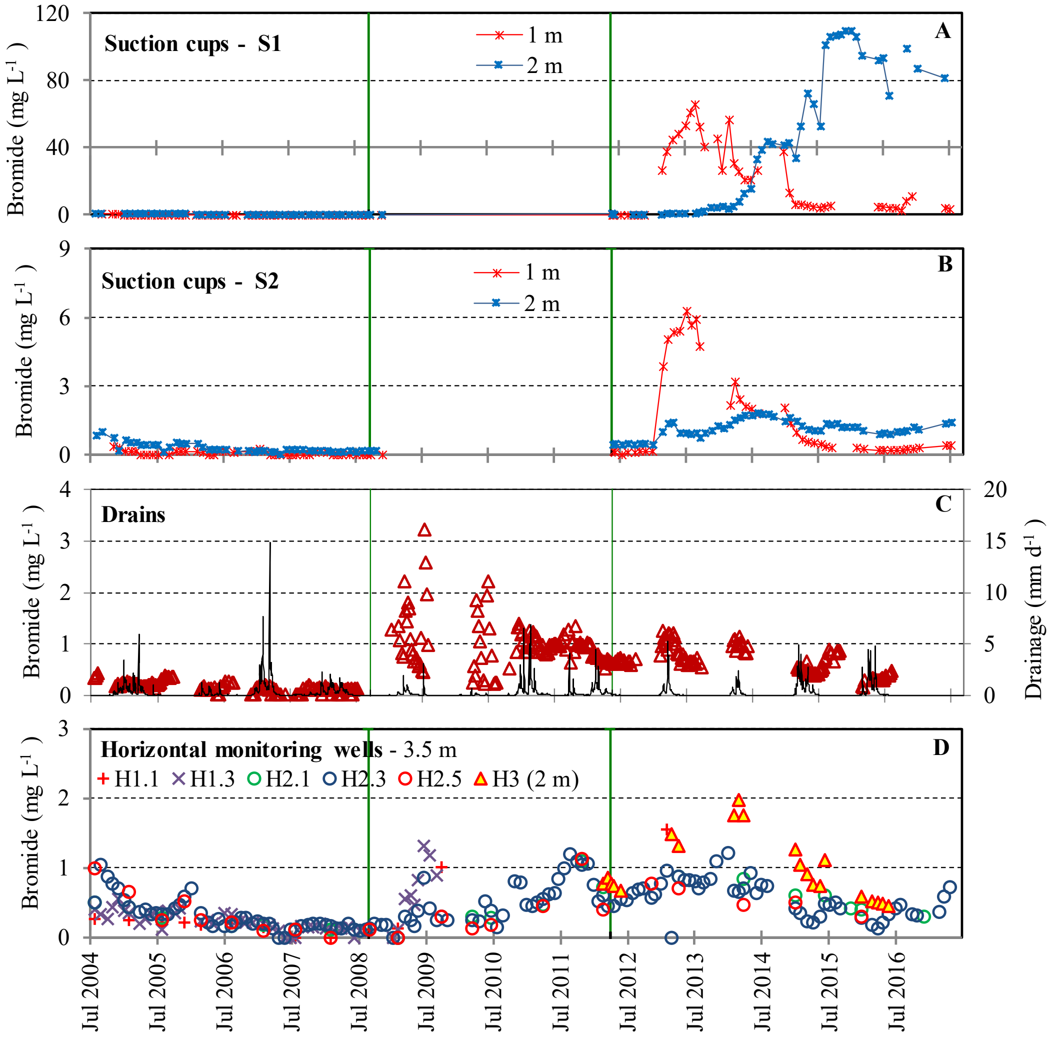


Figure 6.3. Bromide concentrations at **Faardrup** in the period July 2004–June 2017. A and B refer to suction cups located at S1 and S2. The bromide concentration is also shown for drainage runoff (C) and the horizontal monitoring wells. The horizontal wells H1 and H2 are situated 3.5 m b.g.s., and 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.

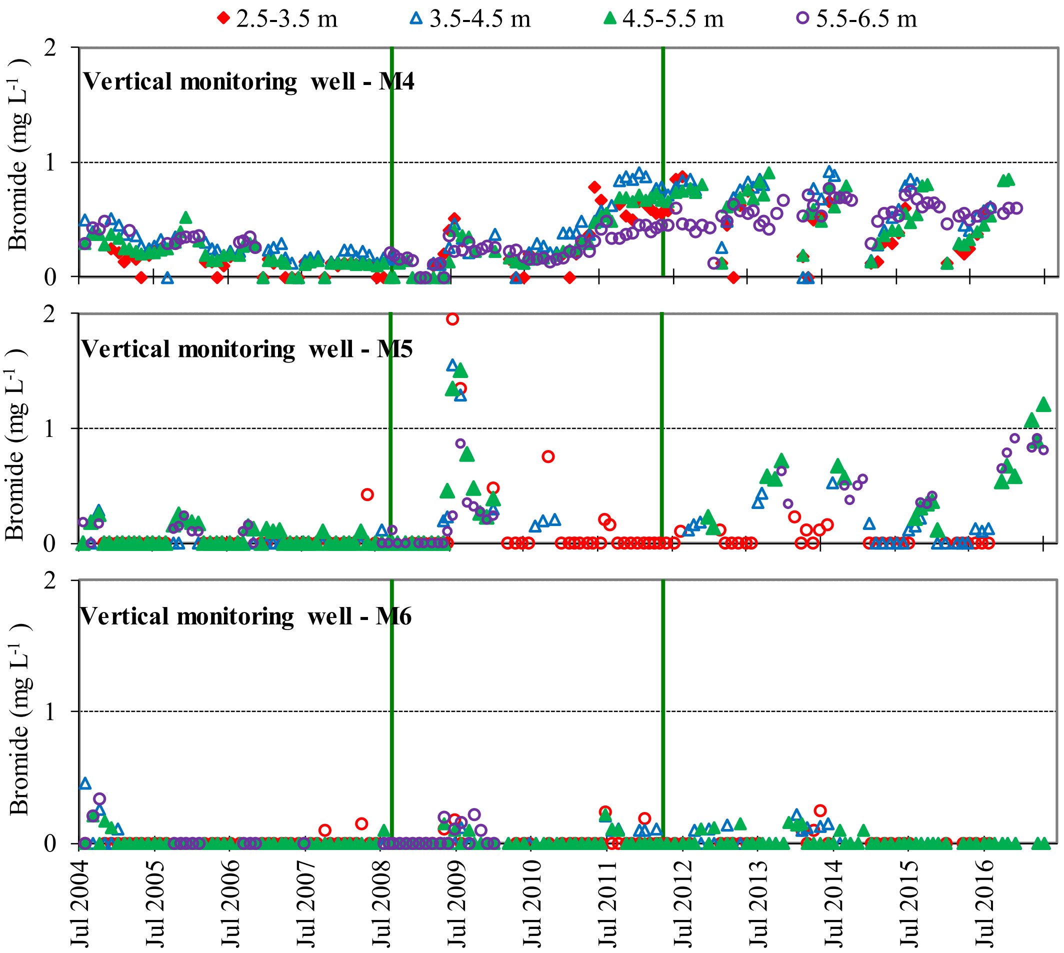


Figure 6.4. Bromide concentrations at **Faardrup** in the period July 2004–June 2017. The data derive from the vertical monitoring wells (M4, M5 and M6). Screen depth is indicated in m b.g.s. The green vertical lines indicate the dates of the two most recent bromide applications.

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/monitor_uk/index.html). Bentazone was included in the monitoring program until September 2015 (Table 6.2). Therefore, the results are included in this report.

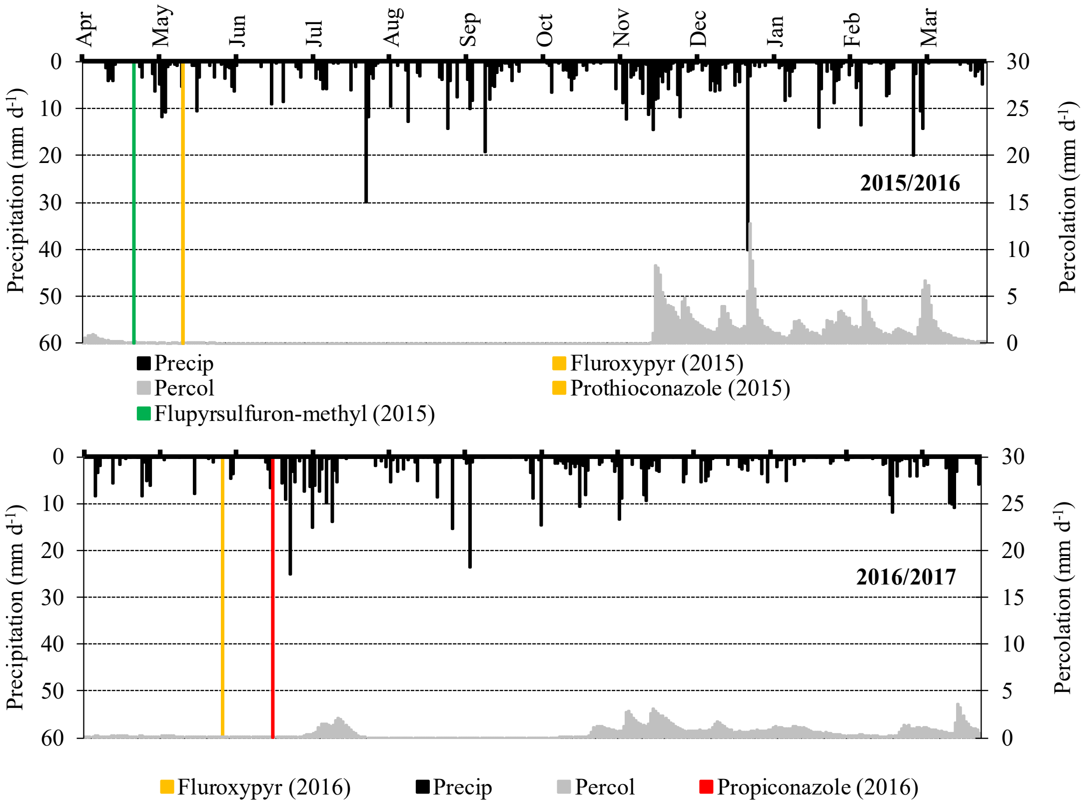


Figure 6.5. Application of pesticides included in the monitoring programme and precipitation (primary axis; Precip) together with simulated percolation (secondary axis; Percol) at **Faardrup** in 2015/2016 (upper) and in 2016/2017 (lower).

Due to too high expenses on analyses, the monitoring of the degradation product 1,2,4-triazole, which may originate from both tebuconazole and prothioconazole, had to be suspended on 9 September 2015 until May 2016 (Figure 6.5). In addition to the economic constraints, new compounds where not 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 years before (in April 2014 and May 2015) there was a risk of some background concentrations stemming from the two degration products. This proved not to be the case as samples of drainage and groundwater contained neither of the two compounds. Until now 17 drainage samples and 71 groundwater samples were collected without detection fluroxypyr pyridinol or fluroxypyr methoxypyridine. Monitoring continues.

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 [$\mu g\ L^{-1}$] 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 Red fescue 2010	Fighter 480	Bentazone(P)	Jun 10	Jun 15*	693	327	49	29	<0.01
	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 White clover 2012	Glyphogan	Glyphosate(P)	Oct 11	Aug 12	425	17	56	17	<0.01
		AMPA(M)	Oct 11	Aug 12	425	17	56	17	<0.01
	Fighter 480	Bentazone(P)	May 12	Sept 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	Sept 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	Oct 16	796	241	94	81	<0.01
		IN-JV460(M)	Nov 14 +Apr 15	Oct 16	796	241	94	81	<0.01
		IN-KY374(M)	Nov 14 +Apr 15	Oct 16	796	241	94	81	<0.01
		IN-KC576(M)	Nov 14 +Apr 15	Oct 16	796	241	94	81	<0.01
Spring Barley 2016	Starane 180S Fluroxypyr(P)	Fluroxypyr methoxy-pyridine(M)	May 15	Jun 17*	785	286	46	0	<0.01
		Fluroxypyr pyrdinol(M)	May 15	Jun 17*	785	286	46	0	<0.01
	Bumper 25 EC Propiconazole(P)1)	1,2,4-triazole(M)	June 16	Jun 17*	621	204	129	23	<0.01
Spring Barley 2017	Zypar Florasulam(P) Halauxifen-methyl (P)	TSA (M) X-575 (M)	June 17	Jun 17*	-	-	-	-	-
	Bumper 25 EC Propiconazole(P)1)	1,2,4-triazole(M)	June 17	Jun 17*	-	-	-	-	-

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 $\mu g\ L^{-1}$) 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 $\mu g\ L^{-1}$) 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 was stopped September 2015.

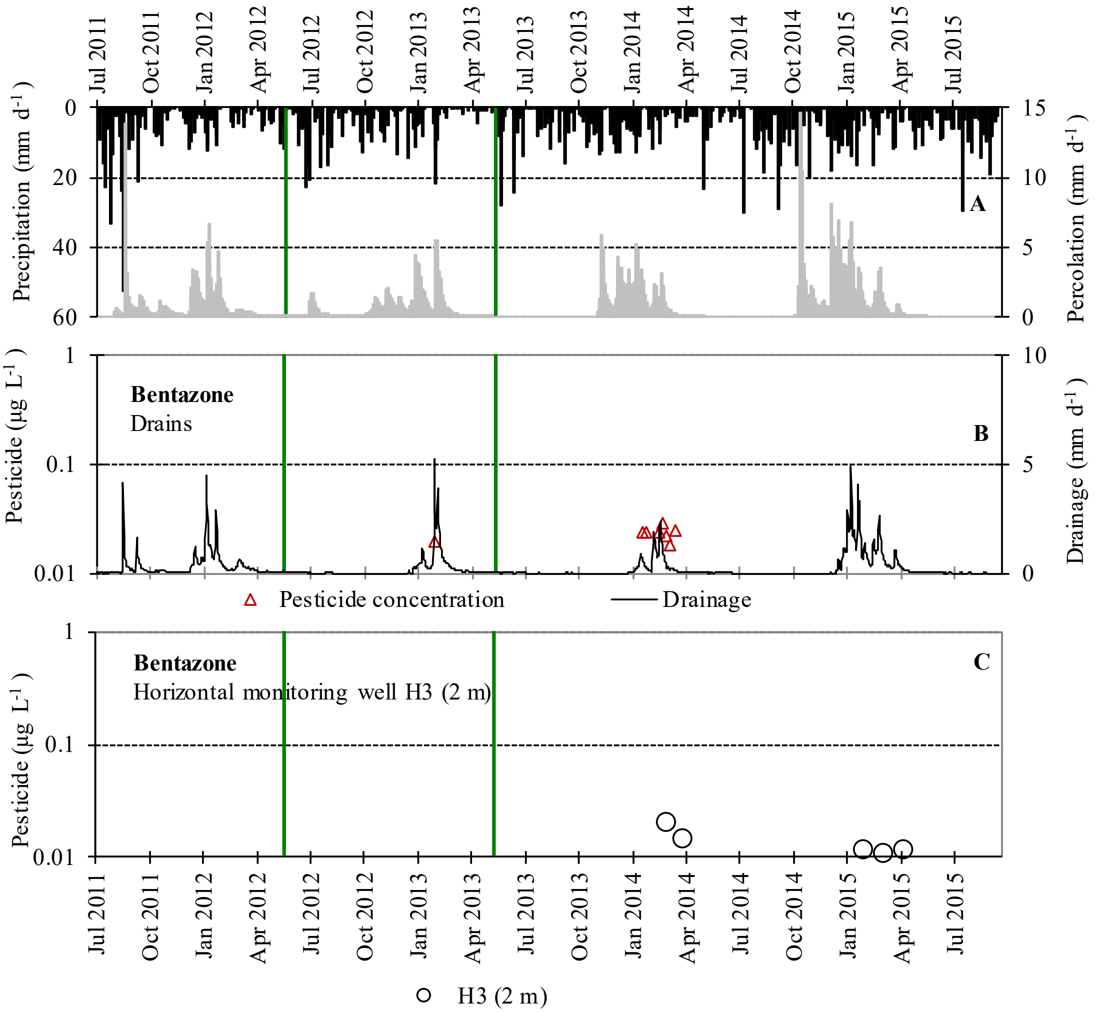


Figure 6.6. **Bentazone** detection at **Faardrup**: Precipitation and simulated percolation 1 m b.g.s. (A) together with the concentration of bentazone detections in water samples collected from drainage (B) and groundwater (C). The green vertical lines indicate the dates of bentazone applications. Water samples without detections of bentazon is not presented.

