

# The Danish Pesticide Leaching Assessment Programme

Monitoring results May 1999–June 2020



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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 several 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 then from the Danish Environmental Protection Agency (EPA) in the period 2010 to 2018. Additionally, funding for establishing a new test field, designated to be included in the monitoring programme for 2016-2018, was provided in the Danish Finance Act for the fiscal year of 2015. The establishment of the new test field was, however, delayed and not initiated until the autumn of 2016. In April 2017, PLAP received funding 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 Ecoscience (ECOS) at Aarhus University, under the direction of a management group comprising Nora Badawi (GEUS), Annette E. Rosenbom (GEUS), Preben Olsen (AGRO), Kirsten Kørup Sørensen (AGRO), Sachin Karan (GEUS), Carsten B. Nielsen (ECOS), Steen Marcher (Danish EPA) and Signe Bonde Rasmussen (Danish EPA).

Maria Sommer Holtze (Danish EPA) chairs the steering group, and the members are Steen Marcher (Danish EPA), Per Kudsk (AGRO), John Jensen (ECOS), Claus Kjøller (GEUS), and the project leader Nora Badawi (GEUS).

This report presents the results for the period May 1999–June 2020 with focus on the leaching risk of pesticides applied during the monitoring period July 2018-June 2020. Results are reported annually, and the present report should therefore be regarded as a continuation of previous reports. All reports covering results from previous years and links to associated peer-reviewed articles are available at [www.plap.dk](http://www.plap.dk).

The report was prepared jointly by Nora Badawi (GEUS), Sachin Karan (GEUS), Eline B. Haarder (GEUS), Annette E. Rosenbom (GEUS), Preben Olsen (AGRO), and Kirsten Kørup (AGRO) with contributions from Lasse Gudmundsson (GEUS), Carl H. Hansen (GEUS), Finn Plauborg (AGRO), and Carsten B. Nielsen (ECOS).

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Nora Badawi  
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## Summary

In 1998, the Danish Parliament initiated the Pesticide Leaching Assessment Programme (PLAP), an intensive monitoring programme aimed at evaluating the leaching risk of pesticides and/or their degradation products under field conditions. The objective of PLAP is to improve the scientific foundation for decision-making in the Danish regulation of pesticides by enabling field studies to be included in the risk assessment of selected pesticides. The specific aim is to evaluate whether approved pesticides applied in accordance with current regulations and maximum permitted dosages, under actual, Danish field conditions can result in leaching of the pesticides and/or their degradation products to the groundwater in concentrations exceeding the maximum allowed concentration of  $0.1 \mu\text{g L}^{-1}$  for groundwater and drinking water.

This report focuses on the results from the monitoring period July 2018–June 2020, comprising 7336 single chemical analyses of water samples collected at the five PLAP-fields: one sandy field (Jyndevad) and four clayey till fields (Silstrup, Estrup, Faardrup, and Lund). From July 2018 to June 2020, 25 different commercial pesticide products containing 22 different active ingredients were applied. Seven active ingredients (for simplicity hereafter referred to as pesticides) and 41 degradation products were included in the monitoring for evaluation of their leaching risk. In total 48 compounds were included in the monitoring and of these, 22 are under evaluation for the first time in PLAP (marked in red in Table 0.1). The remaining 26 were included in the monitoring programme before July 2018, as monitoring of a compound is usually at least two years, and thus overlapping reporting periods. A historical perspective of the full monitoring from 1999 – June 2020 including 151 pesticides and/or degradation products (52 pesticides and 99 degradation products) is presented in Tables 9.1 and 9.2 in Chapter 9, and the previous report (Rosenbom *et al.* 2021; available at [www.plap.dk](http://www.plap.dk)).

Highlights for compounds included in the monitoring period July 2018–June 2020:

### **1,2,4-triazole leaching cannot be linked to specific azole applications presumably because several azole sources are contributing to the continuous detections in groundwater from the fields**

Evaluation of 1,2,4-triazole leaching was initiated in 2014 after the Danish EPA imposed restrictions on certain azole fungicides suspected of degrading into 1,2,4-triazole. Monitoring of 1,2,4-triazole is ongoing since 2014 at Tylstrup (presently on standby), Jyndevad, Estrup, and Faardrup, and since 2016 at Silstrup, and 2017 at Lund. The evaluation included spray applications (sprayings) of five azole fungicides (propiconazole, epoxiconazole, tebuconazole, prothioconazole, metconazole), and from 2017 coated seeds used for sowing were also included in the evaluation. A mixture of tebuconazole and prothioconazole used as seed dressing was evaluated. In the current monitoring period, July 2018 to June 2020, azoles were tested both as sprayings and as seed dressings. Spraying with metconazole was performed at Estrup (2019), and with prothioconazole at Silstrup (2020), and several of the fields were sown with seeds coated with a mix of prothioconazole and tebuconazole. The coated seeds were winter barley at Lund (2018), spring barley at Estrup and Faardrup (both in 2019), and winter wheat at Estrup (2019).

When evaluating leaching of 1,2,4-triazole it is noted that since PLAP started in 1999, all fields were sprayed with azole fungicides on several occasions before monitoring of 1,2,4-triazole was initiated in 2014. In addition, seeds sown in the fields during the entire monitoring period were likely coated with azoles on several occasions, but these were not registered until 2017. Possible azole

accumulation in the plough layer after consecutive applications is mentioned in the EFSA conclusions on tebuconazole and epoxiconazole (EFSA, 2008 and EFSA, 2014). Presence of accumulated azoles in the plough layer from previous sprayings and the use of coated seeds can, therefore, render a continuous degradation of azoles into 1,2,4-triazole and cause long-term leaching to the groundwater. In general, 1,2,4-triazole was detected in samples collected for testing of background concentration before azole applications in the fields. These samples were collected from drainage and groundwater from the uppermost monitoring well screens downstream of the fields immediately before or after the azole applications. From these samples showing 1,2,4-triazole detections before application, it is suspected that azoles are accumulated and still present in the plough layer even several years after the last application, and thus, continuously degraded to 1,2,4-triazole. The present azole content in the plough layer of all fields is currently studied in the research project TRIAFUNG.

1,2,4-triazole is also present in groundwater from the deepest screens in monitoring wells located upstream of fields at Jydevad, Estrup, and Lund. The detections are at a lower concentration level compared to detected levels in monitoring screens located downstream of the fields. However, the presence of 1,2,4-triazole in the deeper groundwater upstream of the fields suggests a contribution of 1,2,4-triazole from azole applications from neighbouring fields, although to a minor extent.

An overall conclusion from the entire monitoring period of 1,2,4-triazole in all fields is that 1,2,4-triazole is omnipresent in water from the variably saturated zone (drainage and water from suction cups), and the uppermost screens of the monitoring wells in all fields. The leaching of 1,2,4-triazole is at a nearly constant concentration level fluctuating in concentrations  $< 0.1 \mu\text{g L}^{-1}$ , except at Estrup. Here, the concentration in groundwater from the uppermost screens of monitoring well M4 are fluctuating in the range of  $0.1\text{--}0.2 \mu\text{g L}^{-1}$ , and a general decreasing trend in concentration level is observed during the period. Based on the continuous 1,2,4-triazole detections and observed concentration levels, leaching of 1,2,4-triazole cannot be related to the current azole sprayings and application of azole coated sowing seeds, or directly to past applications of azoles. To discern between the different azole applications and leaching of 1,2,4-triazole, detailed fate studies of azoles in soil are needed. Monitoring of 1,2,4-triazole is ongoing on all fields.

#### **CyPM detections at Lund show concentration breakthrough $> 0.1 \mu\text{g L}^{-1}$ in drainage six months after azoxystrobin application**

As previously reported (Rosenbom *et al.* 2021), azoxystrobin was applied at Lund in June 2017 to compare with former azoxystrobin applications at Silstrup (June 2004–October 2016) and Estrup (June 2004–April 2017). Azoxystrobin and its degradation product CyPM were included in the monitoring from May 2017 to March 2019. This resulted in detections of both azoxystrobin ( $< 0.1 \mu\text{g L}^{-1}$ ) and CyPM ( $> 0.1 \mu\text{g L}^{-1}$  in three samples) in drainage (1 m depth) during the first drainage period in winter 2017, half a year after application. After these detections, no further leaching of the compounds to drainage was detected during the monitoring period. A total of 240 groundwater samples were collected. Azoxystrobin was not detected in any samples. CyPM was detected in 5% of the groundwater samples, and all detections were within six months after application. At Lund, CyPM was initially detected in the upstream groundwater well M1 in July 2017 and later same year twice in downstream well M7. CyPM was detected in groundwater from M7 in November ( $0.054 \mu\text{g L}^{-1}$ ) and December 2017 ( $0.049 \mu\text{g L}^{-1}$ ). None of the CyPM detections in groundwater were  $> 0.1 \mu\text{g L}^{-1}$  and a contribution of CyPM from upstream fields to the groundwater collected from M7 cannot be excluded. Note that pesticide monitoring data for Lund should still be interpreted with caution. Especially groundwater data obtained before November 2019 might be impacted by poor hydraulic contact due to clogging of the screens.

Azoxystrobin was applied to the Silstrup field in May 2020 and CyPM was included in the monitoring. Monitoring at Silstrup is ongoing and will be evaluated in the next report.

**Leaching of cycloxydim's degradation product, E/Z BH 517-TSO relates to cycloxydim applications and is found in groundwater but in concentrations  $< 0.1 \mu\text{g L}^{-1}$**

The herbicide cycloxydim was applied in May 2017 at Jyndevad in pea, and September 2018 at Silstrup in winter rape, and its two degradation products, BH 517-T2SO<sub>2</sub> and E/Z BH 517-TSO were included in the monitoring programme.

The degradation product E/Z BH 517-TSO was detected in suction cups at Jyndevad, with maximum detected concentration ( $0.53 \mu\text{g L}^{-1}$ ) in June 2017, less than one month after the application. At Silstrup, E/Z BH 517-TSO was detected in drainage in maximum concentration ( $0.11 \mu\text{g L}^{-1}$ ) in November 2018, two months after the application.

E/Z BH 517-TSO was also detected in groundwater from both fields. At Jyndevad, E/Z BH 517-TSO was detected in two out of 12 samples from the horizontal well in concentrations  $< 0.05 \mu\text{g L}^{-1}$ . E/Z BH 517-TSO was not detected in any of the 188 groundwater samples taken from the vertical monitoring wells between May 2017 and March 2019. At Silstrup, E/Z BH 517-TSO was detected in both horizontal and vertical monitoring wells, peaking in December 2018, one month later than in drainage. The maximum groundwater concentration ( $0.052 \mu\text{g L}^{-1}$ ) was detected in water from the horizontal well H1 in December 2018. As E/Z BH 517-TSO was not detected before applications in groundwater samples from upstream wells in both fields, the leaching of E/Z BH 517-TSO relates to the applied cycloxydim. Degradation product, BH 517-T2SO<sub>2</sub> was not detected in any samples from May 2017 to March 2019 at Jyndevad, and from August 2018 to June 2020 at Silstrup. The monitoring at Silstrup is ongoing.

**Two degradation products from flupyrsulfuron-methyl are not detected in the groundwater**

To evaluate the leaching risk of two degradation products from flupyrsulfuron-methyl, IN-KF311 and IN-JE127, the herbicide was sprayed against weeds in winter wheat at the sandy field Jyndevad October 2017 and May 2018. Further, at the clayey till field Silstrup the herbicide was applied in winter barley October 2017, where only the monitoring of IN-KF311 was included. In the analytical method development, IN-JE127 was found unstable in aqueous solutions, and thus omitted from the monitoring program. The degradation product IN-KF311 was not detected during the monitoring period, which ended March 2019 at Jyndevad and March 2020 at Silstrup. Flupyrsulfuron-methyl was banned as an active ingredient in Denmark in December 2018.

**No detections of three mesosulfuron-methyl degradation products in groundwater from the sandy or clayey till fields during two years of monitoring**

The two degradation products from mesosulfuron-methyl, AE-F099095 and AE-F160459 were included for the first time in the PLAP-monitoring in May 2017. Mesosulfuron-methyl was applied in spring barley at the sandy field Tylstrup (monitoring ended in December 2018, when Tylstrup was set on standby). In April 2018, the pesticide was applied to the sandy field Jyndevad and the clayey till fields Silstrup and Estrup, and a third degradation product, AE-F147447 was included in the monitoring. None of the three degradation products were detected in samples from Tylstrup, Silstrup, and Estrup. At Jyndevad, AE-F147447 was detected twice in groundwater from the horizontal well in December 2019 and January 2020 in concentrations  $< 0.1 \mu\text{g L}^{-1}$ . As none of the degradation products were found in water sampled from 1 m depth and only in groundwater in two samples at

Jyndevad during a full two-year monitoring period at the three fields, monitoring was stopped in March 2020.

### **Propyzamide leach in concentrations $> 0.1 \mu\text{g L}^{-1}$ to the groundwater following autumn application**

Propyzamide was for the second time included in the PLAP-monitoring programme at the clay till field Silstrup and sprayed on winter rape in November 2018. Just five days after application and in connection with a precipitation event  $> 20 \text{ mm day}^{-1}$ , a propyzamide concentration of  $5.1 \mu\text{g L}^{-1}$  was detected in drainage. Subsequent detections  $> 0.1 \mu\text{g L}^{-1}$  were observed in drainage and groundwater four months after application. Hereafter, propyzamide was detected only in low concentrations in two drainage samples until September 2019. From September to July 2020 no further detections in drainage or groundwater were observed. Monitoring at Silstrup is ongoing.

Adding to the evaluation of the leaching risk of propyzamide following autumn applications, propyzamide was applied to Lund in December 2019 and monitored together with its degradation products RH-24644 and RH-24580. At Lund, propyzamide and RH-24644 were detected in drainage in concentrations  $> 0.1 \mu\text{g L}^{-1}$  within the first week after application. Hereafter, RH-24644 was detected once in a concentration  $< 0.1 \mu\text{g L}^{-1}$  in a drainage sample, but from January 2020 to the end of the drainage season in March 2020, propyzamide was detected in seven out of 12 drainage samples and twice in concentrations  $> 0.1 \mu\text{g L}^{-1}$ . From December 2019 to July 2020, none of the three compounds were detected in the groundwater samples collected downstream of the field, but propyzamide was detected ( $< 0.1 \mu\text{g L}^{-1}$ ) in two samples from the upstream monitoring well M1 in January-February 2020. The monitoring results indicate that primarily, propyzamide leach through clayey till within the first months after application and in variable concentrations (depending on the weather in connection with application). Monitoring of the three compounds at Lund is ongoing.

### **Selected degradation products from thiophanat-methyl and proquinazid do not leach to groundwater at a sandy and a clayey till field**

The degradation products IN-MM671 and IN-MM991 (from proquinazid) were included in the monitoring programme in April 2019 at the sandy field Jyndevad and clayey till field Faardrup. Carbendazim (from thiophanat-methyl) was included in the monitoring in May 2018 at the clayey till field Estrup and in April 2019 at Jyndevad. None of the compounds were detected in samples collected from the variably saturated zone or groundwater. Analytical methods for IN-MM671 and IN-MM991 were lacking from April 2019 until September 2019, and for carbendazim from May 2018 until September 2018, which is why water samples were stored at  $-20^{\circ}\text{C}$  for analysis. Therefore, results from these periods should be regarded as tentative until further evaluation of the effect of freezing on the quality of analyses is performed (see Chapter 8 for more information).

**Table 0.1.** Result overview. 7 pesticides and 41 degradation products (48 analytes) were analysed in PLAP from July 2018 to June 2020. 22 compounds not previously evaluated in PLAP are marked in red. VZ is variably saturated zone (drains and suction cups), SZ is saturated zone (vertical and horizontal groundwater screens), and irrigation is number of analysed irrigation water samples. Concentrations in irrigation water are presented in brackets in units of  $\mu\text{g L}^{-1}$ . Det. is detections  $> 0.01 \mu\text{g L}^{-1}$  and Max conc. is maximum concentration.

Active ingredient(s)	Analyte	Number of samples			Results of analyses					
		VZ	SZ	Irrigation ( $\mu\text{g L}^{-1}$ )	VZ			SZ		
					Det. n	$>0.1 \mu\text{g L}^{-1}$ n	Max conc. ( $\mu\text{g L}^{-1}$ )	Det. n	$>0.1 \mu\text{g L}^{-1}$ n	Max conc. ( $\mu\text{g L}^{-1}$ )
Acetamiprid	IM-1-4 <sup>IV</sup>	6	25	1 (-)	0	0	-	0	0	-
	IM-1-5 <sup>IV</sup>	6	25	1 (-)	0	0	-	0	0	-
Azoxystrobin	Azoxystrobin	5	72		0	0	-	0	0	-
	CyPM	5	80		1	0	0,02	0	0	-
Bentazone	Bentazone	5	72		0	0	-	0	0	-
Cyazofamid	CCIM <sup>IV</sup>	6	25	1 (-)	0	0	-	0	0	-
	CTCA <sup>IV</sup>	6	25	1 (-)	0	0	-	0	0	-
	DMSA <sup>IV</sup>	6	25	1 (-)	0	0	-	0	0	-
	N,N-DMS <sup>IV</sup>	6	25	1 (0,011)	0	0	-	3	0	0,05
Cycloxydim	BH 517-T2SO2	57	189		0	0	-	0	0	-
	E/Z BH 517-TSO	57	189		10	1	0,11	29	0	0,05
Florasulam	TSA	62	311		0	0	-	0	0	-
	5-OH-florasulam <sup>IV</sup>	2	30		0	0	-	0	0	-
	DFP-ASTCA <sup>IV</sup>	2	30		0	0	-	0	0	-
	DFP-TSA <sup>IV</sup>	2	30		0	0	-	0	0	-
Flupyr-sulfuron-methyl	IN-JE127 <sup>II</sup>	36	118		0	0	-	0	0	-
	IN-KF311	64	176		0	0	-	0	0	-
Foramsulfuron <sup>I</sup>										
Amidosulfuron <sup>I</sup>										
Mesosulfuron-methyl	IN-J0290/AE-F092944	2	12		0	0	-	0	0	-
Flupyr-sulfuron-methyl										
Rimsulfuron <sup>I</sup>										
Glyphosate	Glyphosate	7	107		0	0	-	2	0	0,02
	AMPA	7	106		3	0	0,03	2	0	0,02
Haluxifen-methyl	X-729	53	146		0	0	-	0	0	-
	X-757	27	110		0	0	-	0	0	-
Mesosulfuron-methyl	AE-F099095	149	379	6 (-)	0	0	-	0	0	-
	AE-F147447	106	285	6 (-)	0	0	-	2	0	0,04
	AE-F160459	149	379	6 (-)	0	0	-	0	0	-
Metamitron	Metamitron	33	94		0	0	-	0	0	-
	Desamino-metamitron	33	94		0	0	-	0	0	-
	MTM-126-AMT	31	90		0	0	-	0	0	-
Metconazole	Metconazole	30	62		0	0	-	0	0	-
Picloram	Picloram	21	46		1	0	0,01	0	0	-
Propaquizafop	CGA287422	32	84		0	0	-	0	0	-
	CGA290291	32	84		0	0	-	0	0	-
	CGA294972	32	84		0	0	-	0	0	-
	PPA	32	84		0	0	-	0	0	-
Propyzamide	Propyzamide	75	178		24	9	5,1	20	4	0,22
	RH-24580	22	51		0	0	-	0	0	-
	RH-24644	22	51		2	1	0,11	0	0	-
Proquinazid	IN-MM671	70	195	7(-)	0	0	-	0	0	-
	IN-MM991	70	195	7(-)	0	0	-	0	0	-
Pyroxulam	5-OH-XDE-742 <sup>IV</sup>	2	30		0	0	-	0	0	-
	6-Cl-7-OH-XDE-742 <sup>IV</sup>	2	30		0	0	-	0	0	-
	7-OH-XDE-742 <sup>IV</sup>	2	30		0	0	-	0	0	-
	Amitrol <sup>III</sup>	3	35		0	0	-	0	0	-
	PSA <sup>IV</sup>	2	30		0	0	-	0	0	-
	Pyridin sulfonamid <sup>IV</sup>	2	30		0	0	-	0	0	-
Tebuconazole										
Epoxiconazole <sup>I</sup>										
Propiconazole <sup>I</sup>	1,2,4-triazole	215	672	7(-)	186	46	0,33	397	18	0,20
Prothioconazole										
Metconazole										
Thiencarbazone-methyl	AE1394083	33	93		0	0	-	0	0	-
Thiophanat-methyl	Carbendazim	96	251	7(-)	0	0	-	0	0	-
Subtotal	48 (7 active ingredients, 41 degradation products)	1725	5564	48	227	57		455	22	
Procent		24%	76%	0.7%	13%	3%		8%	0.4%	
Total			7337							

\*IN-JE127 was excluded from the analysis programme when found to be unstable in water. \*\* Amitrol was included in the monitoring of pyroxulam as it was suspected to be a groundwater pollutant in the Danish groundwater monitoring programme 2019 (GRUMO). Pyroxulam was therefore tested as a theoretical source of origin to *amitrol*. The findings of amitrol in the groundwater screening were later shown to be an analytical artefact and the monitoring of *amitrol* in PLAP was thus suspended. \*\*\* The compound was included in PLAP spring 2020 and therefore discussed in the next report covering 2019-2021. <sup>IV</sup> the active ingredient was applied before July 2018 but may still contribute to detections of the monitored analyte.

# 1 Introduction

In Denmark, nearly all drinking water is based on groundwater that has undergone a simple treatment where water has been aerated and passed through a filter of sand. As Denmark is intensively cultivated, there is 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.*, 2021) and the effect of agricultural practices (the Pesticide Leaching Assessment Programme, PLAP). The reported results have and are still continuously addressed in the regulation of pesticides.

The detection of pesticides in groundwater since the 1980s has demonstrated the need for further enhancement of the scientific foundation for the existing approval procedure for pesticides and to improve the present leaching risk assessment tools. The main issue in this respect is that the EU groundwater risk assessment, and hence also the Danish assessment of the risk of pesticides and/or their degradation products leaching to groundwater, is largely based on modelling studies and, if available, lysimeter studies (Gimsing *et al.*, 2019). However, those types of data may not adequately describe the leaching, which may occur under actual field conditions. Although models are widely used within the registration process, their validation requires further work (Gassmann, 2021). The FOCUS models (FORum for Co-ordination of pesticide fate models and their Use) applied in the EU process are one-dimensional, use climate from 1960-1990, apply constant groundwater table at 2 m depth, and have limited inclusion of preferential solute transport added with issues regarding parameter and input estimation caused by the lack of field data (Boesten, 2000; Rosenbom *et al.*, 2015). Moreover, laboratory and lysimeter studies do only to a minor degree include the spatial variability of the soil parameters (hydraulic, chemical, physical, and microbiological soil properties) affecting the pesticide transformation and coherent assessed leaching of the degradation products (Gassmann, 2021). This is of particular importance for silty and clayey till soils, where preferential transport may have a major impact on pesticide leaching (Jacobsen and Kjær, 2007; Rosenbom *et al.*, 2015). 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; Jarvis, 2020).

The inclusion of field studies, i.e., test plots exceeding one hectare, in risk assessment of pesticide leaching to groundwater is considered an important improvement to the assessment procedures. For example, the US Environmental Protection Agency (US EPA) has since 1987 included field-scale studies in its risk assessments (US EPA, 1998). Thus, in the US pesticides that may potentially leach to the groundwater are required to be included in field studies as part of the registration procedure. Hence, the US-EPA has in the period 1987-1998 conducted field studies with more than 50 pesticides. A similar concept was hereafter adopted by the European Union (EU), where Directive 91/414/EEC, Annexe VI (Council Directive 97/57/EC of 22 September 1997) came into force enabling field leaching study results to be included in the risk assessments. This was enforced in 2011 by supplementing Regulation (EC) 1107/2009 with the uniform principles in Regulation 546/2011 (Annex C 2.5.1.2) (European Commission, 2011) allowing simulated groundwater concentrations above the guideline to be discarded if “it is scientifically demonstrated that under relevant field conditions the lower concentration is not exceeded” (Gimsing *et al.*, 2019).

## 1.1 Objective

In 1998, the Danish Government initiated the Pesticide Leaching Assessment Programme (PLAP), an intensive monitoring programme to evaluate 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 or selected degradation products thereof leach in unacceptable concentrations. The programme, which includes currently five active agricultural fields and one field on stand-by, focuses on pesticides used in arable farming and monitors leaching through the agricultural fields (Figure 1.1). All six fields are selected to represent typical Danish geological settings and climatic conditions. Except for one (Lund), all the fields were included in the monitoring since 1999. To increase the representability, the field at Lund (clayey till overlaying chalk), was included in May 2017 based on a one-time special grant. Subsequently, at the end of 2018, monitoring at Lund was continued, while the sandy field (Tylstrup) was put on stand-by, because of the termination of the special grant.

The objective of PLAP is to improve the scientific foundation for decision-making in the Danish registration and approval procedures for pesticides by enabling field studies to be included in the risk assessment of selected pesticides. The specific aim is to evaluate whether approved pesticides applied in accordance with current regulations and maximum permitted dosages, under actual, Danish field conditions can result in leaching of the pesticides and/or their degradation products to the groundwater in concentrations exceeding the maximum allowed concentration of  $0.1 \mu\text{g L}^{-1}$  for groundwater and drinking water.

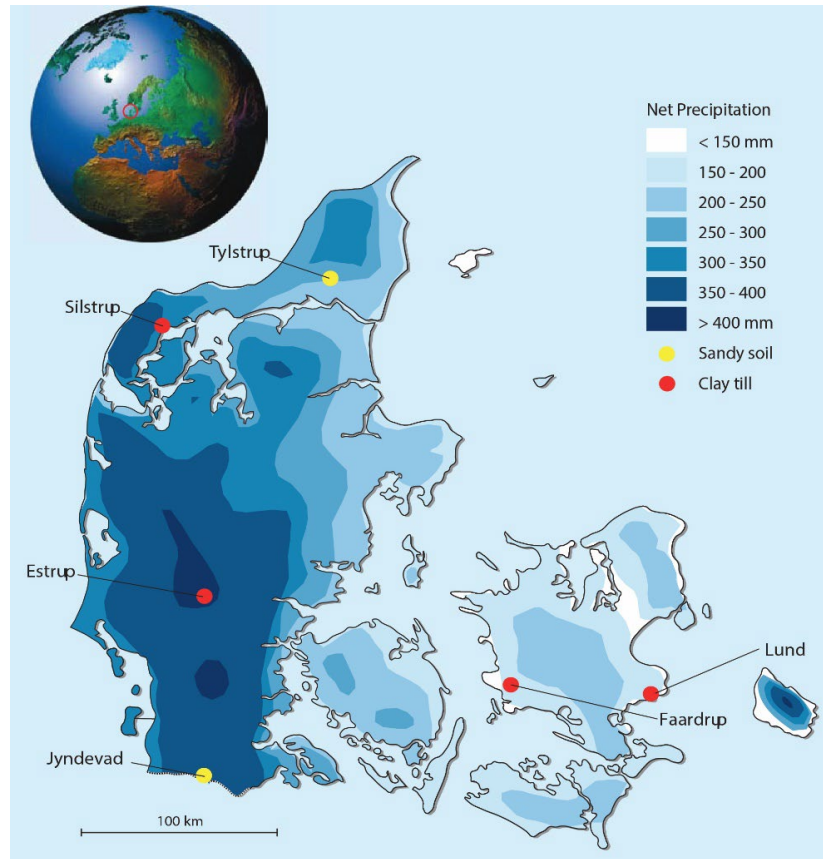
## 1.2 Structure of PLAP

The pesticides included in PLAP were selected based on expert judgement by the Danish EPA. At present, 52 pesticides and 99 degradation products have been included in PLAP. All the compounds (pesticides and degradation products) analysed since 1999 are listed in Appendix 1.

Soil type and climatic conditions are considered some of the most important parameters controlling pesticide leaching. Today, PLAP encompasses six fields that represent dominant soil types and climatic conditions in Denmark (Figure 1.1). As the sandy Tylstrup field was set on stand-by at the end of 2018, no water samples are collected for analysis from this field. The groundwater table is relatively shallow at all the fields, enabling rapid detection of pesticide leaching to groundwater. Cultivation of the PLAP fields is done in accordance with the conventional agricultural practice in the local area. The pesticides are applied at maximum permitted doses as 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 of the given pesticide.

Results and data in the present report comprise the six fields Tylstrup, Jyndevad, Silstrup, Estrup, Faardrup, and Lund. Characteristics of the fields are given in Table 1.1.





**Figure 1.1.** Annual net precipitation across Denmark (Danish EPA, 1992) and location of the six PLAP fields: Tylstrup (sandy), Jyndevad (sandy), Silstrup (clayey till), Estrup (clayey till), and Faardrup (clayey till) included in the monitoring programme from 1999-2020 and the field Lund (clayey till) included from May 2017-2020.