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 in major amounts in soil 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 tebuconazole 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. On 16 June 2016, the fungicide propiconazole (Figure 6.5 and Table 6.2) was applied and the degradation product, **1,2,4-triazole,** was once again included in the monitoring (Figure 6.5). 14 days before application the concentration in drainage was found to be 0.04 µg L^{-1} whereas in groundwater no 1,2,4-triazole was detected. Since the day of the propiconazole application, there has been no water flowing in the tile drain system. Until July 2017, a total of 94 groundwater samples were collected of which seven contained 1,2,4-triazole with maximum concentration being 0.02 µg L^{-1} in the depth 2 to 4 m (Figure 6.7). Monitoring is being continued.

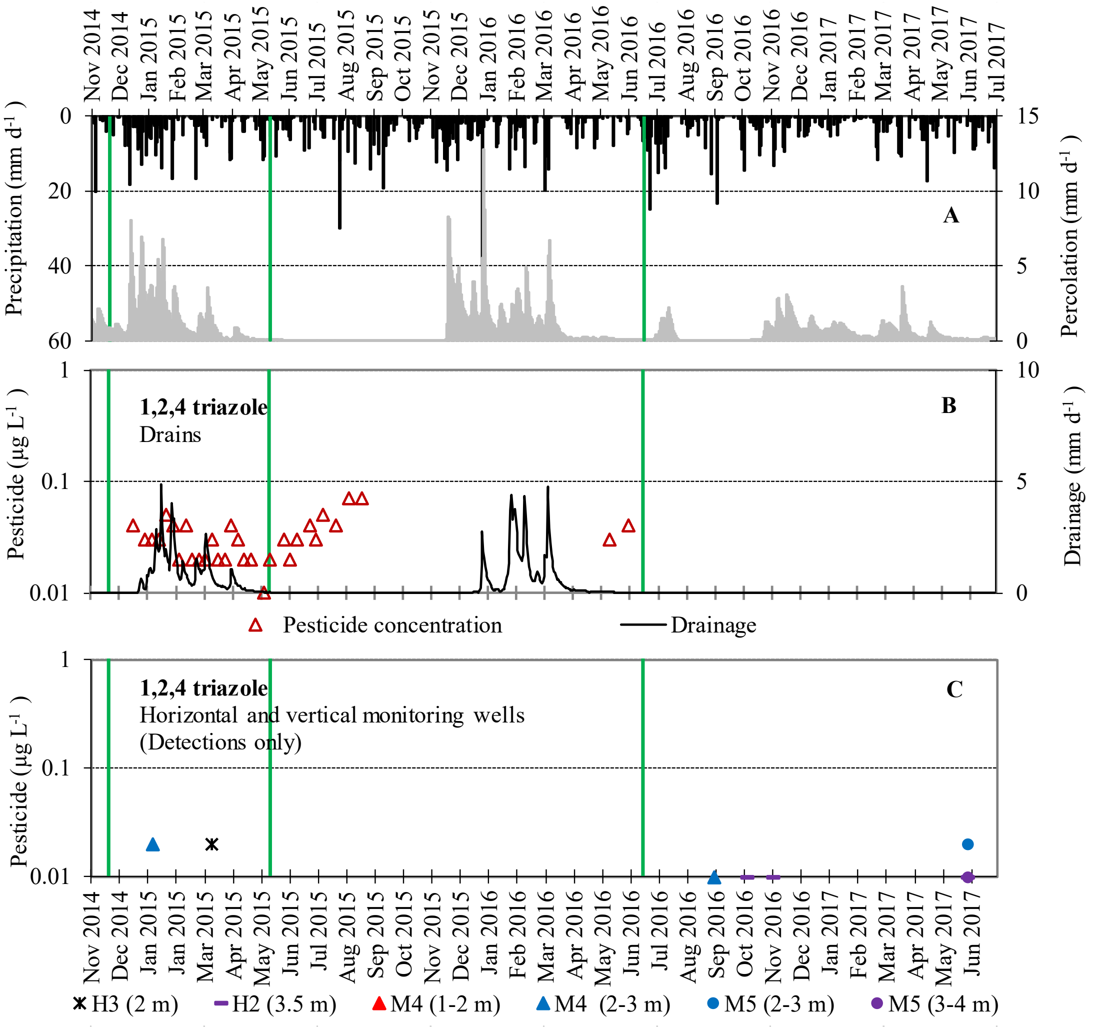


Figure 6.7. **1,2,4-triazole** detections at **Faardrup**: Precipitation and simulated percolation 1 m b.g.s. (A) together with the concentration of 1,2,4-triazole in water samples collected from drainage (B) and groundwater (C). Note that no samples were analysed for 1,2,4-triazole between August 2015 and May 2016 given economic constraints. The green vertical lines indicate the date of the tebuconazole, prothioconazole and propiconazole 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 2016 to June 2017 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 2016 to June 2017, 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 QC 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. Compounds in ampoule no. 1 are dissolved in acetonitrile and in MTBE in no. 2.

Compound	Ampoule concentration [µg L^{-1}]	Ampoules	High-level control [µg L^{-1}]	Low-level control [µg L^{-1}]
1,2,4-triazole	1000	2	0.117	0.050
8-hydroxy-bentazon	1000	1	0.117	0.050
AMBA	1000	1	0.117	0.050
AE F130619	1000	1	0.117	0.050
CGA 192155	1000	1	0.117	0.050
CyPM	1000	1	0.117	0.050
Fluroxypyr-pyridinol	1000	1	0.117	0.050
Fluroxypyr-methoxypyridine	1000	1	0.117	0.050
IN-JV460	1000	1	0.117	0.050
IN-KC576	1000	1	0.117	0.050
Methyl-bentazon	1000	1	0.117	0.050
Triazineamine	1000	1	0.117	0.050

7.2 Results and discussion

7.2.1 Internal QA

Ideally, the analytical procedure provides precise and accurate results. However, in the real world results from analysis are subject to a certain standard deviation. Such standard deviation may be the combined result of several contributing factors. Overall, the accuracy of an analytical result reflects two types of error: Random errors related to precision and systematic errors relating to bias. In a programme like PLAP it is relevant to consider possible changes in analytical “reliability over time”. As random and systematic errors may both change over time it is relevant to distinguish between standard deviations resulting from *within-day* variation as opposed to those associated with *between-day* variation in the analytical 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 20 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 0.009, S_b 0.010 and S_t was 0.014, 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 (6-hydroxy-bentazone S_b/S_w ratio 2.7, 8-hydroxy-bentazone S_b/S_w ratio 3.4, bentazone S_b/S_w ratio 2.1, and IN-JV 460 S_b/S_w ratio 2.1). For these compounds, the results indicate that day-to-day variation makes a significant contribution.
Nine compounds fulfilled 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.

Last year, the compounds: AE-F092944, AE-F130619, flupyrsulfuron-methyl, foramsulfuron, IN-JV460, IN-KC576 and IN-KY374 were introduced in the analytical programme. The data included in this year’s report still rely on few duplicate samples and the methods are still being improved.

This year, five new compounds: 6-hydroxy-bentazone, 8-hydroxy-bentazone, N-methyl-bentazone, fluroxypyr-pyridine and fluroxypyr-pyridinol were included in the QA monitoring programme. Data for these compounds only rely on very few duplicate samples and the methods are still being improved.

6-hydroxy-bentazone and **8-hydroxy-bentazone**: Both compounds have a ratio above two (2.7 and 3.4, respectively), but these high S_b/S_w ratios are caused by the between-day deviation (S_b: 0.013 and 0.014) being relatively high compared to the very low S_w (0.005 and 0.004). However, as both S_w and S_b are still very low and the statistics only rely on data from 12 duplicate samples, this actually indicates an analytical procedure in good control, although there is still room for improvement of the analytical method.

Bentazone and **N-methyl-bentazone**: Although the S_b/S_w-ratio for bentazone is 2.1, the method is still in full control with very low S_b (0.004 µg L^{-1}) and S_w (0.002 µg L^{-1}) deviations. The method for N-methyl-bentazone is similarly in good control, with low deviations in addition to a low S_b/S_w-ratio (1.4).

Fluroxypyr-pyridine, **fluroxypyr-pyridinol**, **flupyrsulfuron-methyl**, and **IN-KY374**: All four compounds have significant day-to-day contribution to the variance in the measurements. The statistical analyses are however based on very few duplicate samples (6 to 12) and not yet sufficient to do a thorough statistical analysis. Data should therefore be considered tentative. Except for a high within-day deviation for IN-KY374 (S_w - 0.026 µg L^{-1}), the standard deviations of the analyses all four compounds were low.

IN-JV460: This year the analysis of the compound meets the criteria of normality, but the S_b/S_w ratio is slightly increased and is now 2.1. However, the method has improved since last year with decreased deviations both within- and between days. The increased S_b/S_w ratio is due to the between-day standard deviation (S_b – 0.012) being relatively high compared to the within-day deviation (S_w – 0.006). Both deviations are, however, acceptable and data only rely on 7 duplicate samples. It still may be possible to improve the analytical procedure for this compound and, especially, bring down the between-day deviations.

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 below 2 during the last three years. The ratio is even further decreased from 1.1 last year to 0.9 this year. 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. Although, MNBA this year has the highest total standard deviation (S_t - 0.028 µg L^{-1}), the method is still improving and this year's results indicate that it may be possible to further improve the analytical procedure for this compound and thus bring down these deviations.

When all compounds are considered, no compounds have S_b/S_w ratios higher than 3.4 (observed for 8-hydroxy-bentazone), and in total only four compounds had ratios > 2.0, which is an improvement compared to the last couple of year's reports. 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 these between-day contributions are, however, significant on the 0.05 significance level. Four compounds had significant between-day contributions, but the number of data-sets was insufficient to do a thorough statistical analysis.

In general, the data suggests that the analytical procedure used for quantification of the compounds in this reporting period is good and in general has improved or is in line with last year's reporting period.

Table 7.2. Internal QA of pesticide analyses carried out in the period 1.7.2016-30.6.2017. Results of the test for normality, one-way analysis of variance (ANOVA), the estimated values of standard deviations (w: within-day, b: between-day, t: total – see text for details), pesticide concentration in internal QA sample (Conc.) and number of duplicate samples (n) are given for each pesticide. For test the P value $\alpha=0.05$ was used.

Compound	Normal Distribut. $\alpha=0.05$	Significant S_b Between day contribut. ANOVA $\alpha=0.05$	S_w ($\mu g\ L^{-1}$)	S_b ($\mu g\ L^{-1}$)	S_t ($\mu g\ L^{-1}$)	Ratio S_b/S_w	n	Conc. ($\mu g\ L^{-1}$)
*1,2,4-triazol**	-	-	0.003	0.004	0.005	1.4	48	0.03
*6-hydroxy-bentazone**	-	-	0.005	0.013	0.014	***2.7***	12	0.05
*8-hydroxy-bentazone**	-	-	0.004	0.014	0.014	***3.4***	12	0.05
*AE-F130619**	yes	-	0.009	0.016	0.018	1.8	26	0.1
*AMBA**	yes	-	0.008	0.011	0.014	1.3	28	0.1
Azoxystrobin	yes	-	0.003	0.004	0.006	1.3	28	0.05
Bentazone	-	-	0.002	0.004	0.004	***2.1***	17	0.05
*CyPM**	-	-	0.010	0.013	0.017	1.4	20	0.05
Flupyrsulfuron-methyl	yes	yes	0.005	0.004	0.007	0.7	6	0.1
*Fluroxypyr-methoxypyridine**	yes	yes	0.004	0.003	0.005	0.6	12	0.05
*Fluroxypyr-pyridinol**	yes	yes	0.006	0.006	0.009	0.9	12	0.05
Foramsulfuron	yes	-	0.008	0.013	0.015	1.6	26	0.1
*IN-JV460**	yes	-	0.006	0.012	0.013	***2.1***	7	0.1
*IN-KC576**	yes	-	0.011	0.018	0.021	1.7	7	0.1
*IN-KY374**	-	yes	0.026	0.004	0.027	0.1	8	0.1
*MNBA**	-	-	0.021	0.019	***0.028***	0.9	26	0.1
Mesotrione	-	-	0.007	0.013	0.014	1.9	28	0.1
*N-methyl-bentazone**	-	-	0.004	0.006	0.007	1.4	14	0.05
*Triazinamin**	-	-	0.013	0.009	0.016	0.7	26	0.11

**Degradation product.*

The total standard deviation (S_t) of the various analyses of pesticides and degradation products lie within the range 0.004-0.028 $\mu g\ L^{-1}$, the highest value observed for MNBA. 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 22 blank samples made from HPLC water were analysed in the period 1st June 2016 to 30th of June 2017 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 1.7.2016-30.6.2017. 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). *Italic* is used for recoveries outside the range of 70-120%.

Compound	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	128	200	131	140	128	186	122	126	100	142	11/11	22
8-hydroxy-bentazone	*40*	*51*	*63*	*60*							56	4*/6	12
AE-F130619					*46*	*40*	80	77			61	6/6	12
CyPM							114	89			101	3/3	6
Fluroxypyr-methoxypyridine									105	112	108	3/3	6
Fluroxypyr-pyridinol									*64*	82	73	3/3	6
N-methyl-bentazone	88	83	84	80							84	6/6	12
Triazinamin					80	83	83	80			81	6/6	12

**The concentration in two of the spiked samples (Low) were below detection limit and therefore missing*

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 30 samples were spiked in this reporting period. In general, the recovery of the spiked compounds is acceptable (i.e. in the range 70% to 120%), but the broad range of average recoveries in the samples indicates for some compounds that 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 QC external data, especially for 8-hydroxy-bentazone and AE-F130619, points to the need of keeping track of these particular compounds.

In 2015, 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 QC (concentration in QC_{low} is 0.05 µg L^{-1}) are within the acceptable range, except for 1,2,4-triazole, 8-hydroxy-bentazone and AE-F130619. The degradation product 1,2,4-triazole has an elevated recovery of up to 200%, which seems to reflect the background concentration (ranging from 0.02 to 0.05 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 22 samples and in combination with the internal QC samples, the QA program confirms that the analytical method is acceptable (refer Appendix 6, Figure A6.1).

The recoveries of 8-hydroxy-bentazone and AE-F130619 in both the external spiked QC_{low} and QC_{high} samples are slightly lower than acceptable, but the internal QC data shows that the analytical method for 8-hydroxy-bentazone and AE-F130619 are acceptable and that the method for AE-F130619 has improved during the reporting period. We will have extra focus on these compounds in the future.

Except 8-hydroxy-bentazone (two QC_{low} samples), were all compounds included in the spiking procedure (Table 7.1) detected in the samples by the commercial laboratory.

During the 2016/2017 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. Analytical data (both internal and external QC samples) for all analytes included in this year's analytical program is presented in Appendix 6.

7.3 Summary and concluding remarks

The QA system showed that:

- The internal QC indicates that the reproducibility of the pesticide analyses was good, and slightly better than last year, with total standard deviation (S_t) in the range 0.005-0.028 $\mu g\ L^{-1}$.

- As demonstrated by the external QA, recovery was generally good in externally spiked samples, except for 8-hydroxy-bentazone.

- 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. No false-positives samples were detected.