**Table 1.1.** Characteristics of the six PLAP fields included in the PLAP-monitoring for the period 1999-2020 (modified from Lindhardt *et al.*, 2001). Tylstrup was set on standby by the end of December 2018

	<b>Tylstrup on stand-by</b>	<b>Jynde vad</b>	<b>Silstrup</b>	<b>Estrup</b>	<b>Faardrup</b>	<b>Lund</b>
Location	Brønderslev	Tinglev	Thisted	Askov	Slagelse	Rødvig
Precipitation <sup>1)</sup> (mm y <sup>-1</sup> )	668	858	866	862	558	
Pot. evapotransp. <sup>1)</sup> (mm y <sup>-1</sup> )	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	100 x 300
Area (ha)	1.2	2.4	1.7	1.3	2.3	2.8
Tile drain	No	No	Yes	Yes	Yes	Yes
Depths to tile drain (m)			1.1	1.1	1.2	1.1
Monitoring initiated	May 1999	Sep 1999	Apr 2000	Apr 2000	Sep 1999	July 2017
<b>Geological characteristics</b>						
– Deposited by	Saltwater	Meltwater	Glacier	Glacier /meltwater	Glacier	Glacier
– Sediment type	Fine Sand	Coarse Sand	Clayey till	Clayey till	Clayey till	Clayey till
– DGU symbol	YS	TS	ML	ML	ML	ML
– Depth to the calcareous matrix (m)	6	5–9	1.3	1–4 <sup>2)</sup>	1.5	1.5
– Depth to the reduced matrix (m)	>12	10–12	5	>5 <sup>2)</sup>	4.2	3.8
– Max. fracture depth <sup>3)</sup> (m)	–	–	4	>6.5	8	>6
– Fracture intensity 3–4 m depth (fractures m <sup>-1</sup> )	–	–	<1	11	4	<1
– Saturated hydraulic conductivity (Ks) in C horizon (m s <sup>-1</sup> )	2.0·10 <sup>-5</sup>	1.3·10 <sup>-4</sup>	3.4·10 <sup>-6</sup>	8.0·10 <sup>-8</sup>	7.2·10 <sup>-6</sup>	5.8·10 <sup>-6</sup>
<b>Characteristics of the plough layer</b>						
– DK classification	JB2	JB1	JB7	JB5/6	JB5/6	JB5/6
– Classification	Loamy Sand	Sand	Sandy clay loam / sandy loam	Sandy loam	Sandy loam	Sandy loam
– Clay content (%)	6	5	18–26	10–20	14–15	10–25
– Silt content (%)	13	4	27	20–27	25	30–35
– Sand content (%)	78	88	8	50–65	57	30–50
– pH	4–4.5	5.6–6.2	6.7–7	6.5–7.8	6.4–6.6	7.4–9.1
– Total organic carbon (TOC, %)	2.0	1.8	2.2	1.7–7.3	1.4	0–1.3

<sup>1)</sup> Based on the 30-year normal for the period 1961–90. The data refer to precipitation measured 1.5 m above ground surface. <sup>2)</sup> Large variation within the field. <sup>3)</sup> 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) for the five fields Tylstrup, Jynde vad, Silstrup, Estrup, and Faardrup, and in Haarder *et al.* (2021) for Lund. The focus of the current report is on the leaching risk of pesticides and/or degradation products included in the July 2018-June 2020 monitoring. Chapter 9 gives a short historical perspective of the results from the entire monitoring period May 1999-June 2020. A detailed description of the earlier monitoring periods from May 1999 to June 2018 is available at [www.plap.dk](http://www.plap.dk). Within PLAP, the leaching risk of pesticides and degradation products is based on approximately two years of monitoring data.

For pesticides applied towards the end of the current reporting period, the present reporting must be considered preliminary, as these compounds have only been monitored for a short period. Thus, monitoring results for these compounds will be further evaluated in the coming reports.

To support the pesticide analysis results, hydrological modelling of the variably saturated zone was conducted with MACRO (version 5.2, Larsbo *et al.*, 2005) to describe and evaluate the soil water

dynamics of the six PLAP fields. Models for the five fields Tylstrup, Jyndevad, Silstrup, Estrup, and Faardrup were calibrated for the monitoring period May 1999–June 2004 and applied for the monitoring period May 1999–June 2020. For Lund, the model is set up and calibrated for the period March 2018–June 2020.

All six fields are fertilized in accordance with agricultural practices and water samples collected within the monitoring period are additionally analysed for inorganic compounds. All fields, except Lund, were subjected to at least three bromide applications and bromide analyses were included in the inorganic analyses. The bromide measurements are used to obtain knowledge about flow and transport pathways underneath the fields and support the hydrological modelling.

Scientifically valid analytical methods are essential to ensure the integrity of PLAP, and thus all chemical analyses of pesticides and degradation products are conducted by an accredited commercial laboratory. The field monitoring work is additionally supported by quality assurance entailing continuous evaluation of the analytical methods employed. Here, it is noted that several compounds that should have been introduced in the analytical programme in May 2018 and April 2019 were not introduced as planned. This was due to a delay in internal procedures regarding the selection of compounds for the monitoring programme in this period, and thus delays in both the procurement of the analytical standards and consequently analytical method development. Therefore, samples collected from May 2018 and onward and from April 2019 and onward for analysis of 11 compounds were stored at -20°C for several months until the analytical methods were ready for sample analysis (Table 8.2). As the stability of these compounds, when frozen for several months, is currently unknown, results from these periods should be considered tentative. Work is presently ongoing to evaluate the stability of these compounds at -20°C. The quality assurance methodology and results are presented in Chapter 8.

In the current report, results from all the bromide applications on the fields are revisited and analysed for the first time in conjunction. The analyses aim to gain further knowledge of transport times and improve the fundamental understanding of hydrogeology in the fields.



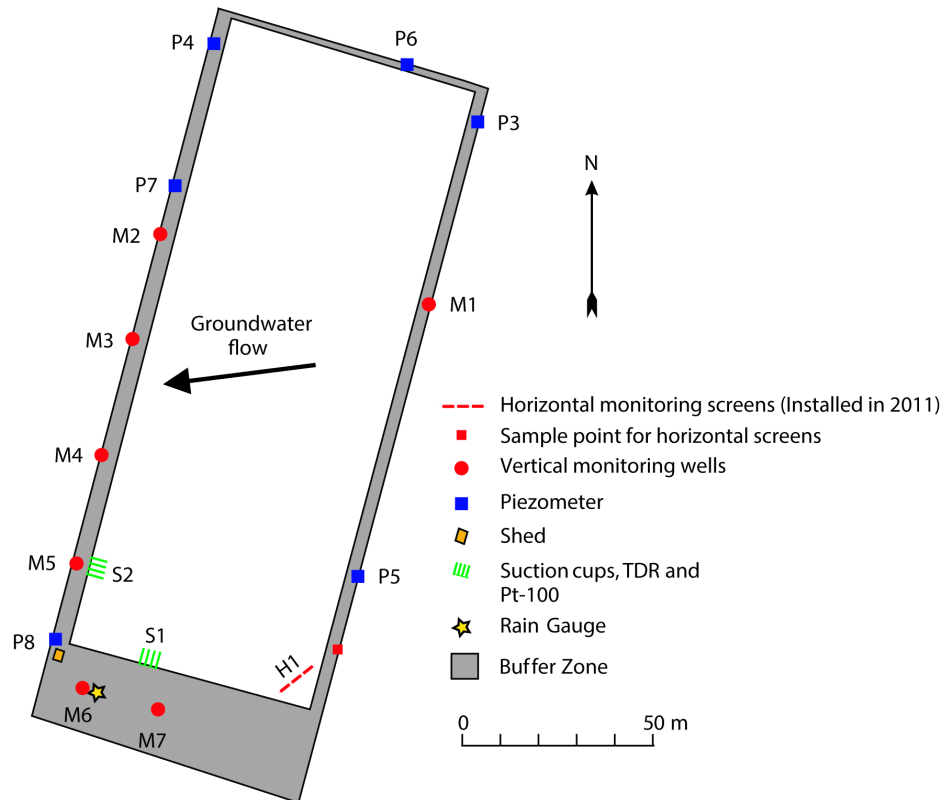
## 2 Pesticide leaching at Tylstrup

Due to economic constraints, the monitoring of pesticides and degradation products were put on stand-by at Tylstrup by the end of 2018. For the sake of comparison, previously published data of 1,2,4-triazole is included.

### 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% total organic carbon (Table 1.1). The aquifer material consists of an approximately 20 m thick layer of marine sand 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 west (Figure 2.1). Since the initiation of the monitoring in 1999, the groundwater table has fluctuated between 2.6–4.8 meters below ground surface, mbgs, (Figure 2.2). In February 2009, water sampling from well M2, M6, and M7 was stopped (Appendix 2). In September 2011, the monitoring system at Tylstrup was extended with three horizontal screens (H1) 4.5 mbgs 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 area surrounded by the buffer zone. Pesticide monitoring was conducted monthly and half-yearly from suction cups and selected vertical and horizontal monitoring screens as described in section 2.1.1 and Appendix 2. At S1 and S2, water content (via TDR) and soil temperature (via Pt100) is measured at four different depths. Additionally, suction cups are installed to collect pore water from the variably saturated matrix for analysis of pH-independent compounds.

The water sampling plan has been revised several times since the beginning of PLAP. During the current monitoring period, water sampling at Tylstrup was done monthly from suction cups in 1 m depth at S1 and S2 and wells M4, M5, and H1, with additional sampling half-yearly from wells M1, M3, and suction cups at 2 m depth at S1 and S2. No sampling is done from wells M2, M6, and M7. Due to earlier budget reduction, only the two uppermost well screens below the groundwater table are sampled. Appendix 2 describes the sampling procedure in more detail.

A new data logger was installed at Tylstrup on May 13, 2019. Unfortunately, the programme of the new data logger was defective and resulted in incorrect TDR-data. Therefore, no TDR-data are presented for the field after this date (Figure 2.2).

### 2.1.2 Agricultural management

As the field was set on standby at the end of 2018, no monitoring was done in the field from January 1, 2019. However, the field is still operated by PLAP and if needed, monitoring can be resumed in due course. Management practice at Tylstrup is found in Table 2.2 and Appendix 3 and 7 (Table A3.1).

### 2.1.3 Model setup and calibration

The one-dimensional numerical model MACRO (version 5.2 Larsbo *et al.*, 2005) represents the treated area of the Tylstrup field covering the upper five meters of the soil profile, always including

the groundwater table. The model is used to simulate water dynamics in the variably saturated zone during the full monitoring period May 1999-June 2020 and to establish an annual water balance.

Compared to the setup in Rosenbom *et al.* (2021), one year of climate and crop data were added to the MACRO setup. The setup was calibrated for the monitoring period May 1999-June 2004 and subsequently used to compare simulated water balance with monitoring results from July 2004 to June 2020. Daily time series of the groundwater table measured in piezometers located in the buffer zone, soil water content measured at three different depths (0.25, 0.6, and 1.1 mbgs) from the two profiles S1 and S2 (Figure 2.1), and the bromide concentration measured in the suction cups located 1 and 2 mbgs were all used in the calibration process. Data acquisition, model setup, and results related to the modelling are described in Barlebo *et al.* (2007).

## 2.2 Results and discussion

### 2.2.1 Soil water dynamics and water balances

The model simulation of the recent hydraulic year (July 2019-June 2020) is 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).

The simulated dynamics of the groundwater table were generally well captured for the recent hydraulic year (Figure 2.2B). Note that, as of January 1, 2019, monitoring of Tylstrup is on standby (Rosenbom *et al.*, 2020) meaning that water balance data will be collected as long as the monitoring equipment is operational – no water sampling is conducted. Measurement of the groundwater table is logged automatically in two piezometer screens P6.1 and P8.2.

Overall, the trends in soil water saturation were simulated successfully with decreasing overestimation with depth (Figure 2.2C-E). Until May 2019, the simulated water saturation was generally slightly overestimated at 0.25 m depth, whereas at 0.6 and 1.1 m depth, the water saturation was well captured. On May 14, 2019, a new data logger system containing a new software programme was installed. Unfortunately, due to a software malfunction, the collected water saturation from the TDR of this new system had errors that could not be corrected, and consequently, comparison between simulated and measured data was not possible.

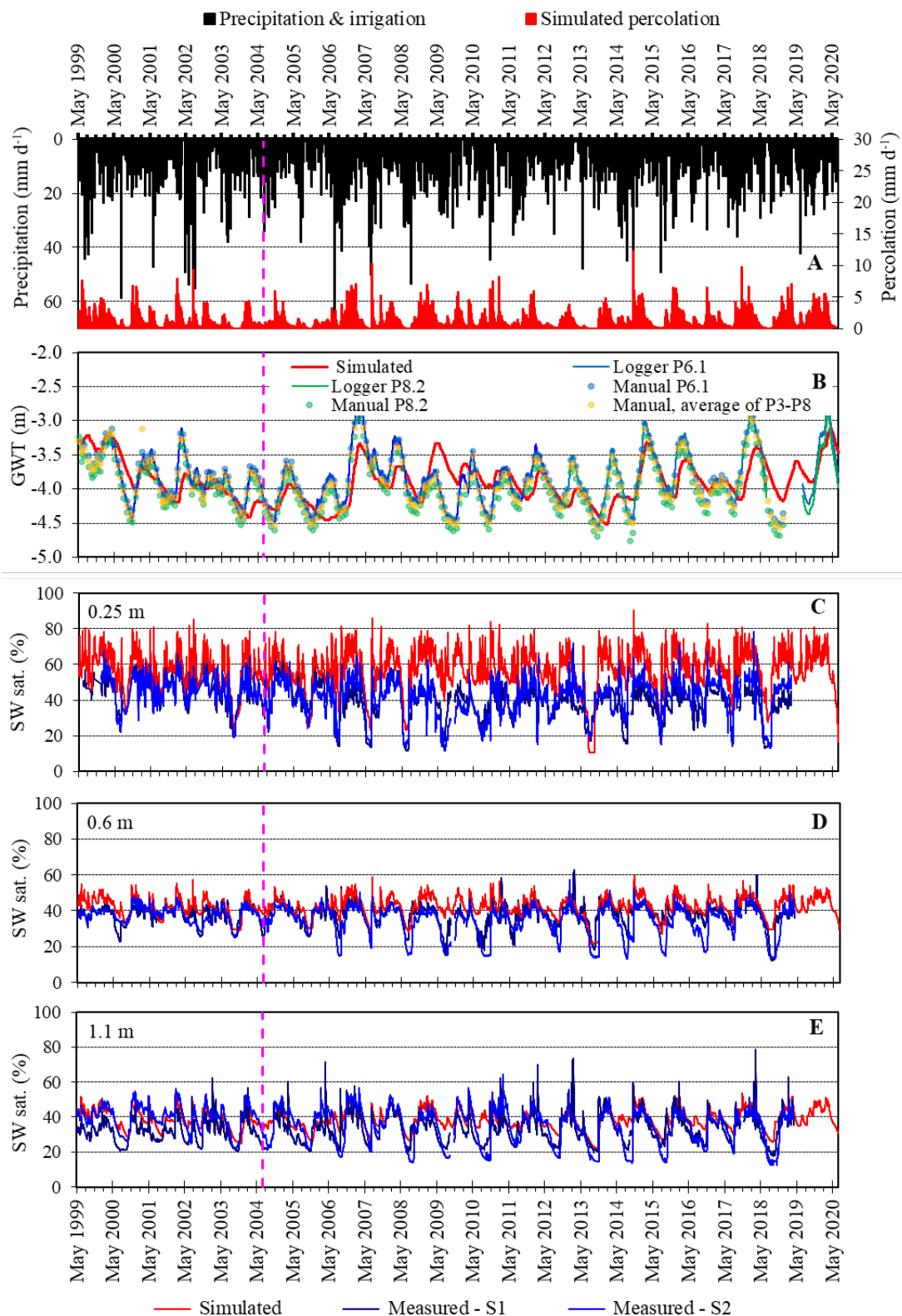
The resulting annual water balance for Tylstrup is shown for each hydraulic year of the monitoring period in Table 2.1. The recent hydraulic year July 2019-June 2020 had annual precipitation of 1047 mm yr<sup>-1</sup>, which is above the average of 924 mm yr<sup>-1</sup> for the entire monitoring period since 1999 (Table 2.1). The actual evapotranspiration of 657 mm yr<sup>-1</sup> was the second-highest calculated since monitoring began at the field (Table 2.1). With the high actual evapotranspiration estimated, the deduced groundwater recharge of 390 mm yr<sup>-1</sup> within the current hydrological year was below the average of 452 mm yr<sup>-1</sup> (Table 2.1). An overview of the monthly precipitation at each of the six PLAP fields is presented in Appendix 4.

**Table 2.1.** Annual water balance for Tylstrup (mm yr<sup>-1</sup>).

Period	Normal precipitation <sup>1)</sup>	Precipitation <sup>2)</sup>	Irrigation	Actual evapotranspiration <sup>3)</sup>	Groundwater Recharge <sup>4)</sup>
01.05.99–30.06.99 <sup>1)</sup>	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
01.07.17–30.06.18	773	1296	110	654	752
01.07.18–30.06.19	773	939	0	669	270
01.07.19–30.06.20	773	1047	0	657	390
<i>Average</i>	<i>773</i>	<i>924</i>	<i>43</i>	<i>514</i>	<i>452</i>

<sup>1)</sup> Normal values based on time series for 1961-1990. <sup>2)</sup> Measured precipitation is corrected to the soil surface according to the method of Allerup and Madsen (1979). <sup>3)</sup> Actual evapotranspiration is estimated by the MACRO-model applying climate data including potential evapotranspiration. <sup>4)</sup> Groundwater recharge is calculated as precipitation + irrigation - actual evapotranspiration.





**Figure 2.2.** Soil water dynamics at Tylstrup: Measured precipitation, irrigation, and simulated percolation 1 mbgs (A); simulated and measured groundwater table, GWT (B); simulated and measured soil water saturation, SW sat., at three different soil depths (C, D, and E). The measured data in B comprises piezometers located in the buffer zone. The measured data in C, D, and E from TDR probes at S1 and S2. The dashed vertical line indicates the end of the calibration period in June 2004.

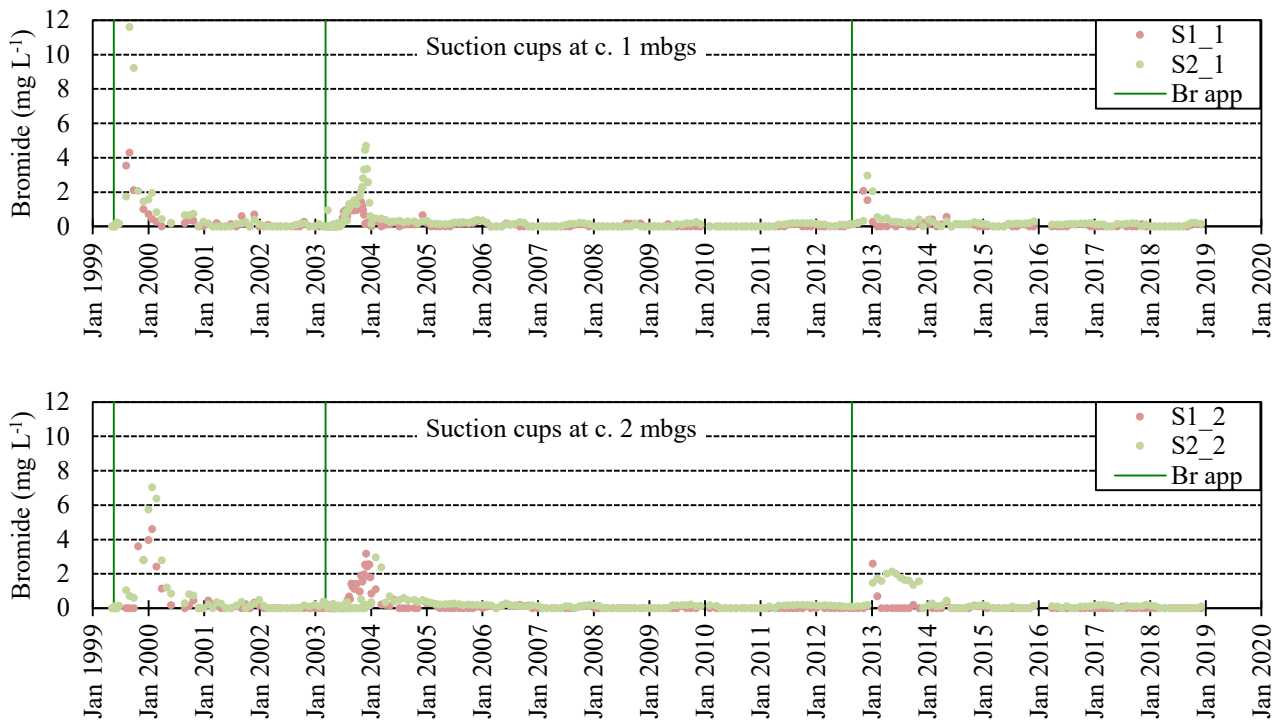
### **2.2.2 Bromide leaching**

As mentioned in Chapter 1, it was decided for the present report to revisit and analyse all bromide data from the fields to possibly improve the fundamental understanding of the hydrogeology at the fields. In the analyses, the time until the maximum concentration of bromide reaches the different depths of water sampling is used to estimate transport times from the surface to the specific filter of interest and allow for comparison between depths. The time of maximum concentration is used in conjunction with the general pattern of breakthrough curves where possible. However, since the number of collected samples differs among the monitored well screens, continuous breakthrough curves are not equally available for all screens. Therefore, the time of maximum concentration is used to achieve transport time ranges within each monitoring depth regardless of the number of samples collected. These transport times are not to be conflated with average transport times. The average transport time (mean breakthrough time) represents when half of the applied mass has passed through the location of measurement which may not necessarily coincide with the breakthrough of maximum concentration. Consequently, bromide detections are generally occurring both before and after the time of the reported maximum concentration breakthroughs.

At Tylstrup, bromide was applied three times (May 1999, March 2003, and August 2012) as 30 kg ha<sup>-1</sup> potassium bromide.

Two nests of suction cups are installed at the field, and therefore measurements from two locations are available for each depth, which in most cases gives reason to a variation in the observed breakthrough of maximum concentrations. In the suction cups located 1 mbgs, the maximum bromide concentrations after May 1999, March 2003, and August 2012 applications are measured within 4, 7-9, and 3-4 months (Figure 2.3). It is noted that bromide concentrations are also measured before the peak concentrations. E.g., within one month after the 2003 application, increased bromide concentrations resulting from the application are measured in S2, whereas the maximum bromide concentration is measured after nine months (Figure 2.3).

In the suction cups located 2 mbgs, the maximum bromide concentrations after May 1999, March 2003, and August 2012 applications are measured within 9, 8-12, and 5-9 months (Figure 2.3). Again, it is noted that increased bromide concentrations are also measured some time before the breakthrough of the maximum bromide concentration. E.g., within three months after the 1999 application, increased bromide concentrations stemming from the application are measured in S2, whereas the maximum bromide concentration is measured after nine months (Figure 2.3).



**Figure 2.3.** Measured bromide concentration in the variably saturated zone at Tylstrup. Water sampling from installations was stopped at the end of 2018 when the field was put on standby.

The maximum bromide concentrations generally reach the suction cup depth of 1 mbgs slower after the March 2003 application compared to the other two applications (Figure 2.3). This is also evident from the general patterns of bromide pulses, where the breakthroughs occur slower after the March 2003 application. The reason is presumably different conditions related to precipitation and temperature, and thus the soil water conditions. That is, bromide transport is dependent on soil saturation, and for instance, with higher temperatures, more evaporation could lead to less soil saturation. In contrast, increased precipitation could lead to more soil saturation. However, at 2 mbgs it seems that the time of bromide detections after all three applications are similar. Overall, the transport time for the maximum bromide concentration to 1 and 2 mbgs in the variably saturated zone is around 5 and 9 months, respectively.

For the groundwater samples, the current analysis is constricted to the monitoring wells; M2, M3, M4, M5, and H1 in the depth interval from around 4 to 8.5 mbgs (Figure 2.1). The measured bromide concentrations in the remaining monitoring wells, M1, M6, and M7 are generally less than 1 mg L<sup>-1</sup> in all depths (not shown but included in previous PLAP reports). M1 is regarded as an upstream well. However, as bromide is measured in M1, although in low concentrations, further analysis of the flow field is needed to fully understand the groundwater flow dynamics across the field. Such analyses are under preparation for all the fields. However, for the sake of simplicity, in the present analysis, M1, M6, and M7 are assumed not to be part of the flow field represented by the remaining wells.

The maximum bromide concentrations measured in the different wells representing different depths are specified. Since the transport time to at a specific depth differs in between wells (wells are located alongside the edges of the field), a time interval for breakthrough of the maximum bromide concentration is given for each depth and each bromide application. In the groundwater samples from

~4 mbgs, the maximum bromide concentrations after May 1999, March 2003, and August 2012 applications are measured within 12-35, 46-51, and 29-41 months, respectively (Figure 2.4).

The groundwater samples from ~4.5 mbgs from the horizontal well only represent bromide applied in August 2012. The maximum bromide concentration is measured 23 months after the application (Figure 2.4).

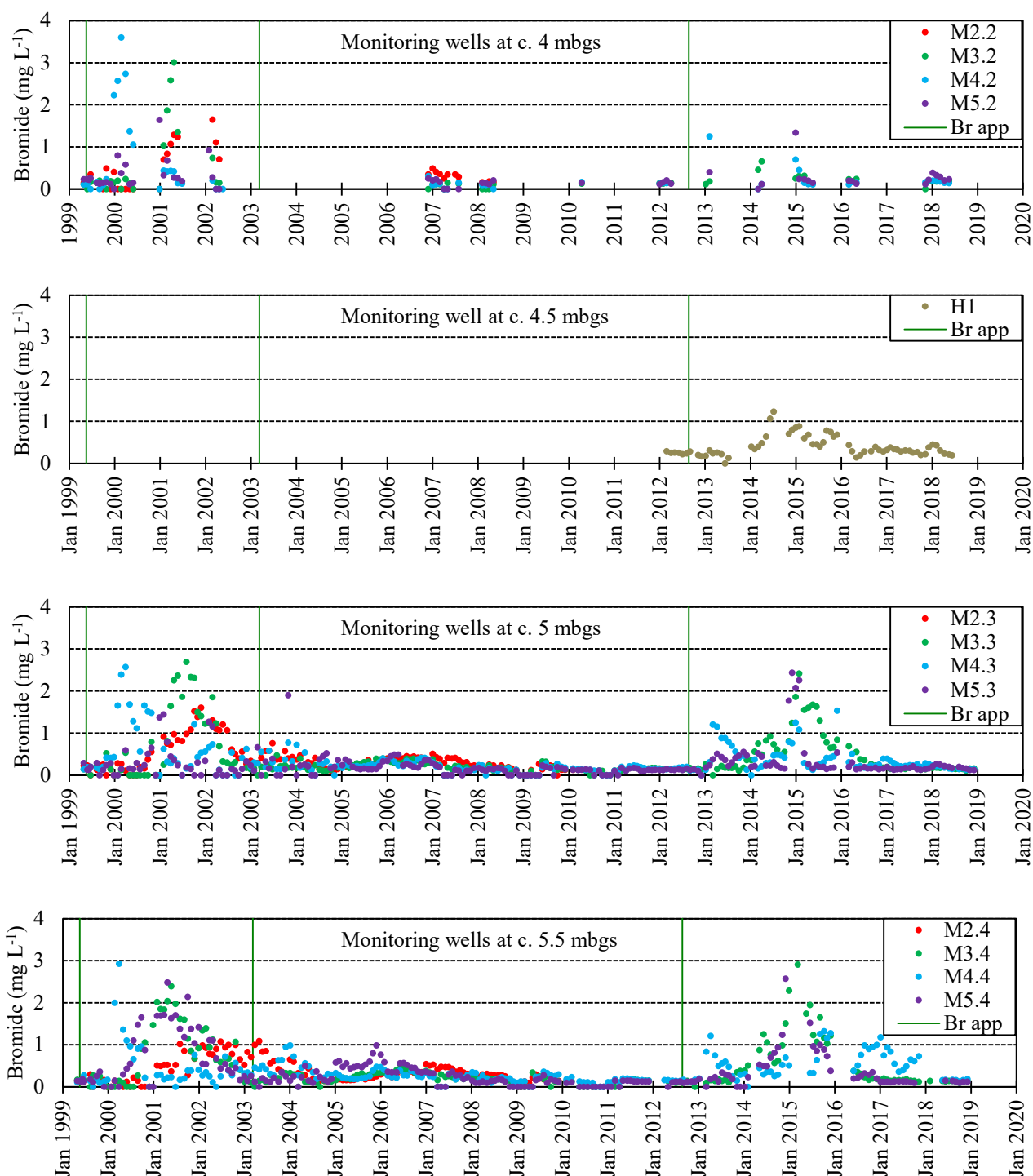
In the groundwater samples from ~5 mbgs, the maximum bromide concentrations after May 1999, March 2003, and August 2012 applications are measured within 12-32, 9-47, and 17-30 months (Figure 2.4).

In the groundwater samples from ~5.5 mbgs, the maximum bromide concentrations after May 1999, March 2003, and August 2012 applications are measured within 12-49, 11-47, and 29-39 months (Figure 2.4).

In the groundwater samples from ~6.5 mbgs, the maximum bromide concentrations after May 1999, March 2003, and August 2012 applications are measured within 30-32, 9-35, and 35 months (Figure 2.4).

In the groundwater samples from ~7.5 mbgs, the maximum bromide concentrations after May 1999, March 2003, and August 2012 applications are measured within 30-46, 12, and 64 months (Figure 2.4).

In the groundwater samples from ~8.5 mbgs, the maximum bromide concentrations after May 1999, March 2003, and August 2012 applications are measured within 29-30, 10-13, and 58 months (Figure 2.4).



**Figure 2.4.** Measured bromide concentration in the groundwater at Tylstrup. Water sampling from installations was stopped at the end of 2018 when the field was put on standby.

Only M4 and M5 are screened deeper than ~5.5 mbgs. Sampling for bromide analysis for the wells extending to ~8.5 mbgs was initiated from 2001, but continuous time series of bromide concentrations from both M4 and M5 are available only for the March 2003 application (Figure 2.5). Considering the general pattern of breakthrough curves to ~5.5 mbgs (Figure 2.4), the measured concentrations after the March 2003 application differ somewhat from the May 1999 and August 2012 applications

by showing substantially lower maximum concentrations. Therefore, the following discussion is separated into the May 1999 and August 2012 applications, and the March 2003 application.

#### *May 1999 and August 2012 applications*

The average breakthrough time for the maximum bromide concentration at a specific depth is calculated from the breakthrough times of maximum concentration within each of the wells representing that particular depth. Hence, for the May 1999 and August 2012 applications, the average time for maximum bromide concentrations reaching depths at around 4, 4.5, 5, and 5.5 mbgs are 23, 23, 29, and 30 months, respectively. However, it is clear that the transport time to the different wells varies considerably, which is illustrated by the intervals in which the maximum concentrations were measured in different screens representing the same depth. E.g., at ~5 mbgs, the maximum concentrations are measured within 12-32 and 17-30 months after the March 1999 and August 2012 applications (Figure 2.4). Further, it is noted that increased concentrations of bromide can be observed in all depths both before and after the breakthrough of maximum concentrations.

In general, the maximum bromide concentration peaks have passed the depth of ~5.5 mbgs around three years after application (Figure 2.4). It is noted that the number of measurements at a depth of ~4 mbgs is relatively sparse compared to the number of measurements at ~5 and ~5.5 mbgs. Nevertheless, the data capture increased bromide concentrations already after one year in depths of 4-5.5 mbgs in all wells. Together with, the rather large variation in the time for breakthrough of maximum bromide concentrations at the same depth for different wells, this indicates that though the field is characterized as a homogenous sandy field, heterogeneity is present and affects the transport of solutes.