8 Summary of monitoring results

This section summarizes the monitoring data from the entire monitoring period, i.e. both data from the two most recent monitoring years (detailed in this report) and data from the previous monitoring years (detailed in previous reports 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 2017, 115 pesticides and/or degradation products (50 pesticides and 65 degradation products) have been analysed in PLAP, comprising five agricultural fields (1.2 to 2.4 ha) cultivated with different crops. The total number of compounds is the same as in the latest PLAP-report (Rosenbom *et al.*, 2017), however metsulfuronmethyl is now correctly given as a degradation product and not as a pesticide like in earlier reports. With 12 new compounds included in the hydrological year 2015-2016, no new compounds could, given economical constrains, be added for an evaluation in the hydrological year 2016-2017. The leaching as a result of the application(s) of 53 pesticides have been evaluated hereamong:

- 16, where only the pesticide was analysed (including epoxiconazole and propiconazole even though their degradation product 1,2,4-triazole is detected, but it is only included as an outcome of tebuconazole in the table 8.2 and 8.4)
- 34, where the pesticide was analysed together with one or more of its degradation products
- 3 (fludioxonil, mancozeb and tribenuron-methyl), where it was only the degradation prodcts of the pesticide, which was analysed

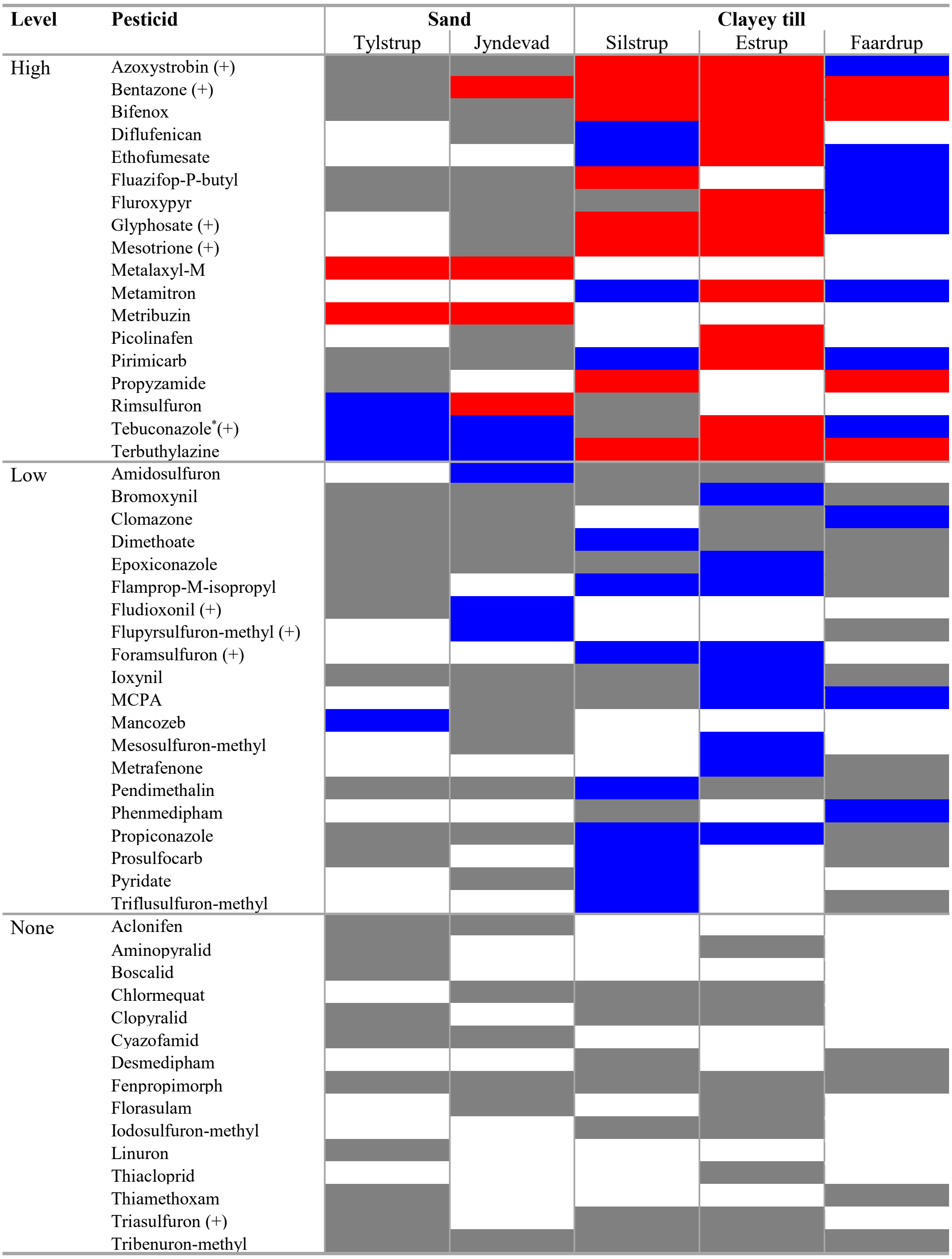
Since it is the application of a specific pesticide on a specific crop, which is under evaluation for the direct application in the pesticide regulatory work of the Danish EPA, all collected monitoring results including analyses of water samples for its degradation products refers to the specific pesticide. Of the 53 pesticides (50+3) being chosen for test in PLAP, 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 above 0.1 µg L^{-1} (Table 8.1 and 8.2). Only five of the 17 pesticides resulted in detections indicating a potential 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 azole fungicides including the use as seed treatment. This is evaluted further in PLAP. The PLAP-results on 1,2,4-triazole have led to a 1,2,4-triazole screening in the Danish National Groundwater Monitoring Programme (GRUMO). Based on the results from GRUMO and PLAP 1,2,4-triazole was included in the Danish Waterworks Drilling Control. The following 10 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, 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 potential 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 previousely 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 756 (Silstrup) + 765 (Estrup) groundwater samples taken at Silstrup and Estrup, 100 (Silstrup) + 41 (Estrup) samples contained CyPM, whereof 12 (Silstrup) + 5 (Estrup) exceeded 0.1 µg L^{-1}. 9 of 12 (Silstrup) and 4 of 5 (Estrup) 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 intersected by 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 more than two and five years to the groundwater at Silstrup and Estrup, respectively, (Jørgensen *et al.*, 2012).

Table 8.1. Level of detections in water collected from drainage and suction cups at **1 m depth** of pesticides and/or their degradation products at the five PLAP fields. Pesticides applied in spring 2017 are not included in the table. (+) indicates that the pesticide and/or its degradation product is included in the monitoring programme July 2015 – June 2017.



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

🟥	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.
🟦	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.
▨	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, propiconazole and prothioconazole.

Table 8.2. Monitoring output from drainage at **1 m depth** and suction cups at **1 m depth** (and 2 m depth for Tylstrup) given for each of the five fields as the total number (T) of samples analysed for the specific analyte (various pesticides and/or their *degradation products*), number of detections (D), number of detections exceeding 0.1 µg L^{-1} (X) and the max conc. M (µg L^{-1}). The pesticide and *degradation products* (if analysed) are listed under Analyte. The pesticides (including degradation products) are listed in regard to the level of detections as in Table 8.1.

Analyte	**Tylstrup**				**Jyndevad**				**Silstrup**				**Estrup**				**Faardrup**			
(Pesticide/*degradation product*)	T	D	X	M	T	D	X	M	T	D	X	M	T	D	X	M	T	D	X	M
Azoxystrobin	95	0	0	-	65	0	0	-	188	23	1	0.11	415	141	15	1.40	106	0	0	-
CyPM	95	0	0	-	65	0	0	-	211	152	24	0.56	415	376	150	2.10	106	4	0	0.06
Bentazone	177	3	0	0.02	213	96	15	4.5	120	45	5	6.4	440	226	16	20	202	28	6	43
2-amino-N-isopropyl-benzamide	72	0	0	-	47	2	0	0.03	65	0	0	-	243	1	0	0.06	68	1	0	0.06
6-hydroxy-bentazone	40	0	0	-	26	0	0	-												
8-hydroxy-bentazone	40	0	0	-	26	0	0	-												
N-methyl-bentazone	40	0	0	-	26	0	0	-												
Bifenox	22	0	0	-	56	2	0	0.04	68	5	2	0.38	95	4	1	0.15	62	6	0	0.09
Bifenox acid	22	0	0	-	53	1	0	0.1	56	20	18	4.8	105	16	10	1.9	42	18	17	8.6
Nitrofen	22	0	0	-	56	0	0	-	68	5	3	0.34	95	0	0	-1	62	6	1	0.16
Diflufenican					38	0	0	-	66	11	1	0.12	57	27	12	0.49				
AE-05422291					38	0	0	-	66	0	0	-	57	0	0	-				
AE-B107137					52	0	0	-	61	5	1	0.13	58	18	0	0.09				
Ethofumesate									201	20	3	0.23	126	35	8	3.36	192	15	6	12
Fluazifop-P-butyl																	128	0	0	-
Fluazifop-P	65	0	0	-	51	0	0	-	175	0	0	-					160	11	3	3.8
TFMP									132	53	23	0.64					91	0	0	-
Fluroxypyr	70	0	0	-	55	0	0	-	50	0	0	-	90	3	2	1.4	256	1	1	0.19
Fluroxypyr-methoxypyridine																	1	0	0	-
Fluroxypyr-pyridinol																	1	0	0	-
Glyphosate					72	0	0	-	257	108	22	4.7	601	343	109	31	236	5	0	0.09
AMPA					72	1	0	0.01	258	203	18	0.35	601	499	120	1.6	236	15	1	0.11
Mesotrione					67	0	0	-	49	13	7	1.10	63	39	10	3.3				
AMBA					67	0	0	-	49	0	0	-	63	4	0	0.04				
MNBA					67	0	0	-	49	8	0	0.09	63	11	1	0.46				
Metalaxyl-M	156	4	0	0.03	95	11	0	0.04												
CGA 108906	153	128	35	4.8	105	68	34	3.7												
CGA 62826	154	35	5	0.12	105	73	20	1.2												
Metamitron									200	49	11	0.55	123	42	15	26.37	192	12	2	1.70
Desamino-metamitron									201	64	7	0.67	125	49	11	5.55	192	16	4	2.50
Metribuzin	91	2	0	0.02	6	0	0	-												
Desamino-diketo-metribuzin	249	81	51	2.1	6	0	0	-												
Desamino-metribuzin	87	0	0	-	4	0	0	-												
Diketo-metribuzin	334	253	61	0.69	6	3	0	0.09												
Picolinafen					36	1	0	0.02					81	17	0	0.07				
CL 153815					36	0	0	-					81	31	11	0.50				
Pirimicarb	82	0	0	-	69	0	0	-	233	14	0	0.05	205	40	0	0.08	228	7	0	0.06
Pirimicarb-desmethyl	81	0	0	-	69	1	0	0.01	233	1	0	0.05	198	0	0	-	129	6	0	0.05
Pirimicarb-desmethyl-formamido	52	0	0	-	69	0	0	-	161	0	0	-	230	26	13	0.38	129	3	0	0.04
Propyzamide	82	0	0	-					66	23	6	1.6					124	4	2	0.51
RH-24580	82	0	0	-					66	2	0	0.02					124	0	0	-
RH-24644	82	0	0	-					66	15	0	0.05					124	4	0	0.02
RH-24655	58	0	0	-					66	0	0	-					124	1	0	0.02
Rimsulfuron	65	0	0	-	52	0	0	-												
PPU	268	194	3	0.15	233	194	64	0.29	1	0	0	-								
PPU-desamino	268	63	0	0.04	233	123	6	0.18	1	0	0	-								
Tebuconazole	77	0	0	-	58	0	0	-	19	2	0	0.08	81	41	17	2.00	54	4	0	0.05
*1,2,4-triazole**	72	12	2	0.16	54	32	8	0.27	3	3	0	0.05	106	106	102	0.45	33	31	0	0.07
Terbuthylazine	72	0	0	-	79	0	0	-	91	60	9	1.55	161	112	34	11.0	110	41	11	10.0
2-hydroxy-desethyl-terbuthylazine	72	5	0	0.02					71	28	1	0.11	131	87	24	6.30	68	8	1	1.00
Desethyl-terbuthylazine	72	2	0	0.01	150	20	0	0.06	116	108	44	1.08	164	146	35	8.20	110	89	7	8.30
Desisopropylatrazine	72	17	0	0.04					71	43	0	0.04	161	71	1	0.44	110	25	1	0.36
Hydroxy-terbuthylazine	72	1	0	0.04					71	26	0	0.04	131	88	16	0.99	110	21	1	0.58
	72	5	0	0.02					71	28	1	0.11	131	87	24	6.3	68	8	1	1.00

Table 8.2 (Continued). Monitoring output from drainage at **1 m depth** and suction cups at **1 m depth** (and 2 m depth for Tylstrup) given for each of the five fields as the total number (T) of samples analysed for the specific analyte (various pesticides and/or their *degradation products*), number of detections (D), number of detections exceeding 0.1 µg L^{-1} (X) and the max conc. M (µg L^{-1}). The pesticide and *degradation products* (if analysed) are listed under Analyte. The pesticides (including degradation products) are listed in regard to the level of detections as in Table 8.1.

Analyte	**Tylstrup**				**Jyndevad**				**Silstrup**				**Estrup**				**Faardrup**			
(Pesticide/*degradation product*)	T	D	X	M	T	D	X	M	T	D	X	M	T	D	X	M	T	D	X	M
Amidosulfuron					23	3	1	0.11	1	0	0	-	100	0	0	-				
Desmethyl-amidosulfuron					23	0	0	-	1	0	0	-								
Bromoxynil	72	0	0	-	61	0	0	-	48	0	0	-	142	3	2	0.60	174	0	0	-
Clomazone	82	0	0	-	23	0	0	-	19	0	0	-	60	0	0	-	85	1	1	0.28
FMC 65317	74	0	0	-	23	0	0	-	19	0	0	-	60	0	0	-	85	1	1	0.30
Clopyralid	107	2	1	0.72					79	4	3	4.09	1	0	0	-	32	1	0	0.08
Dimethoate	65	0	0	-	52	1	0	-	109	1	1	1.42	111	0	0	-	77	0	0	-
Epoxiconazole	74	0	0	-	90	0	0	-	36	0	0	-	49	14	2	0.39	81	0	0	-
Flamprop-M-isopropyl	65	0	0	-					109	12	1	0.11	155	20	0	0.07	71	1	0	0.04
Flamprop	65	0	0	-					108	7	0	0.10	155	13	0	0.03	77	1	0	0.09
Fludioxonil																				
CGA 192155	344	0	0	-	438	2	0	0.05												
CGA 339833	344	0	0	-	416	2	2	0.37												
Flupyrsulfuron-methyl					30	0	0	-									36	0	0	-
IN-JV460					30	0	0	-									36	0	0	-
IN-KC576					30	0	0	-									36	0	0	-
IN-KY374					30	4	3	0.45									36	0	0	-
Foramsulfuron									48	10	2	0.24	62	20	3	0.32				
AE-F092944									48	0	0	-	62	1	0	0.01				
AE-F130619									48	10	0	0.07	62	6	0	0.06				
Ioxynil	72	0	0	-	61	0	0	-	48	0	0	-	142	20	5	0.25	173	1	0	0.01
MCPA					56	0	0	-	51	0	0	-	103	12	2	3.89	143	2	1	0.28
2-methyl-4-chlorophenol					56	0	0	-	51	0	0	-	103	1	0	0.05	143	1	1	0.24
Mancozeb																				
EBIS	27	0	0	-	10	0	0	-												
ETU	44	7	0	0.04																
Mesosulfuron-methyl					78	0	0	-					75	13	0	0.06				
Mesosulfuron					45	0	0	-					74	0	0	-				
Metrafenone													120	20	0	0.07	59	0	0	-
Pendimethalin	144	0	0	-	71	0	0	-	105	14	0	0.06	243	72	29	32.00	57	2	0	0.04
Phenmedipham									160	0	0	-					128	0	0	-
3-aminophenol									109	0	0	-								
MHPC									160	0	0	-					128	2	1	0.19
Propiconazole	89	0	0	-	89	0	0	-	109	6	0	0.03	241	26	3	0.86	251	0	0	-
Prosulfocarb	74	1	0	0.03					74	5	1	0.18					78	0	0	-
Pyridate					39	0	0	-												
PHCP					59	0	0	-	66	4	4	2.69								
Triflusulfuron-methyl									32	0	0	-					63	0	0	-
IN-D8526									32	0	0	-					63	0	0	-
IN-E7710									32	5	0	0.01					63	0	0	-
IN-M7222									32	0	0	-					63	0	0	-
Aclonifen	68	0	0	-	43	0	0	-												
Aminopyralid	91	0	0	-									96	0	0	-				
Boscalid	56	0	0	-																
Chlormequat					28	0	0	-	21	1	0	0.01	46	1	0	0.02				
Clopyralid	107	0	0	-					79	0	0	-	1	0	0	-	32	0	0	-
Cyazofamid	68	0	0	-	32	0	0	-												
Desmedipham									159	0	0	-					128	0	0	-
EHPC									100	0	0	-					99	0	0	-
Fenpropimorph	89	0	0	-	79	1	0	0.04	109	0	0	-	106	1	0	0.01	174	0	0	-
Fenpropimorph acid	75	0	0	-	79	0	0	-	109	1	0	0.02	103	0	0	-	174	0	0	-
Florasulam					54	0	0	-					92	0	0	-				
Florasulam-desmethyl					28	0	0	-					81	0	0	-				
Iodosulfuron-methyl									60	0	0	-								
Metsulfuron-methyl									60	0	0	-	154	1	0	0.05				
Linuron	67	0	0	-	67	0	0	-												
Thiacloprid													47	0	0	-				
M34													55	0	0	-				
Thiacloprid sulfonic acid													56	0	0	-				
Thiacloprid-amide													47	1	0	0.01				
Thiacloprid sulfonic acid													56	0	0	-				
Thiamethoxam	64	0	0	-													68	0	0	-
CGA 322704	64	0	0	-													68	0	0	-
Triasulfuron	82	0	0	-																
Triazinamin	76	0	0	-					66	0	0	-	180	0	0	-				
Tribenuron-methyl																				
Triazinamin-methyl	138	0	0	-	77	0	0	-	109	0	0	-	55	2	0	0.04	77	0	0	-