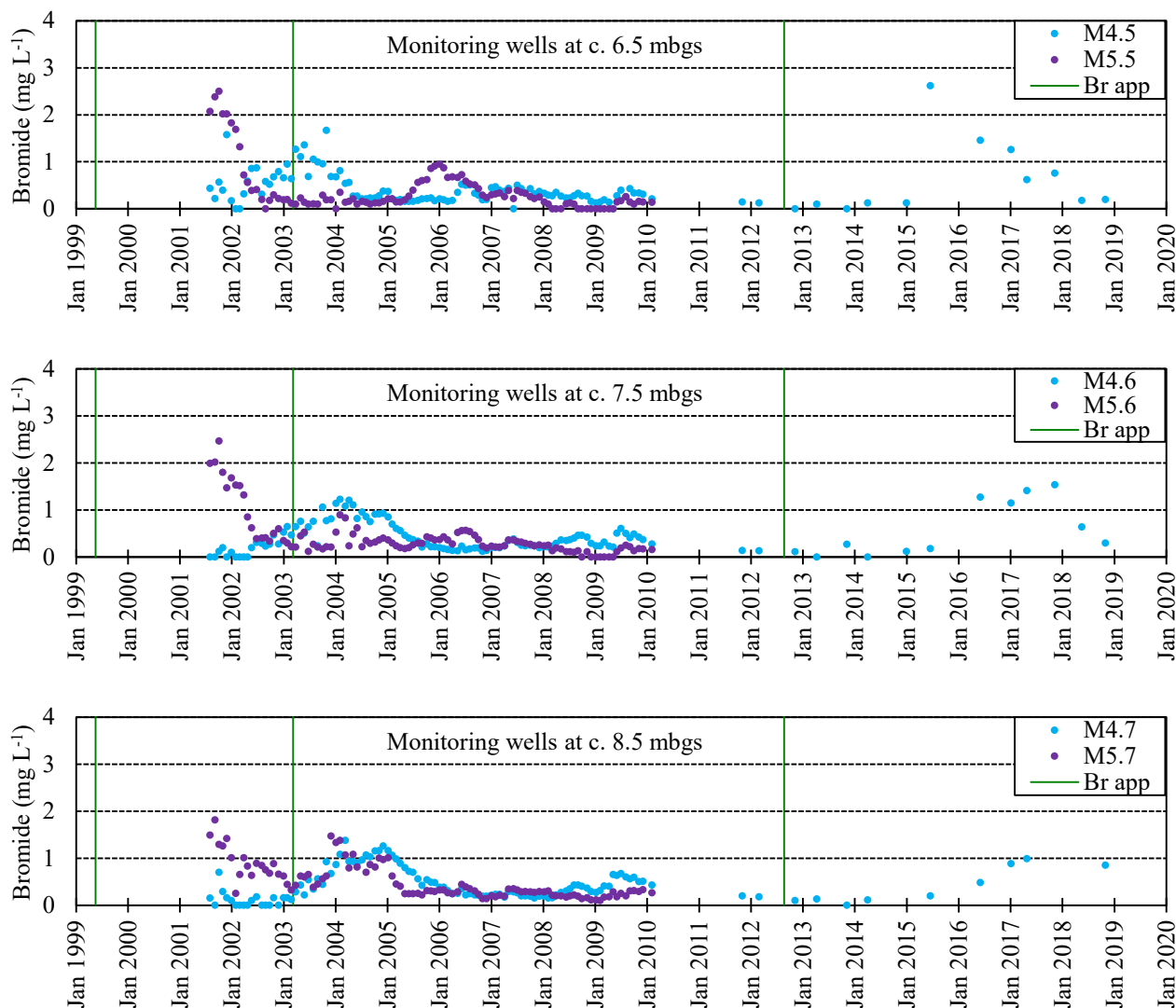
#### *March 2003 application*

In depths down to ~5.5 mbgs, maximum bromide concentrations after the March 2003 application are generally  $< 1 \text{ mg L}^{-1}$  (Figure 2.4). Further, it seems that there are no clear breakthrough curves with maximum concentrations and especially at ~4 mbgs, groundwater samples were not collected in the time immediately after the application. Curiously, the concentration magnitudes in the variably saturated zone are comparable after the March 2003 and August 2012 applications (Figure 2.3) and still, bromide concentrations measured in groundwater differ substantially. As such, bromide concentrations  $> 1 \text{ mg L}^{-1}$  are generally not measured after the March 2003 application, while they are measured after the August 2012 application. The reason for not observing concentrations  $> 1 \text{ mg L}^{-1}$  after the March 2003 application is not readily explained.

In the depths from ~6.5 to ~8.5 mbgs, the measured bromide concentration patterns between the March 2003 and August 2012 applications show breakthrough curves resembling pulse concentrations. The measurements show that maximum bromide concentrations, also  $> 1 \text{ mg L}^{-1}$ , are present deeper than ~5.5 mbgs after the March 2003 application.

While the breakthrough time of maximum concentrations after the March 2003 application is similar in screen depths around 7.5 and 8.5 mbgs, there are pronounced differences between different wells in the breakthrough times of maximum concentrations in the screen depths of ~6.5 mbgs (Figure 2.5). Here, the maximum concentrations after the bromide application are observed at 9 and 35 months in M4 and M5, respectively. The later maximum concentration breakthrough in M5 at ~6.5 mbgs is not consistent with the maximum concentration breakthroughs of its screens around 7.5 and 8.5 mbgs, where the maximum concentrations apparently are observed 12 and 10 months after application (Figure 2.5). However, when looking at the general pattern of bromide reaching M4, there is a pattern

of a pulse moving in depth with time. It seems that the concentrations reaching ~6.5 mbgs in M4 immediately after the March 2003 application is a bromide pulse from the May 1999 application. This pulse is moving downward with time (Figure 2.5). Whether a pulse from the May 1999 application is seen in M5 from ~6.5-8.5 mbgs is not entirely clear. However, there does seem to be a pattern of a pulse in M5 moving downward with time from January 2006. Likewise, the breakthrough of maximum concentrations ~7.5-8.5 mbgs around January 2004 may stem from the May 1999 application as these pulses coincide with pulses observed in M4 (Figure 2.5). Therefore, it seems that bromide concentrations are generally reaching ~6.5-8.5 mbgs around 3-4 years after application.



**Figure 2.5.** Measured bromide concentration in the groundwater at Tylstrup. Water sampling from installations was stopped at the end of 2018 when the field was put on standby.

Overall, the results from the three bromide applications at Tylstrup show that at a depth of ~4-5.5 mbgs, maximum concentrations of bromide can generally be measured in the groundwater monitoring wells up to around three years after application. This is also supported by the general pattern of bromide concentrations reaching these depths showing increased bromide concentrations 1-3 years after application. Deeper than ~5.5 mbgs, increased bromide concentrations are generally present 4-

5 years after application. For all the sampled depths, it is noted that bromide concentrations above the detection limit are measured before and after the breakthrough of maximum concentrations.

### **2.2.3 Pesticide leaching**

Due to economic constraints, the field was not monitored since January 1, 2019, and application of pesticides will only be done if needed from an agricultural management perspective (the field is still cultivated), and only pesticides not relevant for the monitoring program are used.

Pesticide applications from 2014/2015 until the latest growing seasons before the field was set on standby by the end of 2018 are listed in Table 2.2. For information about monitoring of pesticides and degradation products at Tylstrup since the beginning of PLAP in May 1999 until 2014, please refer to Appendix 7.

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 depth) refers to accumulated percolation simulated with the MACRO model.

The leaching risk of pesticides evaluated before January 1, 2019, is presented in Rosenbom *et al.* (2021) and previous monitoring reports (see [www.plap.dk](http://www.plap.dk)).



**Table 2.2.** Pesticides analysed at Tylstrup. Precipitation (precip.) and percolation (percol.) are accumulated within the first year (Y 1<sup>st</sup>), and month (M 1<sup>st</sup>) after application. C<sub>mean</sub> is average leachate concentration at 1 mbgs. See Appendix 2 for calculation method and Appendix 7 (Table A7.1) for previous applications of pesticides.

Crop – Year of harvest	Applied Product	Analysed Pesticide (P) / Degradation product (M)	Application date	End of monitoring	Y 1 <sup>st</sup> precip. (mm)	Y 1 <sup>st</sup> percol. (mm)	M 1 <sup>st</sup> precip. (mm)	M 1 <sup>st</sup> percol. (mm)	C <sub>mean</sub> (µg L <sup>-1</sup> )
<b>Winter wheat 2015</b>	Orius 200 EW Tebuconazole (P)	1,2,4-triazole (M)	Nov 14	Jun 18	1045	467	105	80	x
	Proline EC 250 Prothioconazole (P)	1,2,4-triazole (M)	May 15	Jun 18	1060	504	76	9	x
<b>Spring barley 2016</b>	Fighter 480 Bentazone (P)	Bentazone (P)	May 16	Apr 18	935	464	132	23	<0.01
		6-hydroxy-bentazone (M)	May 16	Apr 18	935	464	132	23	<0.01
		8-hydroxy-bentazone (M)	May 16	Apr 18	935	464	132	23	<0.01
		N-methyl-bentazone (M)	May 16	Apr 18	935	464	132	23	<0.01
<b>Spring barley 2017</b> SD: Redigo Pro 170 FS (Prothioconazole + tebuconazole)	Hussar Plus OD								
	Mesosulfuron-methyl- Na (P)	AE F099095 (M)	May 17	Dec 18	1221	673	110	16	<0.01
		AE F160459 (M)	May 17	Dec 18	1221	673	110	16	<0.01
	Bumper 25 BC* Propiconazole (P)	1,2,4-triazole (M)	Jun 17	Dec 18	1337	682	171	26	x
<b>Winter barley 2018</b>	Standby								
<b>Spring oats 2019</b>	Standby								
<b>Spring barley 2020</b>	Standby								

Systematic chemical nomenclature for the analysed pesticides is given in Appendix 1. SD = Seed dressing.

\* Application both 1<sup>st</sup> June and 14<sup>th</sup> June.

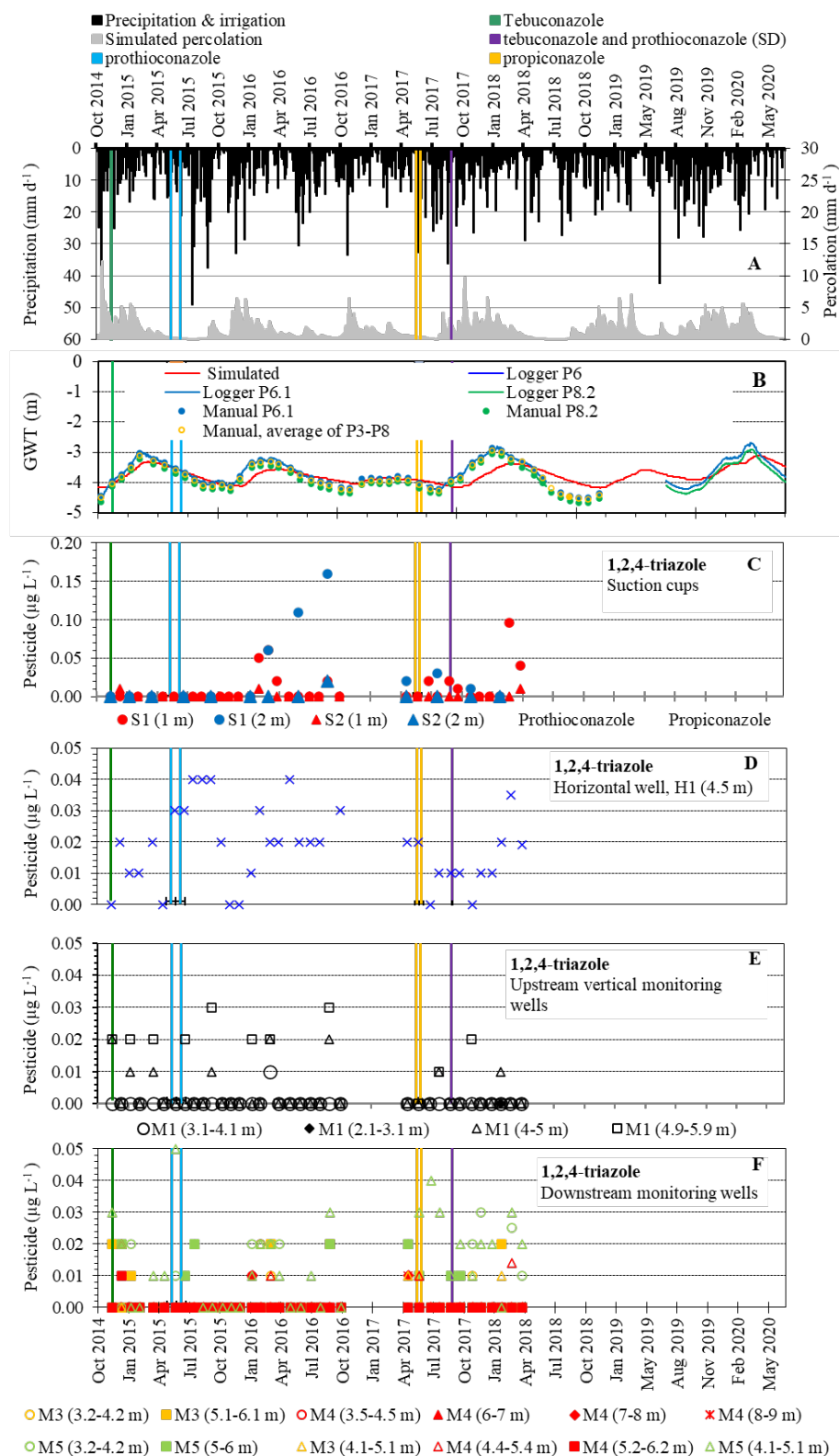
x Due to a high background content of 1,2,4-triazole, the results of the analysis cannot be linked directly to the specific application, why C<sub>mean</sub> is not presented.

## Azole fungicides and 1,2,4-triazole monitoring

This section is included to compare 1,2,4-triazole monitoring from all six fields, although no new data is applied since the last report, albeit all figure formats are changed. Evaluation of 1,2,4-triazole monitoring at Tylstrup, covering the full monitoring period until the field was set on standby, is published in the previous report (Rosenbom *et al.* 2021).

The azole fungicides tebuconazole, propiconazole, prothioconazole, and epoxiconazole were used several times since 1999 in this field, but the monitoring of 1,2,4-triazole, a common degradation product from these azole fungicides, was not introduced until October 2014. From 2017, all seed dressings on sowing seeds used in PLAP are registered. The 1,2,4-triazole data are presented for the full monitoring period starting from 2014 and knowing that the azole fungicides were used before this.

Tebuconazole was sprayed on the field on November 14, 2014, and prothioconazole was sprayed twice: May 14, and June 12, 2015 – both as split applications. Only 1,2,4-triazole was included in the monitoring programme. Prothioconazole was included in PLAP to investigate whether it degrades to 1,2,4-triazole only in minor amounts in soil, as stated in the EFSA conclusion. In addition to spraying of tebuconazole and prothioconazole, azole-containing products may have been applied in the form of seed dressings on the winter wheat sown September 2014, as well as on the spring barley sown April 2016. The amounts and substances applied with these two sowings were not recorded, however. The spring barley sown in March 2017 and winter barley sown in 2017 were coated with tebuconazole and prothioconazole. Monitoring of 1,2,4-triazole stopped in May 2018 and Tylstrup was set on standby by the end of December 2018.



**Figure 2.7.** 1,2,4-triazole monitoring at Tylstrup. Precipitation, irrigation, and simulated percolation 1 mbgs (A); measured and simulated groundwater table (B); concentration in the variably saturated zone (C) and saturated zone (D-F). The vertical lines indicate pesticide application. SD is pesticides applied as seed dressing. Seed dressings before 2017 were not registered. 1,2,4-triazole monitoring stopped in April 2018 and Tylstrup was set on standby by the end of 2018.

## 3 Pesticide leaching at Jyndeved

### 3.1 Materials and methods

#### 3.1.1 *Field description and monitoring design*

Jyndeved 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 mbgs (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 3.1). The geological description points to Jyndeved being a sandy meltwater plain, with local occurrences of thin clay and silt beds.

In September 2011, the monitoring system was extended with three horizontal screens (H1) 2.5 mbgs in the southeastern corner of the field (Figure 3.1). A brief description of the drilling and design of H1 is given in Appendix 8.

The water sampling plan has been altered several times since the beginning of PLAP. During the current monitoring period, water sampling at Jyndeved was done monthly from suction cups at 1 m depth at S1 and S2 and wells M1, M4, M7, and H1. Additional samples from wells M2 and M5 are taken half-yearly. No sampling is done from suction cups at 2 m depth at S1 and S2 and wells M3 and M6. Due to earlier budget reduction, only the two uppermost well screens below the groundwater table are sampled. Appendix 2 describes the sampling procedure in more detail.

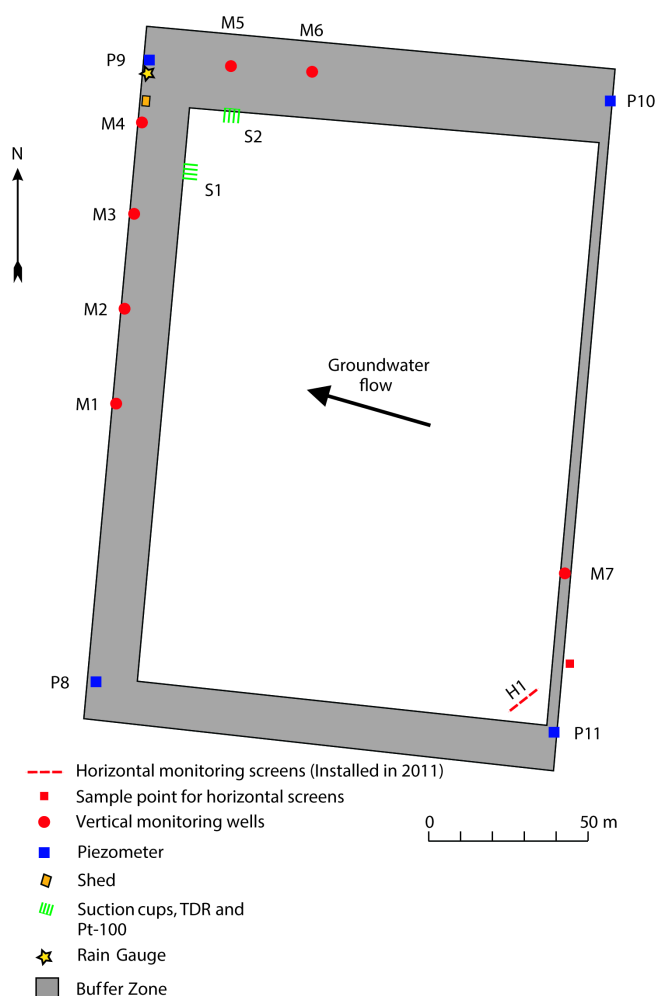
Due to errors in the software of the new data logger installed at Jyndeved on 2 May 2019, erroneous TDR-data were obtained. Therefore, only TDR-data collected before installation of the new data logger on 2 May 2019 is presented for the field (Figure 3.2).

#### 3.1.2 *Agricultural management*

On August 22, 2018, the field was sprayed with glyphosate, which was not included in the monitoring. On October 10, 2018, the field was ploughed and hereafter sown with winter rye (cv. Bono with fludioxonil as a seed dressing). The rye emerged on November 5, 2018. A split application of proquinazid was made on April 25 and May 9, 2019. Two of its degradation products, IN-MM671, and IN-MM991, were included in the monitoring programme. On May 8, 2019, the growth regulator ethephone was used together with the herbicide MCPA – neither of the two were monitored. A dry growing season necessitated irrigation seven times: April 11 and 22 April, May 5 and 24, June 8 and 26, and July 4, 2019 - each time using 30 mm. Harvest of the winter rye was done August 11, 2019, yielding 68.3 hkg ha<sup>-1</sup> of grain (85 % dry matter) and 44.8 hkg ha<sup>-1</sup> of straw (100% dry matter).

The field was ploughed on February 3, 2020, and on April 25 planted with potatoes (cv. Kuras). On May 20, the potatoes were at BBCH 08, and weeds in the field were sprayed with a mixture of glyphosate and clomazone. Neither of these pesticides was monitored. The potatoes emerging May 24 (BBCH 09) were irrigated with 20 mm on June 13 and 21, 2020, and with 30 mm on August 2, 8, and 15, 2020. Spraying against fungi was done with cyazofamid on June 14 and 23, July 17, August

12, and September 1, 10 and 16, 2020. Three of its known degradation products (DMSA, CTCA, and CCIM) and one potential degradation product (N,N-DMS) were monitored. The evaluation of these four degradation products is ongoing and will be reported in upcoming reports. Two additional fungicides were used but not monitored: One containing propamocarb and cymoxanil was used twice (August 6 and 19), and another containing mancozeb was used five times (July 3, 9, and 27, and August 3 and 27, 2020). Pests were sprayed with azadirachtin on both August 12 and September 1, 2020, with the intention of monitoring for the degradation product azadirachtin H\*. However, as azadirachtin H\* was unstable, it could not be analysed and the compound will not be further discussed (Chapter 8). Acetamiprid, another compound for pest control, was applied on June 23 and July 17, 2020, and two of its degradation products, IM-1-4 and IM-1-5, were included in the monitoring. Harvest of potatoes was done on October 21, 2020, yielding 142.84 hkg ha<sup>-1</sup> (100% dry matter).



**Figure 3.1.** Overview of the Jynde vad field. The innermost white area indicates the cultivated area surrounded by the buffer zone. Pesticide monitoring is conducted monthly and half-yearly from selected horizontal and vertical monitoring screens and suction cups as described in section 3.1.1 and in Appendix 2. At S1 and S2, water content (via TDR) and soil temperature (via Pt100) is measured at four different depths. Additionally, suction cups are installed to collect pore water from the variably saturated matrix for analysis of pH-independent compounds.

### 3.1.3 Model setup and calibration

The one-dimensional numerical model MACRO (version 5.2 Larsbo *et al.*, 2005) represents the treated area of the Jynde vad field covering the upper five meters of the soil profile, always including

the groundwater table. The model is used to simulate water dynamics in the variably- saturated zone during the full monitoring period May 1999–June 2020 and to establish an annual water balance.

Compared to the setup in Rosenbom *et al.* (2021), one year of climate and crop data was added to the MACRO setup. The setup was calibrated for the monitoring period May 1999-June 2004 and subsequently used to compare simulated water balance with monitoring results from July 2004 to June 2020. Daily time series of the groundwater table measured in piezometers located in the buffer zone, soil water content measured at three different depths (0.25, 0.6, and 1.1 mbgs) from the two profiles S1 and S2 (Figure 3.1), and the bromide concentration measured in the suction cups located 1 and 2 mbgs were all used in the calibration process. Data acquisition, model setup, and results related to the modelling 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 measured data (i.e., depth to groundwater table and water saturation) 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 (Figure 3.2B). For the previous monitoring period, July 2018-June 2019, groundwater simulations did not capture the measured low groundwater table in the second half of 2018. In this period, precipitation seemed to contribute more to the groundwater recharge increasing the simulated groundwater level compared to the measured. Hence, the model had difficulties in describing the percolation during the warmest year measured in Denmark (DMI, 2019). However, the model does seem to capture the dynamics and the levels measured in the second half of 2019. From May 2019 onwards, the groundwater levels simulated were in accordance with measured levels (Figure 3.2B).

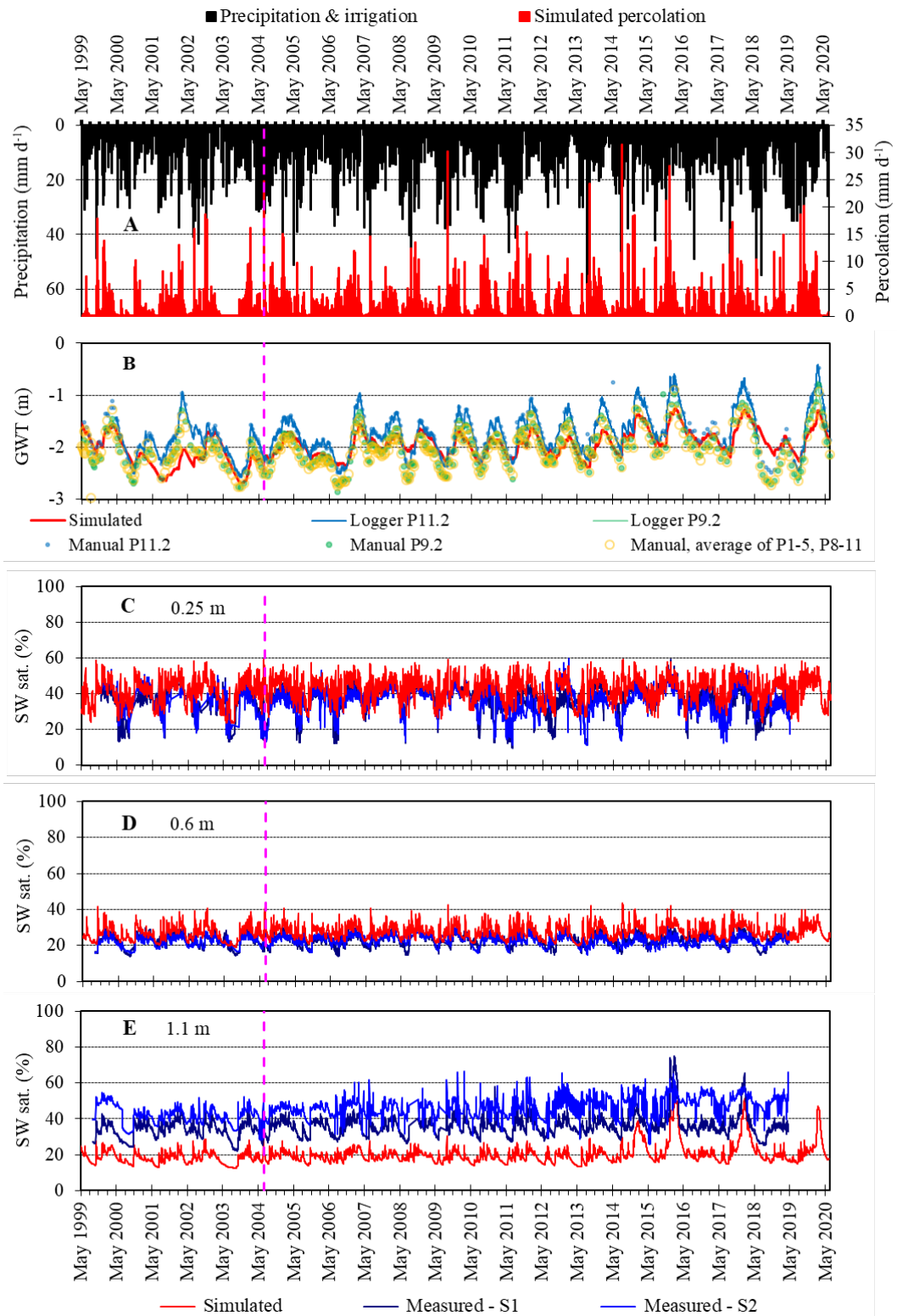
The trends in the measured soil water saturation were in general captured by the model. In all three measured depths, there is an overall offset in the simulated water saturation showing an overestimation within approximately 10% for the TDRs in 0.25 and 0.6 mbgs, respectively. Except for the TDR in 1.1 m, the modelled saturation is too high compared to the measured values. For the TDR in 1.1 m depth, the pattern is consistent with trends from the previous years where the simulation shows a general underestimation of the calculated water saturation (Figure 3.2E). As noted above, water saturation data were not valid from 2 May 2019 and onwards, and therefore not shown.

The resulting water balance for Jyndevad for all the monitoring periods is shown in Table 3.1. The measured precipitation of 1188 mm for the current year 2019-2020 is slightly above average (8%), while the irrigation of 70 mm is lower than the average (-24%). The actual evapotranspiration of 460 mm is less than the average (-12%) while the groundwater recharge of 798 mm is above average (20%). Compared to the warmest year, 2018 (DMI, 2019), the current groundwater recharge indicates that the aquifer is being replenished. An overview of the monthly precipitation of the six PLAP fields is presented in Appendix 4.

**Table 3.1.** Annual water balance for Jynde vad (mm yr<sup>-1</sup>).

	Normal precipitation <sup>1)</sup>	Precipitation <sup>2)</sup>	Irrigation	Actual evapotranspiration <sup>3)</sup>	Groundwater recharge <sup>4)</sup>
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
01.07.17–30.06.18	995	1230	210	570	870
01.07.18–30.06.19	995	805	240	569	477
01.07.19–30.06.20	995	1188	70	460	798
Average	995	1097	92	525	664

<sup>1)</sup> Normal values based on time series for 1961-1990. <sup>2)</sup> Precipitation is corrected to the soil surface according to the method of Allerup and Madsen (1979). <sup>3)</sup> Actual evapotranspiration is estimated by the MACRO-model applying climate data including potential evapotranspiration. <sup>4)</sup> Groundwater recharge is calculated as precipitation + irrigation - actual evapotranspiration.



**Figure 3.2.** Soil water dynamics at Jydevad: Measured precipitation, irrigation, and simulated percolation 1 mbgs (A), simulated and measured groundwater table, GWT (B); simulated and measured soil water saturation (SW sat.) at three different soil depths (C, D, and E). The measured data in B comprises piezometers located in the buffer zone. The measured data in C, D, and E from TDR probes at S1 and S2. The dashed vertical line indicates the calibration period to June 2004.

### 3.2.2 Bromide leaching

As mentioned in Chapter 1, it was decided for the present report to revisit and analyse all bromide data from the fields to possibly improve the fundamental understanding of the hydrogeology at the fields. In the analysis, the time until the maximum concentration of bromide reaches the different depths of water sampling is used to estimate transport times from the surface to the specific filter of interest and allow for comparison between depths. The time of maximum concentration is used in conjunction with the general pattern of breakthrough curves where possible. However, since the number of collected samples differs among the monitored well screens, continuous breakthrough curves are not equally available for all screens. Therefore, the time of maximum concentration is used to achieve transport time ranges within each monitoring depth regardless of the number of samples collected. These transport times are not to be conflated with average transport times. The average transport time (mean breakthrough time) represents when half of the applied mass has passed through the location of measurement which may not necessarily coincide with the breakthrough of maximum concentration. Consequently, bromide detections are generally occurring both before and after the time of the reported maximum concentration breakthroughs.