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

Table 8.3. Level of 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 2015 – June 2017.

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

🟥 The pesticide (or its degradation products) leached to groundwater in a concentration exceeding 0.1 µg L^{-1} within the first season after application.

🟦 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.

▨ 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, propiconazole and prothioconazole.

Table 8.4. Monitoring output from the **groundwater monitoring screens** given for each of the five fields as the total number (T) of samples analysed for the specific analyte (various pesticides and/or their *degradation products*), number of detections (D), number of detections exceeding 0.1 µg L^{-1} (X) and the max conc. M (µg L^{-1}). The pesticide and degradation products (if analysed) are listed under Analyte. The pesticides (including degradation products) are listed in regard to the level of detections as in Table 8.3.

Analyte	**Tylstrup**				**Jyndevad**				**Silstrup**				**Estrup**				**Faardrup**			
	T	D	X	M	T	D	X	M	T	D	X	M	T	D	X	M	T	D	X	M
Azoxystrobin	216	0	0	-	233	0	0	-	644	8	0	0.03	766	3	0	0.04	286	0	0	-
CyPM	216	0	0	-	233	0	0	-	756	100	12	0.52	766	41	5	0.46	286	0	0	-
Bentazone	440	0	0	-	811	1	0	0.01	406	29	3	0.44	744	44	0	0.05	527	21	4	0.60
*2-amino-N-isopropyl-benzamid*e	191	0	0	-	178	0	0	-	205	0	0	-	351	1	0	0.03	193	0	0	-
N-methyl-bentazone	110	0	0	-	138	0	0	-												
8-hydroxy-bentazone	110	0	0	-	138	0	0	-												
6-hydroxy-bentazone	110	0	0	-	138	0	0	-												
Bifenox	49	0	0	-	222	2	0	0.05	183	5	0	0.10	193	0	0	-	104	0	0	-
Bifenox acid	49	0	0	-	170	0	0	-	182	27	20	3.10	197	1	1	0.11	104	1	1	0.19
Nitrofen	49	0	0	-	222	0	0	-	183	0	0	-	193	0	0	-	104	0	0	-
Diflufenican					152	0	0	-	201	1	1	0.47	71	0	0	-				
AE-05422291					152	0	0	-	201	0	0	-	71	0	0	-				
AE-B107137					152	0	0	-	201	1	0	0.02	89	2	0	0.03				
Ethofumesate									529	5	0	0.04	204	0	0	-	362	31	6	1.4
Fluazifop-P-butyl																	232	0	0	-
Fluazifop-P	178	0	0	-	190	0	0	-	442	1	0	0.07					299	6	1	0.17
TFMP	3	0	0	-	3	0	0	-	435	87	16	0.29					238	0	0	-
Fludioxonil																				
CGA 192155	182	0	0	-	232	1	0	0.05												
CGA 339833	182	0	0	-	221	1	1	0.37												
Glyphosate					223	0	0	-	646	40	0	0.05	1017	53	6	0.67	451	5	0	0.03
AMPA					223	2	0	0.02	646	40	0	0.08	1018	8	0	0.07	451	2	0	0.03
Mesotrione					237	0	0	-	177	0	0	-	123	5	1	0.13				
AMBA					237	0	0	-	177	0	0	-	123	0	0	-				
MNBA					237	0	0	-	177	0	0	-	121	1	0	0.02				
Metalaxyl-M	352	21	0	0.08	392	88	23	1.30												
CGA 108906	352	288	47	1.50	393	278	84	2.70												
CGA 62826	352	17	0	0.04	393	174	9	0.68												
Metamitron									529	29	2	0.17	204	0	0	-	362	24	4	0.63
Desamino-metamitron									529	30	4	0.19	203	0	0	-	362	48	12	1.30
Metribuzin	388	1	0	0.01	26	0	0	-												
Desamino-diketo-metribuzin	525	236	5	0.20	26	20	13	1.83												
Desamino-metribuzin	366	0	0	-	26	0	0	-												
Diketo-metribuzin	526	453	315	0.55	26	26	19	1.37												
Propyzamide	221	0	0	-					227	9	2	0.14					360	1	0	0.03
RH-24580	221	0	0	-					227	0	0	-					360	0	0	-
RH-24644	221	0	0	-					227	2	0	0.03					360	0	0	-
RH-24655	157	0	0	-					227	0	0	-					360	0	0	-
Pyridate					116	0	0	-												
PHCP					184	0	0	-	189	14	4	0.31								
Rimsulfuron	178	0	0	-	189	0	0	-												
PPU	656	58	0	0.05	863	374	12	0.23												
PPU-desamino	656	9	0	0.03	863	98	0	0.09												
Tebuconazole	196	1	0	0.01	214	1	0	0.01	38	0	0	-	162	5	2	0.12	174	1	0	0.01
1,2,4-triazole[*]	196	80	0	0.06	308	185	1	0.15	25	0	0	-	176	158	48	0.26	211	10	0	0.04
Terbuthylazine	179	0	0	-	260	0	0	-	316	36	1	0.12	286	1	0	0.02	283	51	21	1.90
2-hydroxy-desethyl-terbuthylazine	191	1	0	0.03					236	1	0	0.02	230	0	0	-	193	7	0	0.09
Desethyl-terbuthylazine	191	0	0	-	517	27	0	0.02	375	161	2	0.14	298	7	0	0.05	283	66	30	0.94
Desisopropylatrazine	191	1	0	0.01					236	4	0	0.05	286	27	0	0.03	283	60	0	0.04
Hydroxy-terbuthylazine	191	0	0	-					236	0	0	-	230	0	0	-	283	34	0	0.07

Table 8.4 (*Continued*). Monitoring output from the **groundwater monitoring screens** given for each of the five fields as the total number (T) of samples analysed for the specific analyte (various pesticides and/or their *degradation products*), number of detections (D), number of detections exceeding 0.1 µg L^{-1} (X) and the max conc. M (µg L^{-1}). The pesticide and degradation products (if analysed) are listed under Analyte. The pesticides (including degradation products) are listed as in Table 8.3.

Analyte	**Tylstrup**				**Jyndevad**				**Silstrup**				**Estrup**				**Faardrup**			
	T	D	X	M	T	D	X	M	T	D	X	M	T	D	X	M	T	D	X	M
Aminopyralid	212	2	0	0.06									152	0	0	-				
Clopyralid	138	0	0	-					286	1	0	0.03					96	0	0	-
Desmedipham									348	1	0	0.03					232	0	0	-
EHPC									207	0	0	-					176	0	0	-
Dimethoate	176	0	0	-	190	0	0	-	222	1	0	0.09	200	0	0	-	207	0	0	-
Epoxiconazole	199	0	0	-	324	1	0	0.01	179	0	0	-	88	0	0	-	209	0	0	-
Fenpropimorph	313	0	0	-	258	1	0	0.03	222	0	0	-	189	0	0	-	306	1	0	0.02
Fenpropimorph acid	276	0	0	-	264	0	0	-	222	0	0	-	158	0	0	-	306	0	0	-
Flamprop-M-isopropyl	176	0	0	-					222	1	0	0.02	263	0	0	-	199	0	0	-
Flamprop					222	0	0	-	263	0	0	-	207	0	0	-				
Fluroxypyr	194	0	0	-	193	0	0	-	216	0	0	-	155	1	0	0.06	515	1	0	0.07
Fluroxypyr-methoxypyridine																	88	0	0	-
Fluroxypyr-pyridinol																	88	0	0	-
Foramsulfuron									169	4	0	0.04	119	0	0	-				
AE-F092944									169	0	0	-	119	0	0	-				
AE-F130619									169	9	0	0.03	119	0	0	-				
Ioxynil	198	0	0	-	218	0	0	-	159	0	0	-	166	0	0	-	306	1	0	0.01
MCPA					210	0	0	-	190	0	0	-	146	1	0	0.02	365	0	0	-
2-methyl-4-chlorophenol					210	0	0	-	191	0	0	-	146	0	0	-	365	0	0	-
Mancozeb																				
EBIS	78	0	0	-	99	0	0	-												
ETU	200	2	0	0.02																
Metrafenone													189	1	0	0.04	168	0	0	-
Phenmedipham									348	0	0	-					232	2	0	0.03
3-aminophenol									245	0	0	-								
MHPC									348	0	0	-					232	1	0	0.05
Pirimicarb	301	0	0	-	251	0	0	-	646	3	0	0.01	293	1	0	0.02	437	2	0	0.04
Pirimicarb-desmethyl	301	0	0	-	251	0	0	-	646	0	0	-	289	0	0	-	232	3	0	0.04
Pirimicarb-desmethyl-formamido	173	0	0	-	251	0	0	-	468	0	0	-	337	0	0	-	232	2	0	0.08
Propiconazole	313	0	0	-	297	0	0	-	222	0	0	-	397	2	0	0.02	511	1	0	0.04
Prosulfocarb	168	4	0	0.03					226	1	0	0.03					187	0	0	-
Triasulfuron	168	4	0	0.03																
Triazinamin	291	0	0	-					300	0	0	-	314	1	0	0.04				
Triflusulfuron-methyl									158	0	0	-					130	0	0	-
IN-D8526									158	0	0	-					130	0	0	-
IN-E7710									158	0	0	-					130	0	0	-
IN-D7222									158	1	0	0.05					130	0	0	-
Aclonifen	127	0	0	-	171	0	0	-												
Amidosulfuron					88	0	0	-					143	0	0	-				
Desmethyl-amidosulfuron					88	0	0	-												
Boscalid	111	0	0	-																
Bromoxynil	192	0	0	-	218	0	0	-	159	0	0	-	166	0	0	-	306	0	0	-
Chlormequat					14	0	0	-	102	0	0	-	74	0	0	-				
Clomazone	230	0	0	-	104	0	0	-	49	0	0	-	98	0	0	-	235	0	0	-
FMC 65317	208	0	0	-	105	0	0	-	49	0	0	-	98	0	0	-	235	0	0	-
Cyazofamid	127	0	0	-	135	0	0	-												
Florasulam					191	0	0	-					160	0	0	-				
Florasulam-desmethyl													130	0	0	-				
Flupyrsulfuron-methyl					229	0	0	-									174	0	0	-
IN-JV460					229	0	0	-									174	0	0	-
IN-KC576					229	0	0	-									174	0	0	-
IN-KY374					229	0	0	-									174	0	0	-
Iodosulfuron-methyl									250	0	0	-								
Metsulfuron-methyl									250	0	0	-	263	0	0	-				
Linuron	271	0	0	-																
Mesosulfuron-methyl					285	0	0	-					126	0	0	-				
Mesosulfuron					12	0	0	-					107	0	0	-				
Pendimethalin	436	0	0	-	257	0	0	-	344	0	0	-	140	0	0	-	180	0	0	-
Picolinafen					35	0	0	-					158	0	0	-				
CL153815					35	0	0	-					158	0	0	-				
Thiacloprid													100	0	0	-				
M34													100	0	0	-				
Thiacloprid sulfonic acid													100	0	0	-				
Thiacloprid-amide													100	0	0	-				
Thiamethoxam	175	0	0	-													184	0	0	-
CGA 322704	175	0	0	-													184	0	0	-
Tribenuron-methyl																				
Triazinamin-methyl	446	0	0	-	252	0	0	-	222	0	0	-	107	0	0	-	205	0	0	-

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

- **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 twice at 1 m depth 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. In the period from 2001 to July 2017, bentazone was detected in concentrations exceeding 0.1 µg L^{-1} in three groundwater samples from Silstrup in 2003 and in four groundwater samples from Faardrup in 2005. Bentazone has been detected in 100 out of 3169 analysed groundwater samples. In total bentazone has been analysed in 4394 water samples from drainage and groundwater. Especially application of bentazone on pea at Silstrup and maize at Faardrup 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}). The leaching of bentazone has been monitored at Faardrup until September 2015, where no detections in the water samples from drainage nor groundwater were made within the latter five months. The detections in water from the horizontal well in 2 m depth are clearly linked to periods of drainage in connection with snowmelt. In May 2016, bentazone was applied to spring barley at both Tylstrup and Jyndevad to test, whether bentazone and/or 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. However, none of the three degradation products were detected (keeping in mind that the analyses of the water samples for 8-hydroxy-bentazone has a high uncertainty). After the application of bentazone in May 2016, detections of bentazone were again monitored in the suction cups but not in the groundwater samples. At Tylstrup bentazone is detected twice in the spring 2017 in water from the suction cups at 1 m depth, whereas the detections at Jyndevad starts from August 2016. Generally, the bentazone concentration at Jyndevad seem to level off after February 2017. With a bentazone application in May 2017 at Jyndevad, the concentration level in water from 1 m depth, however, rose to 4.6 µg L^{-1} at S2 (Figure 3.7). The bentazone concentration in water from suction cups after the application in May 2017, hence, seem to be follow the leaching pattern of the application in 2012 and 2013 and differ from the previous applications, where bentazone concentrations appeared after approximately three months. This evaluation 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 once during the monitoring period extending to August 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: 0.048 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 (Figure 4.7) and Estrup (Figure 5.7) 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} 173 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 2.0 m depth at Estrup (Figure 5.7). Monitoring at Silstrup and Estrup was stopped by the end of May 2017.