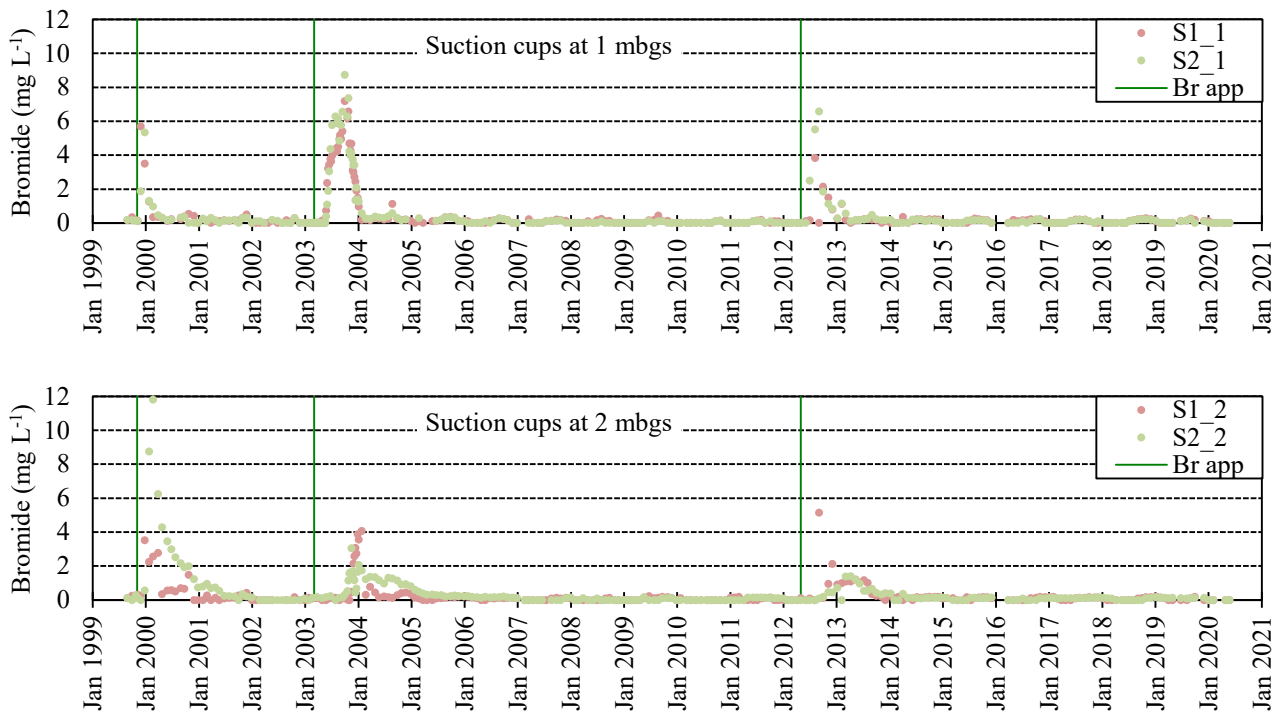
At Jyndevad, bromide was applied three times (November 1999, March 2003, and May 2012) as 30 kg ha<sup>-1</sup> potassium bromide.

In the suction cups located 1 mbgs, the maximum bromide concentrations after November 1999, March 2003, and May 2012 application are measured within 1-2, 7, and 3-4 months, respectively (Figure 3.3).

In the suction cups located 2 mbgs, the maximum bromide concentrations after November 1999, March 2003, and May 2012 applications are measured within 2-3, 8-11, and 4-11 months, respectively (Figure 3.3).

The maximum bromide concentrations generally reach the suction cup depth of 1 mbgs slower after the March 2003 application compared to the other applications. A similar pattern is seen at the Tylstrup field, and the reason is likely related to different precipitation and temperature conditions in 2003, resulting in different soil water conditions. That is, bromide transport is dependent on soil saturation, and for instance, with higher temperatures, more evaporation could lead to less soil saturation. In contrast, increased precipitation could lead to more soil saturation. Overall, the transport time for the maximum bromide concentration to 1 and 2 mbgs in the variably saturated zone is around 4 and 7 months, respectively.





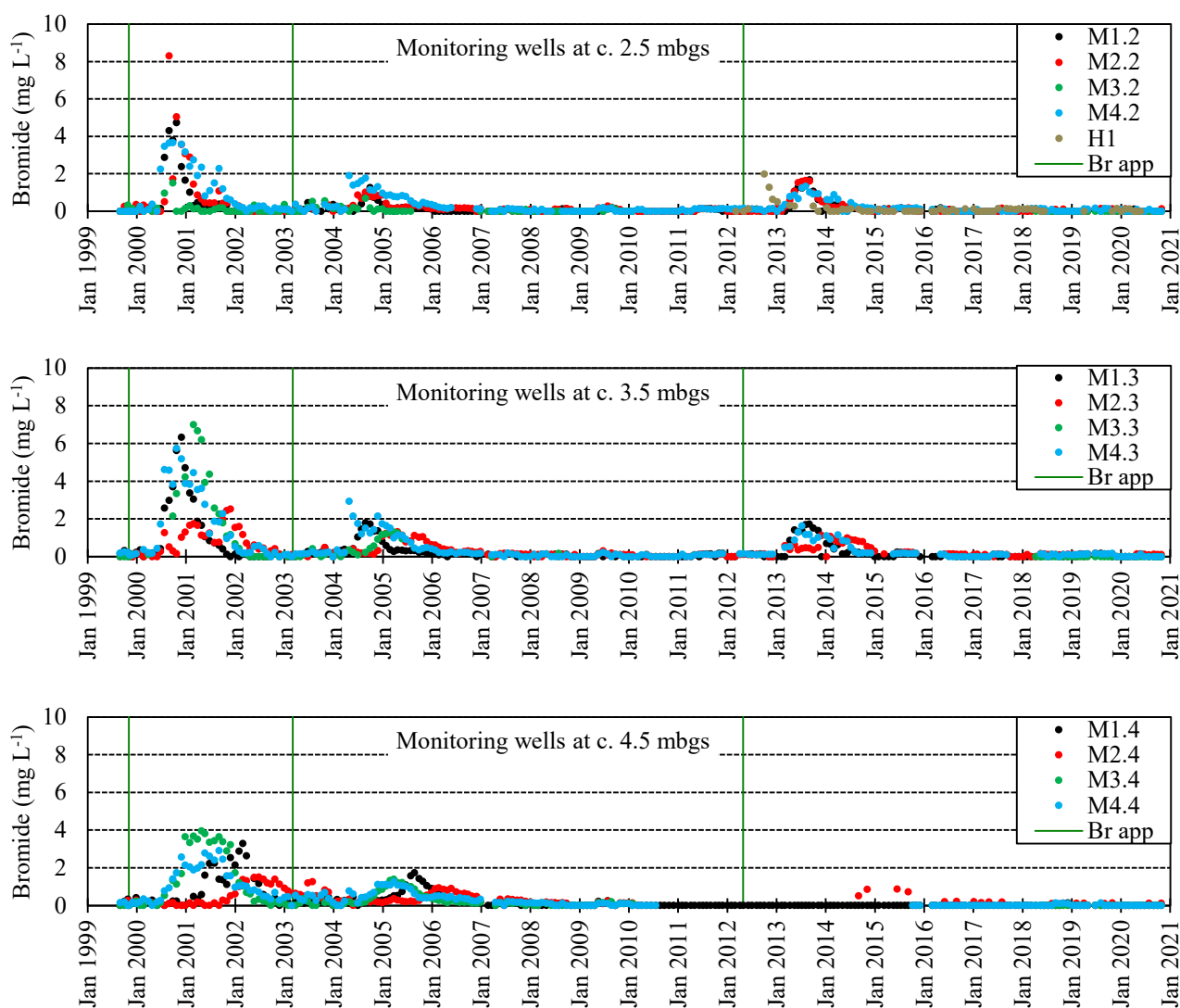
**Figure 3.3.** Measured bromide concentration in the variably saturated zone at Jyndevad.

For the groundwater samples, the current analysis is constricted to the monitoring wells; M1, M2, M3, M4, and H1 in the depth interval from around 2.5 to 4.5 mbgs (Figure 3.1). Sampling is conducted from ~1.5 mbgs in these wells also, but as measured concentrations are generally close to the detection limit or below (not shown but included in previous PLAP reports, e.g., Rosenbom *et al.*, 2021) the results are not included in the analysis. The measured bromide concentrations in the remaining monitoring wells, M5, M6, and M7 are generally less than 1 mg L<sup>-1</sup> in all depths (not shown but included in previous PLAP reports, e.g., Rosenbom *et al.*, 2021). M7 is regarded as an upstream well and as bromide is measured in M7, further analysis of the flow field is needed to fully understand the groundwater flow dynamics across the field. Such analyses are under preparation for all the fields. However, for the sake of simplicity, in the present analysis, M5, M6, and M7 are not assumed to be part of the flow field represented by the remaining wells.

In the groundwater samples from ~2.5 mbgs, the maximum bromide concentrations after November 1999, March 2003, and May 2012 applications are measured within 10-11, 13-19, and 5-16 months (Figure 3.4).

In the groundwater samples from ~3.5 mbgs, the maximum bromide concentrations after November 1999, March 2003, and May 2012 applications are measured within 11-25, 13-25, and 14-19 months (Figure 3.4).

In the groundwater samples from ~4.5 mbgs, the maximum bromide concentrations after November 1999, March 2003, and May 2012 applications are measured within 18-32, 5-29, and 37-87 months (Figure 3.4).



**Figure 3.4.** Measured bromide concentration in the groundwater at Jynde vad.

For a specific depth, the average breakthrough time for the maximum bromide concentration is calculated from the breakthrough time of the maximum concentration within each of the wells representing that particular depth. Thus, for the November 1999, March 2003, and May 2012 applications, the average time for maximum bromide concentrations reaching the screens at around 2.5, 3.5, and 4.5 mbgs are 14, 18, and 35 months, respectively. For the screens in  $\sim 4.5$  mbgs, it is noted that the interval of 37-87 months in which the breakthrough of maximum concentrations is observed after the May 2012 application is relatively large compared to the intervals of maximum concentration breakthrough from the other applications. The relatively large interval in which maximum concentrations are observed after the May 2012 application is mainly due to lack of bromide detections in M3 and M4 up to four years after the application (Figure 3.4). The maximum concentrations do not exceed  $0.14 \text{ mg L}^{-1}$  in M1 and M4, and the concentrations are substantially lower compared to the maximum concentration of  $0.87 \text{ mg L}^{-1}$  measured after 37 months in M2. If the maximum concentrations from M1 and M4 after the May 2012 application are omitted in calculating the average time for maximum bromide concentrations reaching  $\sim 4.5$  mbgs, the average time is changed from 35 months to 24 months.

Overall, the average breakthrough time of measured maximum concentrations within the different depths and locations coincides with the general breakthrough patterns. At ~2.5-3.5 mbgs, bromide pulses generally show breakthrough 0.5-1.5 years after application and at ~4.5 mbgs, the time of breakthrough is generally 1-2 years after application (Figure 3.4). For all the sampled depths, it is noted that bromide concentrations above the detection limit are measured before and after the transport times representing maximum concentrations.

### **3.2.3 Pesticide leaching**

Monitoring at Jyndevad began in September 1999 and encompasses the pesticides and degradation products shown in Appendix 7. Several azole fungicides have had great focus since the beginning of the programme, but especially their common degradation product 1,2,4-triazole is intensively monitored since it was introduced in 2014. All pesticide applications since 2014 are therefore listed in Table 3.2. The recent two years are shown together with precipitation and simulated percolation from 2018/2019 and 2019/2020 in Figure 3.6. It is noted that precipitation is corrected to the soil surface according to Allerup and Madsen (1979), whereas percolation (1 mbgs) refers to accumulated percolation simulated with the MACRO model (Table 3.1). Moreover, due to the very short monitoring period and few data points, pesticides applied after 1 April 2020 are not evaluated in this chapter, although presented in Table 3.2 and Figure 3.6.

For all pesticides and degradation products (except 1,2,4-triazole where the full monitoring period is evaluated), this chapter evaluates the monitoring from July 2018 to June 2020 at Jyndevad. The leaching risk of pesticides evaluated before this period is available in previous monitoring reports (see [www.plap.dk](http://www.plap.dk)). As all seeds sown in PLAP are purchased from a commercial agribusiness supplier, these have most likely been coated with seed dressing containing one or more of the pesticides included for testing in PLAP. Seed dressing information was, however, not registered in PLAP until 2017. Seed dressings used from 2017 and onwards are listed in Table 3.2.

### **Pesticides applied in 2020**

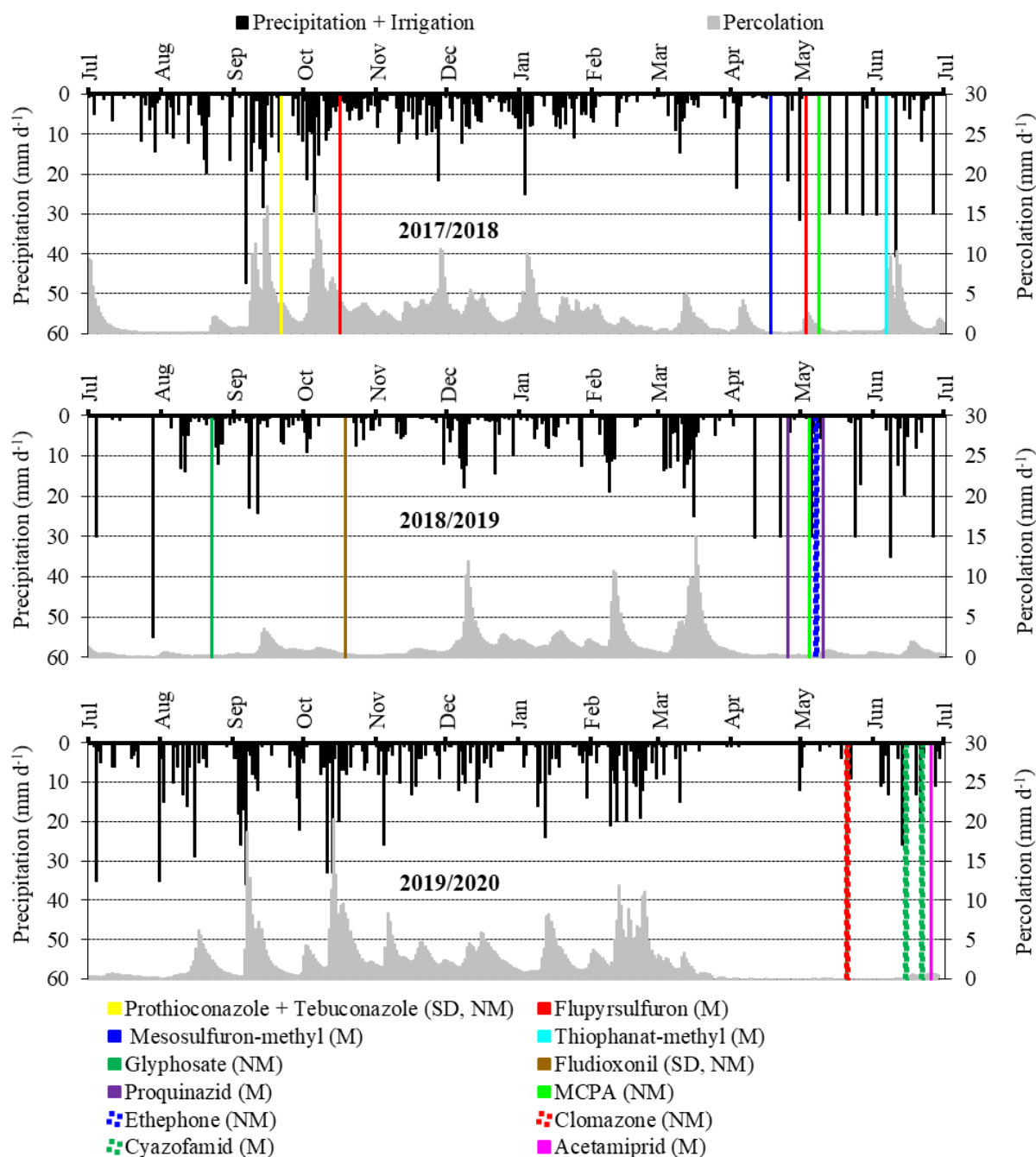
Two pesticides, acetamiprid and cyazofamid, were used in the potato crop in 2020. Two degradation products from acetamiprid, IM-1-4 and IM-1-5, and one known degradation product, DMSA, and one suggested degradation product N,N-DMS from cyazofamid were introduced in the monitoring in May 2020. As the reporting period ends June 30, 2020, the monitoring period is too short for an evaluation of these pesticides and degradation products, but they will be included in next year's report.