- 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 5.8) 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 azole fungicides as spray or 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 one detection (0.01 µg L^{-1}) 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 (suction cups) exceeding 0.1 µg L^{-1} (Figure 3.8). With the half-dose application of propiconazole in 2016, more detections were generally obtained. Water from the upstream well at Jyndevad revealed high concentrations of 1,2,4-triazole at depth 3-5 m depth, why this impact on the detections in groundwater from the downstream wells can not be neglected (Figure 3.8). Water of high concentrations are, however, obtained from the suction cups in 1 m depth, why there is a contribution from the field. Following the half-dose application of propiconazole at Faardrup groundwater detections (three samples) were again (last time in Marts 2015) obtained in low concentration in a period with no drainage and hence no drainage samples to be analysed. The outcome reveals 1,2,4-triazole leaching through the variably saturated zone (1 m depth) at both of the sandy fields but also at the fractured clayey till field Faardrup. 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:

- 18 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).
- 15 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).
- 17 pesticides resulted in no detections in groundwater; here among 10, 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 hydrogeochemical 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.

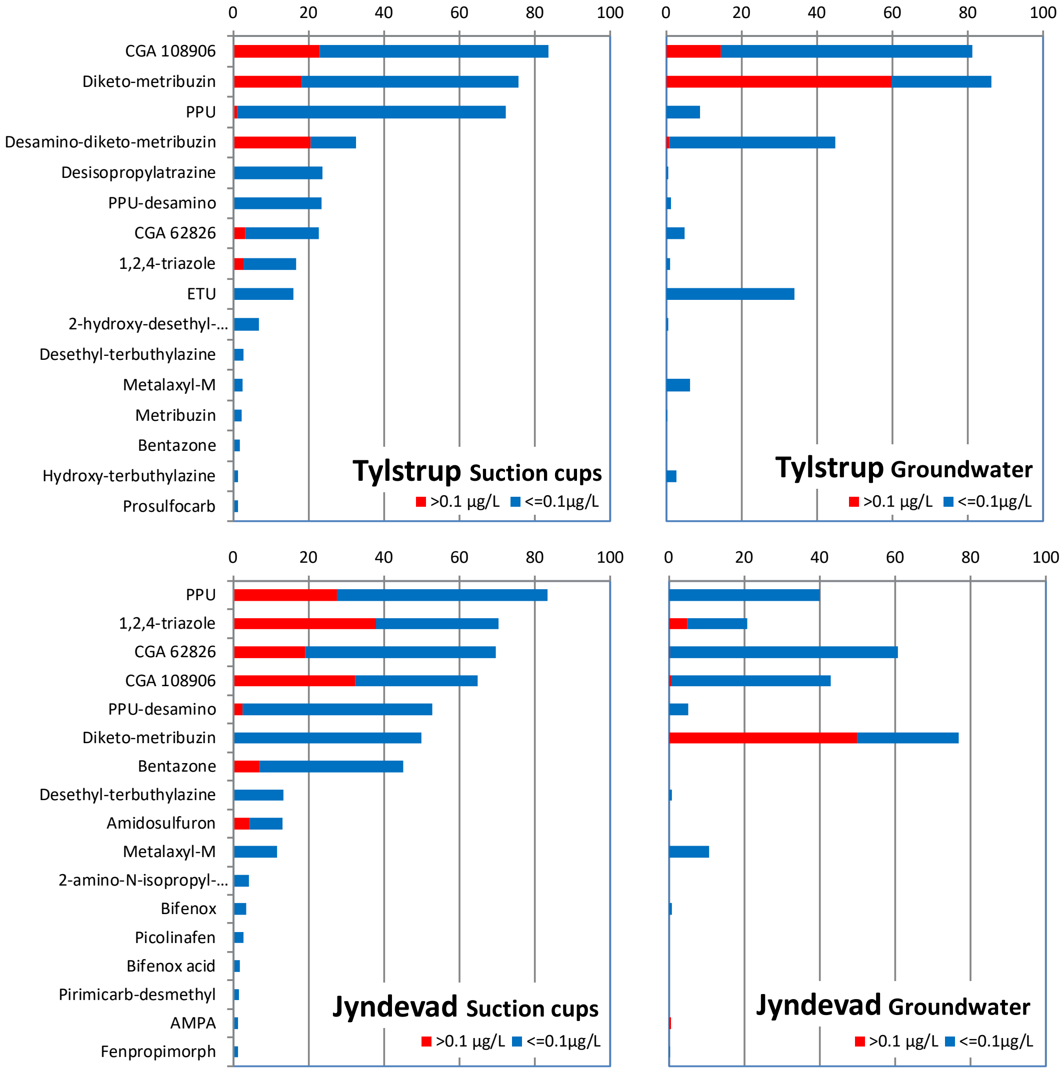

Figure 8.1. Frequency of detection in samples from the suction cups (left) and groundwater monitoring screens located deeper than the suction cups (right) at the **sandy fields: Tylstrup** and **Jyndevad.** Frequency is estimated for the entire monitoring period up to July 2017. The time the different 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.

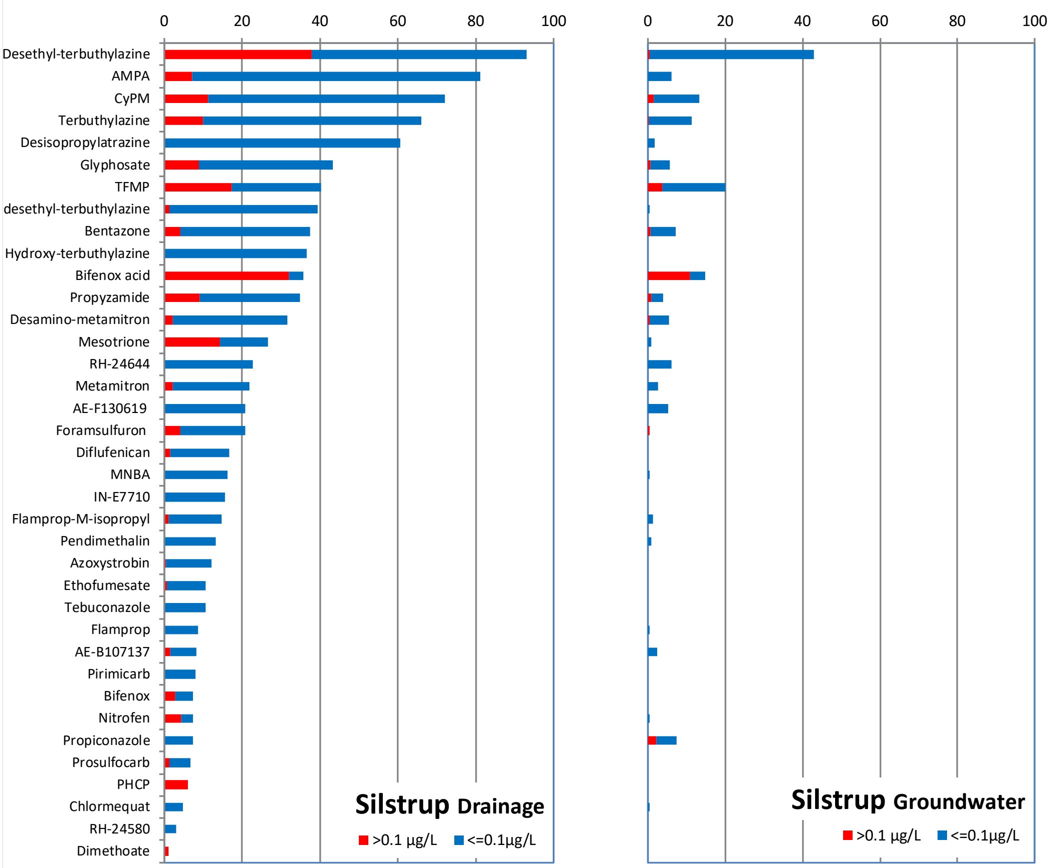

Figure 8.2A. Frequency of detection in samples from the drainage system (left) and groundwater monitoring screens located deeper than the drainage system (right) at the **clayey till field Silstrup**. Frequency is estimated for the entire monitoring period up to July 2017. The time the different pesticides have been included in the programme and the number of analysed samples varies. The figure includes pesticides detected in drainage and groundwater.

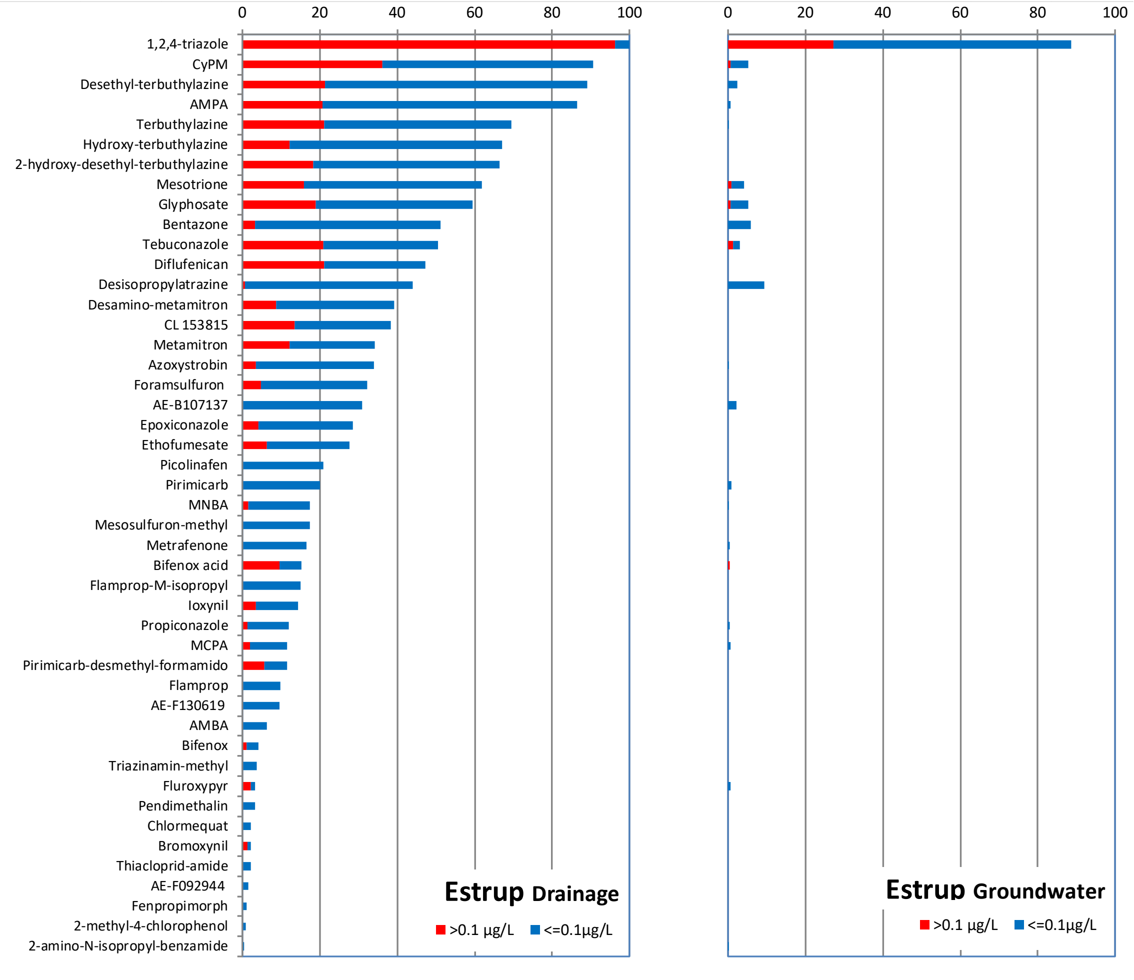

Figure 8.2B. Frequency of detection in samples from the drainage system (left) and groundwater monitoring screens located deeper than the drainage system (right) at the **clayey till field Estrup**. Frequency is estimated for the entire monitoring period up to July 2017. The time the different pesticides have been included in the programme and the number of analysed samples varies. The figure includes pesticides detected in drainage and groundwater.

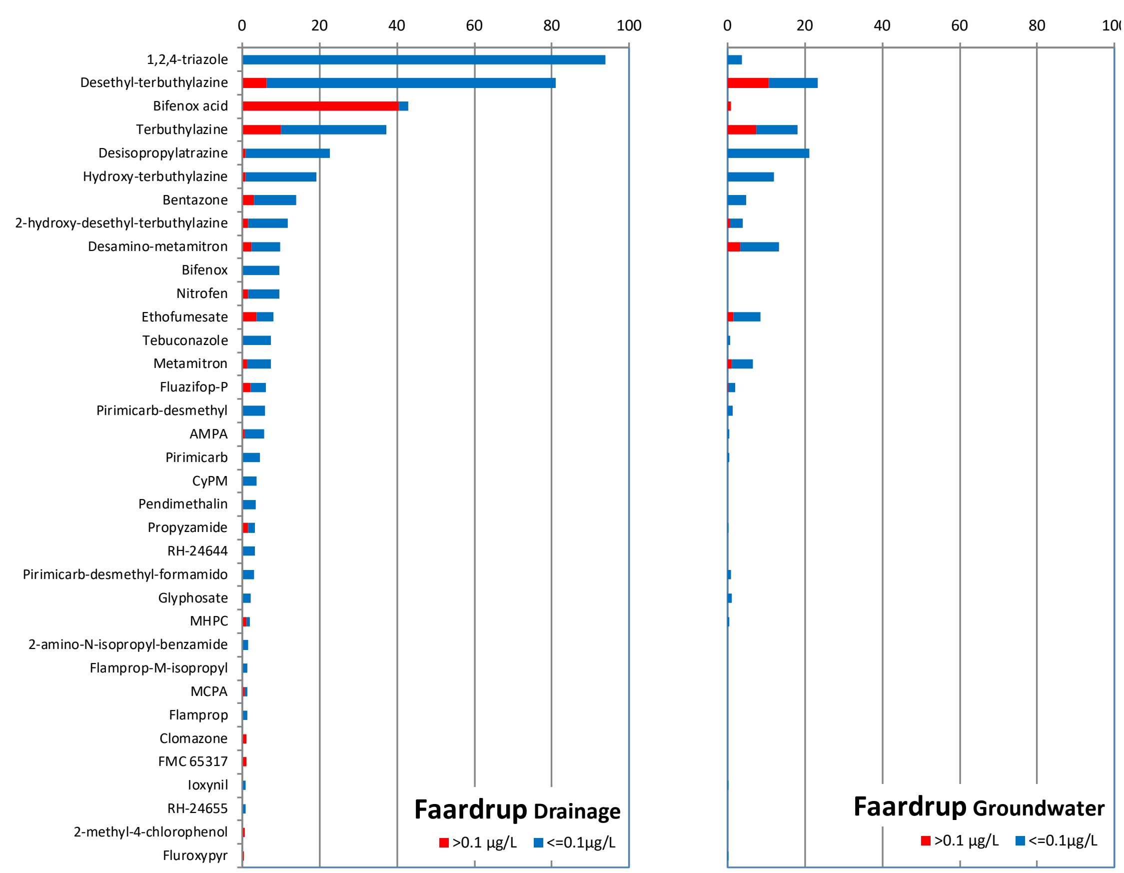

Figure 8.2C. Frequency of detection in samples from the drainage system (left) and groundwater monitoring screens located deeper than the drainage system (right) at the **clayey till field Faardrup**. Frequency is estimated for the entire monitoring period up to July 2017. The time the different pesticides 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 2015–June 2017. Within that period (Table 8.5):

- A total of 7,269 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).
- PLAP has evaluated the leaching risk of 6 pesticides and 18 degradation products after the applicaton of the maximum allowed dose of the 13 specific pesticides in connection with the specific crops with the exception of the propiconazole application in 2016 where by mistake only half of the dosage was used. All 24 compounds included in the monitoring have been evaluated in previous PLAP reports.

Results covering the period May 1999–June 2016 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; Rosenbom *et al.*, 2017). 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 2015 - June 2017. 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)*** 6 pesticides and 18 *degradation products* have been analysed in PLAP in the period July 2015 - June 2017 of which all compounds were included in the latest PLAP-report. 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.**
Azoxystrobin	Azoxystrobin	84	216		0	0	-	1	0	0.01
	CyPM	84	216		74	5	0.16	14	0	0.03
Bentazone	Bentazone	94	340	3 (0.011;-;-)	24	1	4.5	1	0	0.02
	6-hydroxy-bentazone	66	275	3(-)	0	0	-	0	0	-
	8-hydroxy-bentazone	66	275	3(-)	0	0	-	0	0	-
	N-methyl-bentazone	66	275	3(-)	0	0	-	0	0	-
Fludioxonil	*CGA 192155*	44	160	1 (-)	0	0	-	1	0	0.05
	CGA 339833	44	160	1 (-)	0	0	-	1	1	**0.37**
Flupyrsulfuron-methyl	Flupyrsulfuron-methyl	45	255	1 (-)	0	0	-	0	0	-
	IN-JV460	45	255	1 (-)	0	0	-	0	0	-
	IN-KC576	45	255	1 (-)	0	0	-	0	0	-
	IN-KY374	45	255	1 (-)	4	3	0.45	0	0	-
Foramsulfuron	Foramsulfuron	100	249	1 (-)	27	5	0.32	4	0	0.04
	AE-F092944	100	249		1	0	0.01	0	0	-
	AE-F130619	100	249		15	0	0.07	9	0	0.03
Glyphosat	Glyphosate	65	116		12	0	0.05	3	1	**0.13**
	AMPA	65	116		51	2	0.14	2	0	0.02
Mesotrione	Mesotrione	100	249		44	10	1.30	2	0	0.07
	AMBA	100	249		3	0	0.04	0	0	-
	MNBA	100	247		12	0	0.06	0	0	-
Tebuconazole 2014 Epoxiconazole 2015 Prothioconazole 2015 Propiconazole 2016	*1,2,4-triazole*	168	600	4 (-)	114	73	0.45	282	24	**0.19**
Fluroxypyr	*Fluroxypyr-methoxypyridine*	1	88		0	0	-	0	0	-
	Fluroxypyr-pyridinol	1	88		0	0	-	0	0	-
Triasulfuron	*Triazinamin*	47	131		0	0	-	0	0	**-**
Sub total	24 (6 Pesticides; 18 *Degradation products*)	1675	5568	26	**381**	**99**		**320**	**26**	
Percent		23%	77%	0.4%	**23%**	**6%**		**6%**	**0%**	
Total			**7269**							

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Appendixes

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

Appendix 2
Pesticide monitoring programme – Sampling procedure

Appendix 3
Agricultural management

Appendix 4
Monthly precipitation data for PLAP fields

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

Appendix 6
Laboratory internal control cards and external control sample results

Appendix 7
Pesticides analysed at five PLAP fields in the period up to 2009/2010

Appendix 8
New horizontal wells

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

Appendix 1

Chemical abstracts nomenclature for the pesticides encompassed by the PLAP

Table A1.1. Systematic chemical nomenclature for the pesticides and degradation products encompassed by the PLAP. P (parent). M (degradation product). N: Total number of samples analysed in PLAP including QC samples. Monitoring is ongoing if latest analysis date is in June 2017.

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	08.04.15	619
Azoxystrobin	P	Azoxystrobin	131860-33-8	Methyl (E)-2-{2-[(6-(2-cyanophenoxy)-4-pyrimidin-4-yloxy]phenyl}-3-methoxyacrylate	07.06.17	3458
Azoxystrobin	M	CyPM	1185255-09-7	E-2-(2-[6-cyanophenoxy)-pyrimidin-4-yloxy]-phenyl) – 3-methoxyacrylic acid	07.06.17	3611
Bentazone	P	Bentazone	25057-89-0	3-(1-methylethyl)-1H-2,1,3-benzothiadiazin-4(3H)-one 2,2 dioxide	07.06.17	5007
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	07.06.17	375
Bentazone	M	6-hydroxy-bentazone	60374-42-7	6-Hydroxy-3-isopropyl-1H-2,1,3-benzothiadiazin-4(3H)-one 2,2-dioxide	07.06.17	375
Bentazone	M	8-hydroxy-bentazone	60374-43-8	8-Hydroxy-3-(1-methylethyl)-1H-2,1,3-benzothiadiazin-4(3H)-one 2,2-dioxide	07.06.17	375
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	13.03.15	1989
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	Methyl 2-[(4,6-dimethoxypyrimidin-2-ylcarbamoyl)sulfamoyl]-6-(trifluoromethyl)nicotinate monosodium salt monosodium salt	11.10.16	512
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	11.10.16	512
Flupyrsulfuron-methyl	M	IN-KC576	-		11.10.16	512
Flupyrsulfuron-methyl	M	IN-KY374	-	N-(4,6-dimethoxypyrimidine-2-yl)-N-(3-methoxycarbonyl-6-trifluoromethylpyridine-2-yl)-amine	11.10.16	512
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	28.06.17	100
Fluroxypyr	M	Fluroxypyr-pyridinol	94133-62-7	4-amino-3,5-dichloro-6-fluoro-2-pyridinol	28.06.17	100
Foramsulfuron	P	Foramsulfuron	173159-57-4		14.06.17	444
Foramsulfuron	M	AE-F092944	36315-01-2	2-amino-4,6-dimethoxypyrimidine	14.06.17	444
Foramsulfuron	M	AE-F130619	-	4-amino-2-[3-(4,6-dimethoxypyrimidin-2-yl)ureidosulfonyl]-N, N-dimethylbenzamide	14.06.17	444
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
Iodosulfuron-methyl-natrium	M	Metsulfuron-methyl	74223-64-6	Methyl-2-(4-methoxy-6-methyl-1,3,5-triazin-2-ylcarbamoylsulfamoyl)benzoate	22.12.10	1346
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	14.06.17	799
Mesotrione	M	MNBA	110964-79-9	methylsulfonyl-2-nitrobenzoic acid	14.06.17	797
Mesotrione	M	AMBA	393085-45-5	2-amino-4-methylsulfonylbenzoic acid	14.06.17	799
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
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

Pesticide	**P/M**	**Analyte**	**CAS no.**	**Systematic name**	**Latest analysis**	**N**
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
Propyzamide	P	Propyzamide	23950-58-5	3,5-dichloro-N-(1,1-dimethylprop-2-ynyl)benzamide	08.04.15	1233
Propyzamide	M	RH-24644	-	2-(3,5-dichlorophenyl)-4,4-dimethyl-5-methylene-oxazoline	08.04.15	1233
Propyzamide	M	RH-24655	-	3,5-dichloro-N-(1,1-dimethylpropenyl)benzamide	08.04.15	1134
Propyzamide	M	RH-24580	-	N-(1,1-dimethylacetonyl)-3,5-dichlorobenzamide	08.04.15	1233
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	28.06.17	1304
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	14.06.17	1924
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 contains 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:

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

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

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 2012 to 2017 growing seasons. The active ingredients of the various pesticides are indicated in parentheses.

Date	Management practice and growth stages – **Tylstrup**
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
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 removed, 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

Date	Management practice and growth stages – **Tylstrup**
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 removed, 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
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

Date	Management practice and growth stages – **Tylstrup**
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
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

Date	Management practice and growth stages – **Tylstrup**
10-06-2016	Biomass 414.8 g m^{-2} – 100% DM
24-06-2016	BBCH stage 54
04-07-2016	BBCH stage 58
13-07-2016	BBCH stage 75
13-07-2016	Biomass 1099.5 g m^{-2} - 100% DM
21-07-2016	BBCH stage 80-81
27-07-2016	BBCH stage 87
19-08-2016	BBCH stage 91
19-08-2016	Harvest of spring barley. Stubleheight 15 cm, grainyield 61.9 hkg ha^{-1} - 85% DM
29-08-2016	Straw remowed, yield 27.0 hkg ha^{-1} - 100% DM
10-03-2017	Rotor harrowed - depth 7 cm
22-03-2017	Ploughed - depth 23 cm
28-03-2017	BBCH stage 0
28-03-2017	Spring barley sown, CV Laurikka coated with Redigo Pro 170 FS, seeding rate 165 kg ha^{-1}, sowing depth 4 cm, row distance 13 cm. Final plantnumber not determined.
04-04-2017	BBCH stage 6
06-04-2017	Fertilisation - 133 N, 19 P, 63 K, kg ha^{-1}
11-04-2017	BBCH stage 9 - emergence
27-04-2017	BBCH stage 12
08-05-2017	BBCH stage 22
08-05-2017	Biomass 57.3 g m^{-2} - 100% DM
09-05-2017	BBCH stage 22
09-05-2017	Hussar Plus OD (Iodosulfuron-mesosulfuron) - weeds - 0.07 L ha^{-1} (i.e. 3.5 g idosulfuron and 0.525 g mesosulfuron, a.i. ha^{-1})
11-05-2017	BBCH stage 23
23-05-2017	BBCH stage 31
29-05-2017	BBCH stage 37
01-06-2017	BBCH stage 41
01-06-2017	Bumper 25 EC (propiconazole) - fungi - 0.5 L ha^{-1} (i.e. 125 g propiconazol a.i. ha^{-1})
14-06-2017	BBCH stage 55
14-06-2017	Biomass 629.5 g m^{-2} - 100% DM
14-06-2017	Bumper 25 EC (propiconazole) - fungi - 0.5 L ha^{-1} (i.e. 125 g propiconazol a.i. ha^{-1})

Table A3.2. Management practice at **Jyndevad** during the 2012 to 2017 growing seasons. The active ingredients of the various pesticides are indicated in parentheses.

Date	Management practice and growth stages – **Jyndevad**
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
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

Date	Management practice and growth stages – **Jyndevad**
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
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

Date	Management practice and growth stages – **Jyndevad**
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}
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.

Date	Management practice and growth stages – **Jyndevad**
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
06-07-2016	BBCH stage 72
12-07-2016	BBCH stage 75
12-07-2016	Biomass 1148.7 g m^{-2} - 100% DM
25-07-2016	BBCH stage 89
01-08-2016	BBCH stage 90
08-08-2016	BBCH stage 95
17-08-2016	Harvest of spring barley. Seed yield 48.3 hkg ha^{-1} 85% DM, stubble height 15 cm
30-08-2016	Removal of straw, straw yield 27.4 hkg ha^{-1} 100% DM
03-02-2017	Ploughing - 22 cm depth
20-02-2017	Rolled with concrete roller
15-03-2017	Fertilization 28 P, 147 K, kg ha^{-1}
23-03-2017	Sowing pea cultivare Mascara, depth 6.0 cm, rowdistance 12 cm, seed rate 235 kg ha^{-1},using a combine drill, final plant number 74 m^{-2}
08-04-2017	BBCH stage 09 - emergence
08-04-2017	BBCH stage 10
17-04-2017	BBCH stage 11
23-04-2017	BBCH stage 12
09-05-2017	BBCH stage 33
09-05-2017	Stomp CS (pendimethalin) - weeds - 1.0 L ha^{-1} (ie.e. 455 gr a.i. ha^{-1}) (not included)
09-05-2017	Fighter 480 (bentazone) - weeds - 1.0 L ha^{-1} (i.e. 480 gr a.i. ha^{-1})
19-05-2017	BBCH stage 52
19-05-2017	Biomass 335.1 g m^{-2} - 100% DM
19-05-2017	Focus Ultra (cycloxydim) - weeds - 5.0 L ha^{-1} (i.e. 500 g a.i. ha^{-1})
27-05-2017	BBCH stage 59
	Irrigation - 30 mm ha^{-1}
30-05-2017	BBCH stage 60
08-06-2017	BBCH stage 64
08-06-2017	Biomass 64.8 g m^{-2} - 100% DM
16-06-2017	BBCH stage 69
22-06-2017	BBCH stage 70
	Irrigation - 30 mm ha^{-1}
27-06-2017	BBCH stage 71
27-06-2017	Biomass 704.3 g m^{-2} - 100% DM

Table A3.3. Management practice at **Silstrup** during the 2012 to 2017 growing seasons. The active ingredients of the various pesticides are indicated in parentheses.

Date	Management practice and growth stages – **Silstrup**
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}
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

Date	Management practice and growth stages – **Silstrup**
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}
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

Date	Management practice and growth stages – **Silstrup**
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
06-07-2016	BBCH stage 31
13-07-2016	BBCH stage 32-33
20-07-2016	BBCH stage 34-50
25-07-2016	BBCH stage 51
25-07-2016	Biomass 428.1 g m^{-2} - 100% DM
15-08-2016	BBCH stage 67
15-08-2016	Biomass 925.8 g m^{-2} - 100% DM
15-09-2016	BBCH stage 75
20-09-2016	Dry mattet determination - 27.25%
29-09-2016	Dry mattet determination - 29,74%
05-10-2016	Dry mattet determination - 31.2%
11-10-2016	Harvest of maiz. Stubble height 33 cm. Total harvested yield 120.86 hkg ha^{-1} 100% DM.
13-10-2016	Maiz stubble chrushed with a cutter
14-10-2016	Stuble cultivated - depth 6 cm
12-11-2016	Ploughed - 24 cm depth
28-04-2017	Seedbed preparation - depth 5 cm
28-04-2017	Fertilization 30.5 N, 4.4 P, 14.5 K, kg ha^{-1}
29-04-2017	BBCH stage 0
29-04-2017	Spring barley sown, cv. KWS Irina coated with Redigo Pro 170 FS, seeding rate 160 kg ha^{-1}, sowing depth 3.4 cm, row distance 12.5 cm. Final plantnumber not determined.
11-05-2017	BBCH stage 9
15-05-2017	BBCH stage 12
29-05-2017	BBCH stage 21-22
29-05-2017	Pig slurry application - accidified at application - trail hose applied at surface - 30 t ha^{-1} - 110.4 Total-N, 69.3 NH4-N, 44.4 P, 51.9 K, kg ha^{-1}, DM of slurry 4.88 %
29-05-2017	Biomass 50.7 g m^{-2} - 100% DM
12-06-2017	BBCH stage 32
15-06-2017	BBCH stage 33
15-06-2017	

Date	Management practice and growth stages – **Silstrup**
27-06-2017	Zypar (halauxifen-methyl + florasulam (not monitored)) - weeds - 1.0 L ha^{-1} (6.25 g a.i.ha^{-1} halauxifen-methyl + 5 g florasulam)
27-06-2017	BBCH stage 50
27-06-2017	Biomass 526.1 g m^{-2} - 100% DM
	Bumper 25 EC (propiconazol) - fungi - 0.5 L ha^{-1} (125 g a.i. ha^{-1} propiconazol)

Table A3.4. Management practice at **Estrup** during the 2012 to 2017 growing seasons. The active ingredients of the various pesticides are indicated in parentheses.

Date	Management practice and growth stages – **Estrup**
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}
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

Date	Management practice and growth stages – **Estrup**
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
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

Date	Management practice and growth stages – **Estrup**
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
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
13-07-2016	BBCH stage 51
13-07-2016	Biomass 3069.0 g m^{-2} - 100% DM
27-07-2016	BBCH stage 57
09-08-2016	BBCH stage 65
09-08-2016	Biomass 8118.8 g m^{-2} - 100% DM
10-08-2016	BBCH stage 65
24-08-2016	BBCH stage 71
07-09-2016	BBCH stage 80
21-09-2016	BBCH stage 86
30-09-2016	Harvest of maize. Stubble height 43 cm. Total harvested yield 184.76 hkg ha^{-1} 100% DM.
04-04-2017	Fertilization 28 P, 147 K, kg ha^{-1}
08-04-2017	Sowing peas - cv. Mascara - depth 7 cm, rowdistance 13 cm seeding rate 220 kg ha^{-1}. Final plantnumber 72 m^{-2}
14-04-2017	BBCH 09 - emergence
15-04-2017	BBCH stage 12
15-04-2017	Stomp CS (pendimethalin) - weeds - 1.0 L ha^{-1} (i.e. 455 g a.i.ha^{-1}) - not included in monitoring
15-04-2017	Fighter 480 (bentazone) - weeds - 1.0 L ha^{-1} (i.e. 480 g a.i. ha^{-1})

Date	Management practice and growth stages – **Estrup**
08-05-2017	BBCH stage 12
15-05-2017	BBCH stage 32
22-05-2017	BBCH stage 35
22-05-2017	Biomass 26.7 g m^{-2} - 100% DM
08-06-2017	BBCH stage 51
12-06-2017	BBCH stage 60
12-06-2017	Biomass 162.8 g m^{-2} - 100% DM
22-06-2017	BBCH stage 62
29-06-2017	BBCH stage 64

Table A3.5. Management practice at **Faardrup** during the 2012 to 2017 growing seasons. The active ingredients of the various pesticides are indicated in parentheses.

Date	Management practice and growth stages – **Faardrup**
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
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

Date	Management practice and growth stages – **Faardrup**
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
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
04-07-2016	BBCH stage 69
22-07-2016	BBCH stage 71
22-07-2016	Biomass 391.2 g m^{-2} - 100% DM
11-08-2016	BBCH stage 87
11-08-2016	Roundup PowerMax (glyphosate) - weeds - 2.0 kg ha^{-1} (i.e. 1440 g a.i. ha^{-1} - not included in
22-08-2016	monitoring)
26-08-2016	BBCH stage 87
26-08-2016	Harvest of spring barley. Grain yield 57.7 hkg ha^{-1} 85% DM - stubbleheight 13 cm.
27-08-2016	Biomass 369.3 g m^{-2} - 100% DM
20-12-2016	Straw removed from the field - yield 54.0 hkg ha^{-1} fresh weight.
07-04-2017	Ploughing - depth 24 cm
02-05-2017	Fertilization 132 N, 17 P, 61 K, kg ha^{-1}
02-05-2017	BBCH stage 0
10-05-2017	Rotor harrowed at the time of sowing the spring barley. CV Quench. Depth 4 cm, seeding rate 180 kg ha^{-1}, row distance 13.0 cm. Final plant number 365 m^{-2} . Seed coated with Fungazil A (imazalil)
11-05-2017	BBCH stage 09 - emergence
18-05-2017	BBCH stage 10-11
02-06-2017	BBCH stage 12-13
02-06-2017	BBCH stage 22
14-06-2017	Hussar Plus OD (iodosulfuron-methyl-Na and mesulfuron-methyl) - weeds - 0.035 L ha^{-1} (ie 1.75 g a.i. ha^{-1} iodosulfuron-methyl-Na and 0.27 g a.i. ha^{-1} mesulfuron-methyl)

Date	Management practice and growth stages – **Faardrup**
19-06-2017	BBCH stage 43 BBCH stage 45 Biomass 115.8 g m^{-2} - 100% DM Bumper 25 EC (propiconazol) - fungi - 0.5 L ha^{-1} (i.e. 125 g ai ha^{-1}) Zypar (haluuxifen-methyl + florasulam) - weeds - 0.5 L ha^{-1} (i.e 3.125 g ai ha^{-1} halauxifen-methyl and 2.5 g ai ha^{-1} florasulam)

Appendix 4

Monthly precipitation data for the PLAP fields

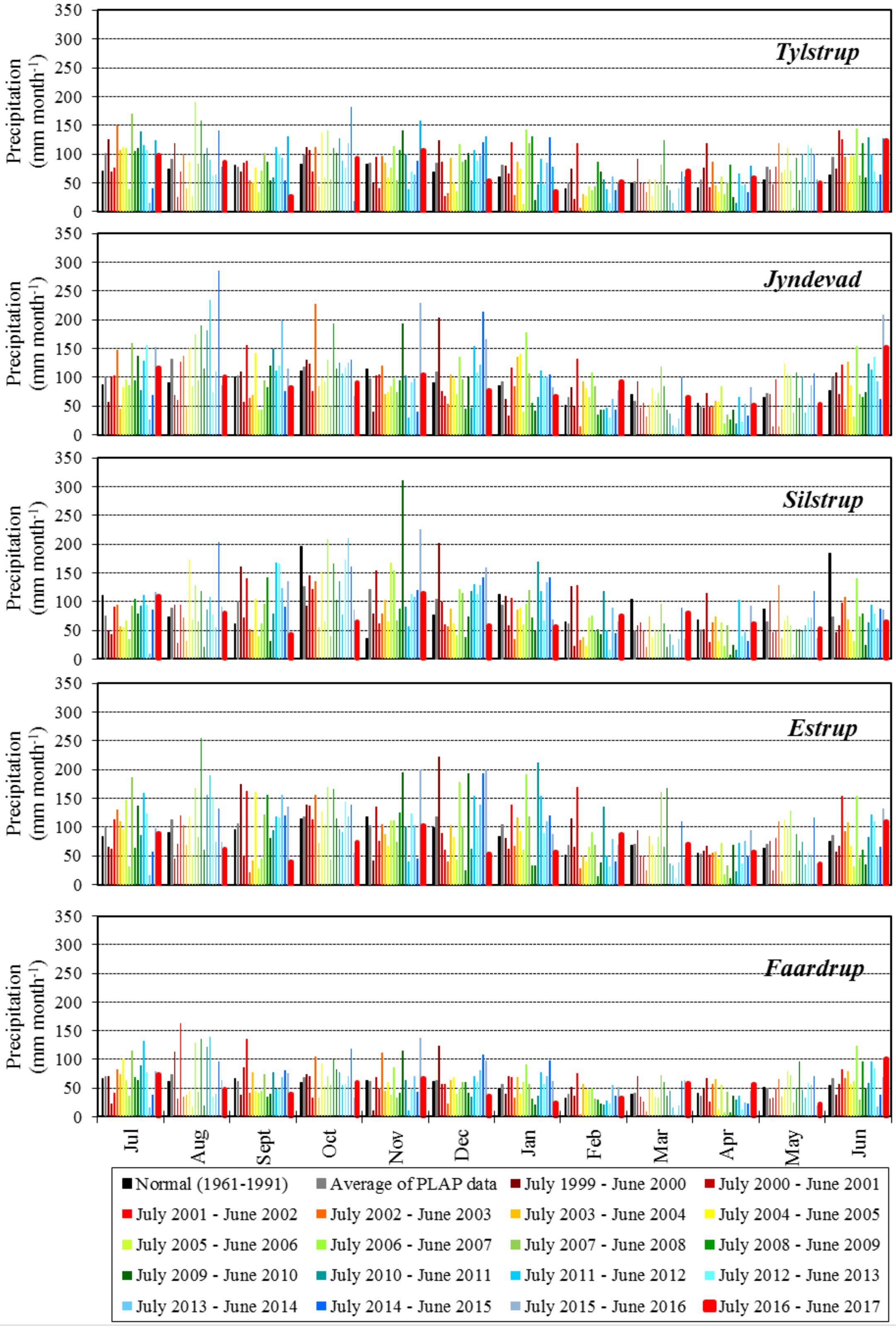


Figure A4.1. Monthly precipitation at all fields for the monitoring period July 2000–June 2017. Regional normal values (1961–1990) are included for comparison.

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	14	-	-	96	-	-	40	-	-
	8-hydroxy-bentazone	14	-	-	96	-	-	40	-	-
	Bentazone	14			426	-	-	174	3	-
	N-methyl-bentazone	14	-	-	96	-	-	40	-	-
Bifenox	Bifenox	8	-	-	41	-	-	22	-	-
	Bifenox acid	8	-	-	41	-	-	22	-	-
	Nitrofen	8	-	-	41	-	-	22	-	-
Boscalid	Boscalid	9	-	-	102	-	-	56	-	-
Bromoxynil	Bromoxynil				192	-	-	72	-	-
Clomazone	Clomazone				230	-	-	82	-	-
	FMC 65317				208	-	-	74	-	-
Clopyralid	Clopyralid				83	-	-	81	-	-
Cyazofamid	Cyazofamid	4	-	-	123	-	-	68	-	-
Dimethoate	Dimethoate				176	-	-	65	-	-
Epoxiconazole	Epoxiconazole				199	-	-	74	-	-
Fenpropimorph	Fenpropimorph				313	-	-	89	-	-
	Fenpropimorph acid				276	-	-	75	-	-
Flamprop-M-isopropyl	Flamprop				176	-	-	65	-	-
	Flamprop-M-isopropyl				176	-	-	65	-	-
Fluazifop-P-butyl	Fluazifop-P				178	-	-	65	-	-
	TFMP				3	-	-			
Fludioxonil	CGA 192155	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	22	-	112	58	-	60	10	2
	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	14	-	-	124	-	-	26	-	-
	8-hydroxy-bentazone	14	-	-	124	-	-	26	-	-
	Bentazone	43	1	-	767	-	-	117	81	15
	N-methyl-bentazone	14	-	-	124	-	-	26	-	-
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	28	-	-	201	-	-	30	-	-
	IN-JV460	28	-	-	201	-	-	30	-	-
	IN-KC576	28	-	-	201	-	-	30	-	-
	IN-KY374	28	-	-	201	-	-	26	1	3
Fluroxypyr	Fluroxypyr				193	-	-	55	-	-
Glyphosate	AMPA				221	2	-	71	1	-
	Glyphosate				223	-	-	72	-	-
Ioxynil	Ioxynil				218	-	-	61	-	-
MCPA	2-methyl-4-chlorophenol				210	-	-	56	-	-
	MCPA				210	-	-	56	-	-
Mancozeb	EBIS	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	16	20	-	107	164	1	22	24	28
	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 $\mu g\ L^{-1}$ (<0.1 $\mu g\ L^{-1}$) or detected in concentrations above 0.1 $\mu g\ L^{-1}$ (>=0.1 $\mu g\ L^{-1}$) 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	165	22	1	231	3	-	405	5	-			
	CyPM	59	128	24	224	41	6	432	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	1	-	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	48	-	-	57	-	-	112	-	-			
	AE-F130619	38	10	-	51	6	-	109	3	-			
	Foramsulfuron	38	8	2	54	3	-	111	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	49	-	-	61	-	-	116	-	-			
	MNBA	41	8	-	61	-	-	116	-	-			
	Mesotrione	36	6	7	61	-	-	116	-	-			
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	1,2,4-triazole		3		6			19					
	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	66	-	-	100	-	-	200	-	-			
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 $\mu g\ L^{-1}$ ($<0.1\ \mu g\ L^{-1}$) or detected in concentrations above 0.1 $\mu g\ L^{-1}$ ($>=0.1\ \mu g\ L^{-1}$) 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	274	126	15	240	1	-	523	2	-			
	CyPM	39	226	150	207	29	5	518	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	61	1	-	49	-	-	70	-	-			
	AE-F130619	56	6	-	49	-	-	70	-	-			
	Foramsulfuron	42	17	3	49	-	-	70	-	-			
Glyphosate	AMPA	79	379	120	291	1	-	719	7	-	23	-	-
	Glyphosate	235	234	109	284	6	1	680	41	5	23	-	-
Iodosulfuron-methyl	Metsulfuron-methyl	131	-	-	55	-	-	208	-	-	22	1	-
Ioxynil	Ioxynil	119	15	5	41	-	-	125	-	-	3	-	-
MCPA	2-methyl-4-chlorophenol	102	1	-	34	-	-	112	-	-			
	MCPA	91	10	2	34	-	-	111	1	-			
Mesosulfuron-methyl	Mesosulfuron	74	-	-	24	-	-	83	-	-			
	Mesosulfuron-methyl	62	13	-	27	-	-	99	-	-			
Mesotrione	AMBA	59	4	-	51	-	-	72					
	MNBA	52	10	1	51	-	-	69	1	-			
	Mesotrione	24	29	10	48	2	1	70	2	-			
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	102	-	65	9	20	43	39			
	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	158	-	-	76	-	-	237	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	-	-	51	-	-	123	-	-			
	IN-JV460	36	-	-	51	-	-	123	-	-			
	IN-KC576	36	-	-	51	-	-	123	-	-			
	IN-KY374	36	-	-	51	-	-	123	-	-			
Fluroxypyr	Fluroxypyr	182	-	1	146	1	-	368	-	-	73	-	-
	Fluroxypyr.methoxypyridine	1	-	-	17	-	-	71	-	-			
	Fluroxypyr-pyridinol	1	-	-	17	-	-	71	-	-			
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	-	49	4	-	152	6	-			
	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

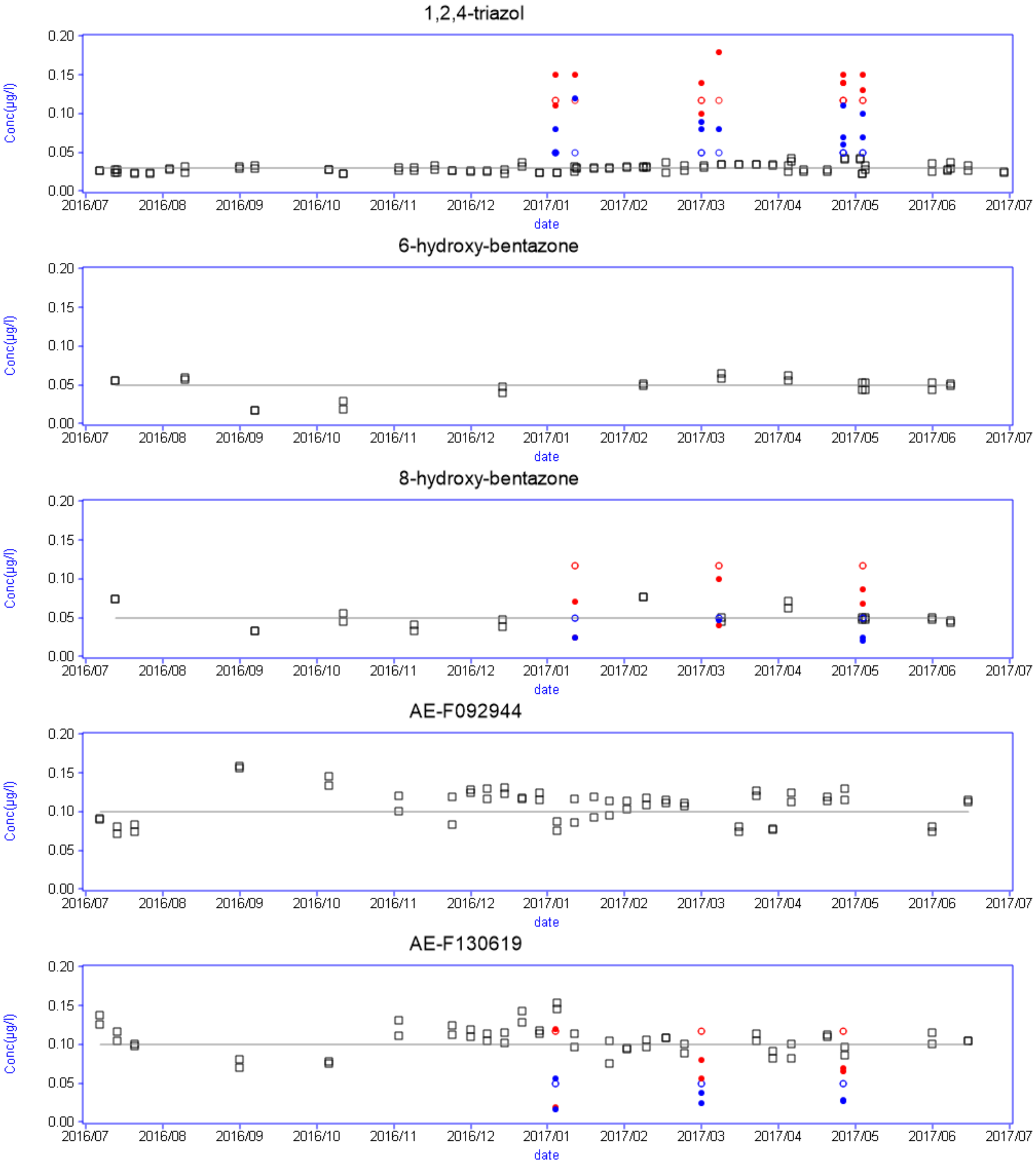


Figure A6.1. Quality control data for pesticide analysis by laboratory 1. Internal laboratory control (IQ) samples are indicated by square symbols and the nominal level is indicated by the solid grey line (□ IQ measured, — IQ nominal concentration). External control (EQ) samples are indicated by circles.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

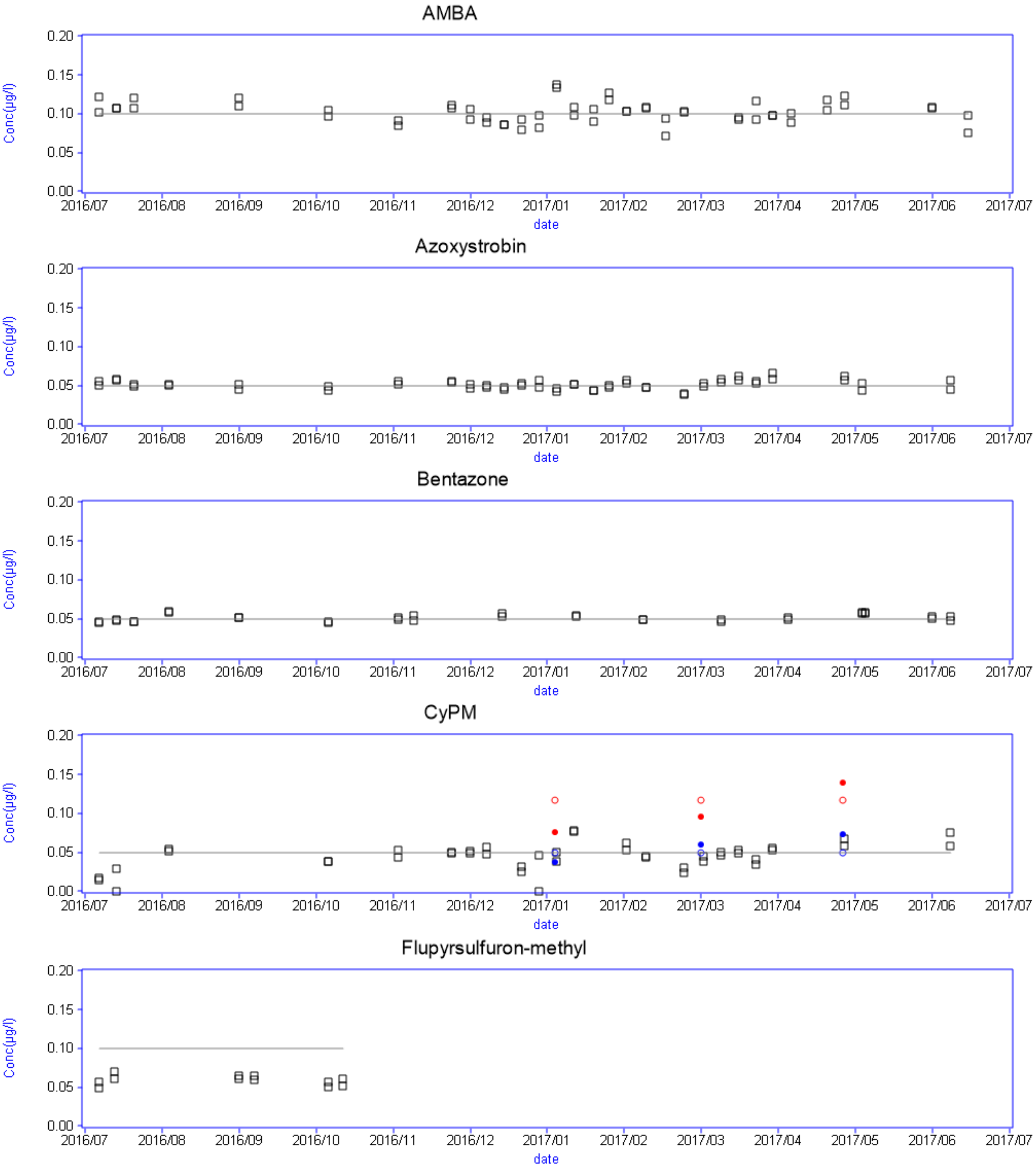
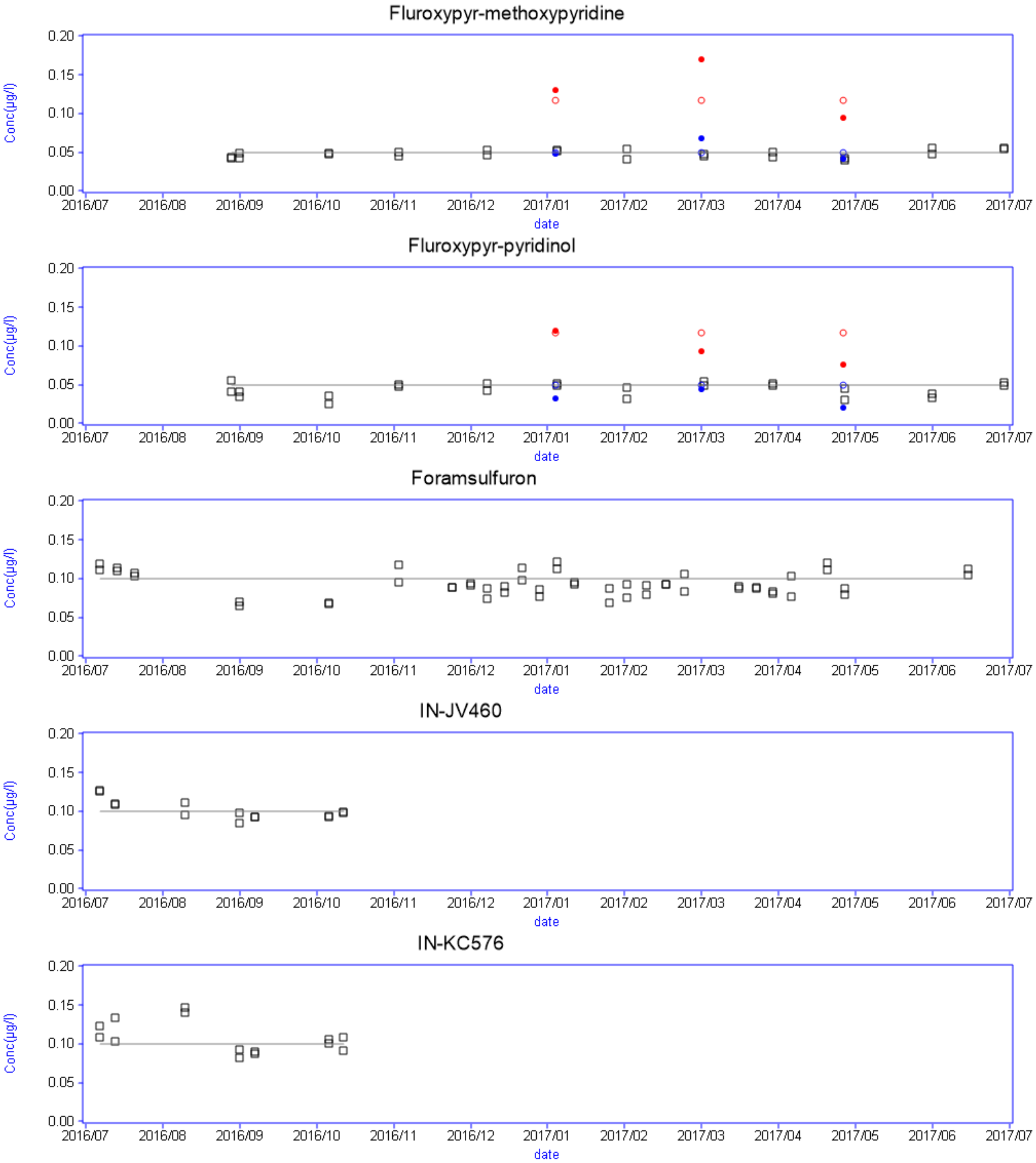


Figure A6.1. Quality control data for pesticide analysis by laboratory 1. Internal laboratory control (IQ) samples are indicated by square symbols and the nominal level is indicated by the solid grey line (□ IQ measured, — IQ nominal concentration). External control (EQ) samples are indicated by circles.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



Fluroxypyr-methoxypyridine

Fluroxypyr-pyridinol

Foramsulfuron

IN-JV460

IN-KC576

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

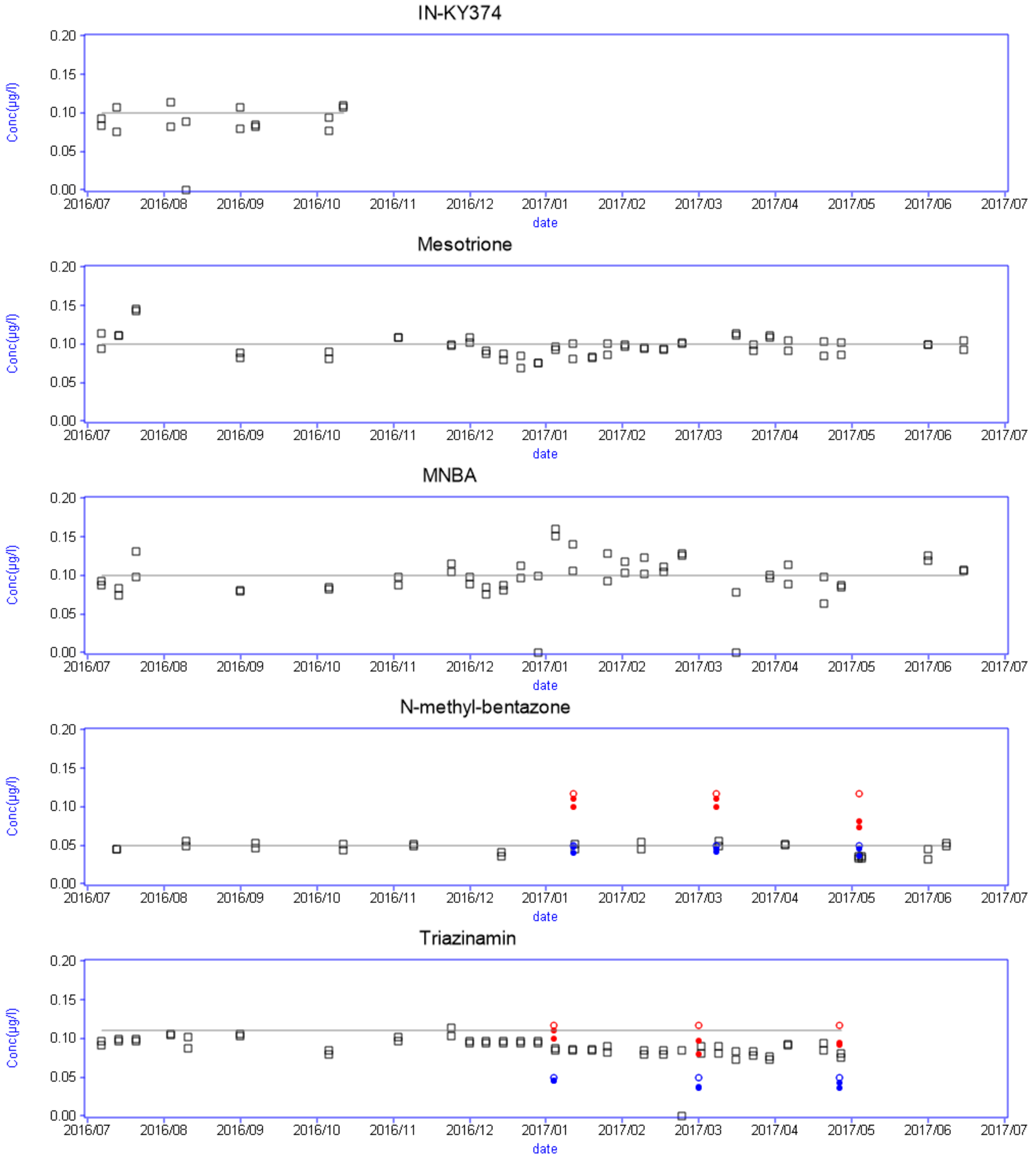


Figure A6.1. Quality control data for pesticide analysis by laboratory 1. Internal laboratory control (IQ) samples are indicated by square symbols and the nominal level is indicated by the solid grey line (□ IQ measured, — IQ nominal concentration). External control (EQ) samples are indicated by circles. 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} ($\mu g\ L^{-1}$)
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 [$\mu g\ L^{-1}$] 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
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**

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} (µg 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} ($\mu g\ L^{-1}$)
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 [$\mu g\ L^{-1}$] 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. 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})
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} ($\mu g\ L^{-1}$)
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 [$\mu g\ L^{-1}$] 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} ($\mu g\ L^{-1}$)
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 (^{3}H/^{3}He), chlorofluorocarbons (CFCs) and sulphurhexafluoride (SF_6). Preliminary studies using the latter two methods were, however, unable to produce sufficiently accurate results to permit direct comparison, due to:

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

The tritium-helium method was tested in 2010 at 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 (^{3}H), half-life 12.5 years, and its daughter product helium-3 (^{3}He) in the water.

The tritium-helium age and the recharge model age differ less than one year for most wells over the entire depth interval and no systematic difference in age can be observed (Figure A9.1). Wells including both 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.

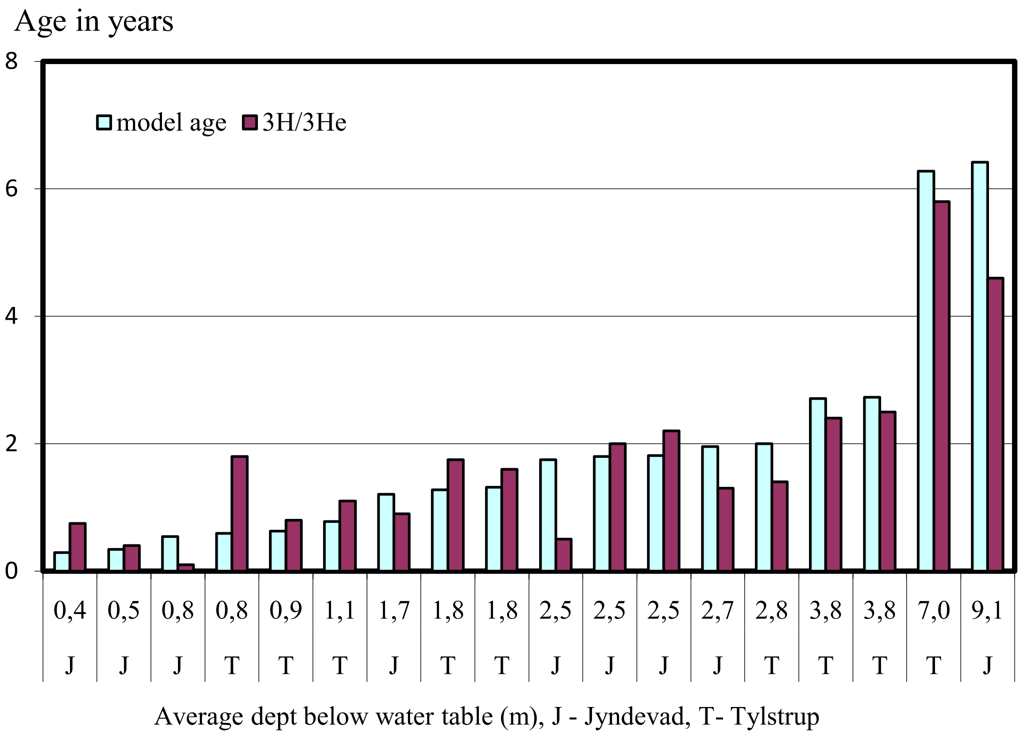


Figure A9.1. Groundwater age at Jyndevad and Tylstrup. Recharge model age assumes water velocity of 1.4 m per year, except for the deep filter at Tylstrup (1.1 m per year).

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.