**Table 3.2.** Pesticides analysed at Jyndevad. Precipitation (precip.) and percolation (percol.) are accumulated within the first year (Y 1<sup>st</sup>), and month (M 1<sup>st</sup>) after application. C<sub>mean</sub> is average leachate concentration at 1 mbgs. See Appendix 2 for calculation method and Appendix 7 (Table A7.2) for previous applications of pesticides.

Crop – Year of harvest	Applied Product	Analysed Pesticide (P) / Degradation product (M)	Application date	End of monitoring	Y 1 <sup>st</sup> precip. (mm)	Y 1 <sup>st</sup> percol. (mm)	M 1 <sup>st</sup> precip. (mm)	M 1 <sup>st</sup> percol. (mm)	C <sub>mean</sub> (µg L <sup>-1</sup> )
<b>Winter wheat 2015</b>	Lexus 50 WG Flupyrifluron-methyl	Flupyrifluron-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 Opus	1,2,4-triazole (M)	Nov 14	Jun 20*	1253	645	86	35	- <sup>3</sup>
	Epoxiconazole Proline EC 250	1,2,4-triazole (M)	May 15	Jun 20*	1323	754	81	10	- <sup>3</sup>
	Prothioconazole	1,2,4-triazole (M)	Jun 15	Jun 20*	1435	789	103	10	- <sup>3</sup>
<b>Spring barley 2016</b>	Fighter 480 Bentazone	Bentazone(P)	May 16	Apr 18	1174	633	85	6	0.01
		6-hydroxy-bentazone (M)	May 16	Apr 18	1174	633	85	6	<0.01
		8-hydroxy-bentazone (M)	May 16	Apr 18	1174	633	85	6	<0.01
		N-methyl-bentazone (M)	May 16	Apr 18	1174	633	85	6	<0.01
	Bumper 25 EC Propiconazole <sup>1</sup>	1,2,4-triazole (M)	Jun 16	Jun 18	1171	631	247	112	- <sup>3</sup>
<b>Peas 2017</b>	Fighter 480 Bentazone	Bentazone (P)	May 17	Apr 18	1386	849	148	6	0.35
		6-hydroxy-bentazone (M)	May 17	Apr 18	1386	849	148	6	<0.01
		8-hydroxy-bentazone (M)	May 17	Apr 18	1386	849	148	6	<0.01
		N-methyl-bentazone (M)	May 17	Apr 18	1386	849	148	6	<0.01
	Focus Ultra Cycloxydim	BH 517-T2SO2 (M)	May 17	Mar 19	1430	866	132	27	<0.01
		E/Z BH 517-TSO (M)	May 17	Mar 19	1430	866	132	27	0.07
<b>Winter wheat 2018</b> SD: Redigo Pro 170 FS (Prothioconazole + tebuconazole)	Lexus 50WG Flupyrifluron-methyl	IN-KF311 (M)	Oct 17	Mar 19	1194	650	100	90	<0.01
		IN-JE127 (M) <sup>2)</sup>	Oct 17	Mar 19	1194	650	100	90	<0.01
	Hussar Plus OD Mesosulfuron-methyl	AE F099095 (M)	Apr 18	Mar 20	1139	548	90	18	<0.01
		AE F160459 (M)	Apr 18	Mar 20	1139	548	90	18	<0.01
		AE F147447 (M)	Apr 18	Mar 20	1139	548	90	18	<0.01
	Topsin WG Thiophanate-methyl	Carbendazim (M)	Jun 18	Jun 20*	1089	543	196	82	<0.01
<b>Winter rye 2019</b> SD: Celeste Formula M (fludioxonil)	Proquinazid (P)	IN-MM671 (M)	Apr 19	Jun 20*	1333	821	86	12	<0.01
		IN-MM991 (M)							
<b>Potatoes 2020</b>	Ranman Top Cyazofamid	N,N-DMS (M) <sup>4</sup>	Jun 20	Jun 20*	-	-	-	-	-
		DMSA (M) <sup>4</sup>	Jun 20						
	Mospilan SG Acetamiprid	IM-1-4 (M) <sup>4</sup>	Jun 20	Jun 20*	-	-	-	-	-
		IM-1-5 (M) <sup>4</sup>	Jun 20						

Systematic chemical nomenclature for the analysed pesticides is given in Appendix 1. SD = Seed dressing.

\*Monitoring continues the following year—<sup>1)</sup> Propiconazole applied in half of the maximum allowed dose. <sup>2)</sup> The degradation product IN-JE127 was discontinued due to instability in aqueous solution (Chapter 8). <sup>3)</sup> Due to a high background content of 1,2,4-triazole, the results of the analysis cannot be linked directly to the specific application, and c<sub>mean</sub> is not presented. <sup>4)</sup> Parent compound was applied in spring 2020. Data evaluation is not included in this report but will be discussed in next year's report covering 2019-2021



**Figure 3.6.** Application of pesticides at Jynde vad from July 2017-June 2020. Pesticides are marked (M) if the pesticide and/or its degradation products are included in the monitoring programme, or (NM) if they are used but not monitored. Pesticides applied as seed dressing are marked SD. Measured precipitation including artificial irrigation is given on the primary axis and simulated percolation 1 mbgs on the secondary axis.

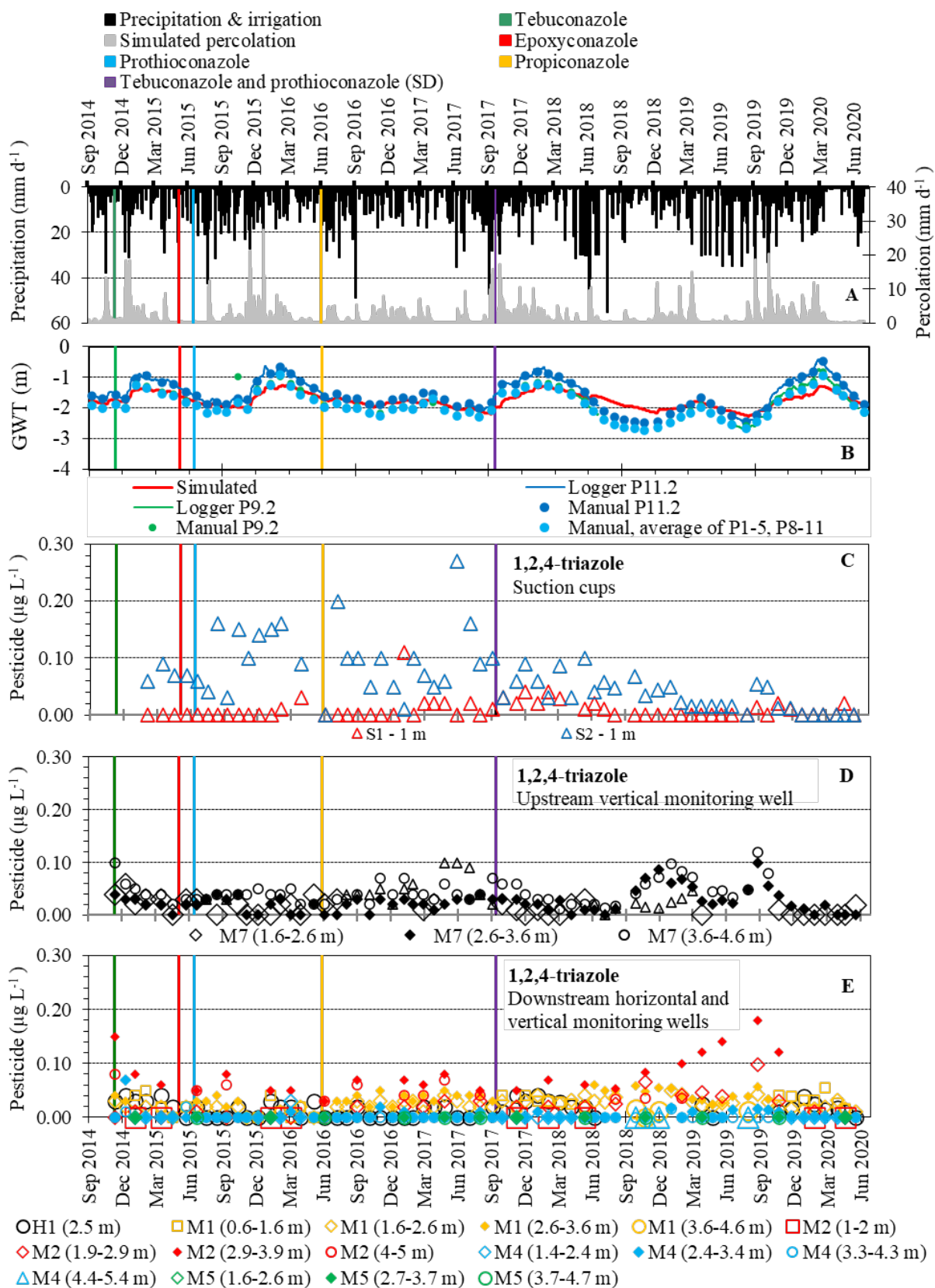
### Azole fungicides and 1,2,4-triazole monitoring

Tebuconazole was applied on winter wheat in November 2014 to test the leaching potential of its degradation product 1,2,4-triazole (a common azole degradation product) which is still ongoing on several VAP fields. In this report, results from 1,2,4-triazole monitoring at Jynde vad are thus reported from November 2014 to July 2020. As previous use of azole-fungicides might contribute to 1,2,4-triazole leaching, it is noted that the azoles were used seven times in the field before 2014, the most recent being epoxiconazole in May 2008. These previous azole-sprayings comprised tebuconazole

(once), propiconazole (three times), and epoxiconazole (three times) (see Table 3.2 and Appendix 3 in previous reports). Furthermore, seeds sown in the field during the entire monitoring period were presumably coated with azoles. However, seed dressings used at the PLAP fields were not registered until 2017 and onwards.

Before the monitoring of 1,2,4-triazole started in 2014, leaching of azole fungicides was monitored in a total of 382, 272, and 413 samples, and tested for propiconazole (1999-2002), tebuconazole (2007-2010), and epoxiconazole (2006-2009). Only tebuconazole and epoxiconazole were detected, and both only once in groundwater in concentrations of  $0.014 \mu\text{g L}^{-1}$  and  $0.011 \mu\text{g L}^{-1}$ , respectively (data shown in previous reports). A crop of winter wheat was sprayed with tebuconazole in November 2014, and epoxiconazole and prothioconazole in May and June 2015, respectively. In June 2016, propiconazole was applied in spring barley (Figure 3.7). The winter wheat sown September 2017 was coated with a seed dressing containing tebuconazole and prothioconazole. As mentioned, seeds sown before 2017 were presumably also coated with azoles.

Background samples were not taken before the application of tebuconazole in November 2014 but a 1,2,4-triazole concentration of  $0.15 \mu\text{g L}^{-1}$  was observed in a groundwater sample two days after the application. However, as tebuconazole is classified as medium persistent and with less than 2 mm of precipitation in the two days between the day of spraying (11 November 2014) and the first day of sampling (13 November 2014), it is unlikely that the 1,2,4-triazole concentration from 2.9-3.9 mbgs in the downstream monitoring well M2 (Figure 3.7D and 3.7E) relates to this particular spraying. Soil content of azoles from past azole sprayings and seed dressings are more likely contributors to the 1,2,4-triazole detection. This is also supported by the bromide measurements showing that the average time is  $\sim 1.5$  years for breakthrough of maximum bromide concentrations reaching a depth of  $\sim 3.5$  mbgs (section 3.2.2.). Additional 1,2,4-triazole input sources may come from upstream fields, as observed on the first day of monitoring in November 2014, where water from the upstream screen in M7 (situated at 3.6-4.6 m depth) contained  $0.1 \mu\text{g L}^{-1}$  1,2,4-triazole (Figure 3.7D).



**Figure 3.7.** 1,2,4-triazole monitoring at Jynde vad. Precipitation, irrigation, and simulated percolation 1 mbgs (A); measured and simulated groundwater level (B); 1,2,4-triazole concentration in the variably saturated zone (C) and saturated zone (D-E). Vertical lines indicate the dates of pesticide application. SD is pesticides applied as seed dressing. Seed dressings used before 2017 were not registered.

Following the applications of tebuconazole (November 2014), epoxiconazole (May 2015), prothioconazole (June 2015), and propiconazole (June 2016), a pattern of increased concentration of 1,2,4-triazole in water from S2 was observed in the period from August 2015 to June 2017. Here, the concentration peaked at  $0.27 \mu\text{g L}^{-1}$  in June 2017. Although the concentrations were  $> 0.1 \mu\text{g L}^{-1}$  on three occasions thereafter, they generally fluctuated  $< 0.1 \mu\text{g L}^{-1}$  for the rest of the monitoring period. As no water from the suction cups was available before the November 2014 tebuconazole application and the following three months, the background level of 1,2,4-triazole in water from 1 m depth is not known. The 1,2,4-triazole leaching pattern in suction cup S2 was not reflected in S1. Here, only few samples contained 1,2,4-triazole and the concentration was only once  $> 0.1 \mu\text{g L}^{-1}$  (January 2017;  $0.11 \mu\text{g L}^{-1}$ ) (Figure 3.7.C). As the suction cups are situated 1 mbgs they are apparently not affected by inputs from upstream fields, and thus, 1,2,4-triazole concentrations in S2 and S1 are assumed to originate from the use of azoles in the field. However, it is not possible to relate the observed leaching of 1,2,4-triazole to specific applications.

1,2,4-triazole was present in upstream and downstream groundwater samples two days after tebuconazole spraying in November 2014 (Figure 3.7D and E). 1,2,4-triazole concentrations were fluctuating  $< 0.1 \mu\text{g L}^{-1}$  from November 2014 to September 2018 in the downstream monitoring wells (Figure 3.7E). In the upstream well M7, the fluctuating trend was similar, except for three samples at the largest depth (4.6-5.6 m), where the concentrations peaked at  $0.1 \mu\text{g L}^{-1}$  around the summer of 2017 (Figure 3.7D). From September 2018 and onward, the fluctuating trend in the downstream wells continued except in well M2, where the concentration of 1,2,4-triazole increased and peaked at  $0.18 \mu\text{g L}^{-1}$  in September 2019. From the analyses of bromide measurements, it is shown that peak concentrations reaching  $\sim 3.5$  mbgs can take up to  $\sim 1.5$  years. This coincides with the timing of the observed 1,2,4-triazole peak in September 2019 compared to the most recent azole application around September 2017 (Figure 3.7D). However, it is noted that a pattern of increasing 1,2,4-triazole  $\sim 1.5$  years after the recent azole application is not observed in groundwater samples from other wells. Therefore, the observed increase in 1,2,4-triazole may be explained by other sources than the application in September 2017. Further, an increase in concentration was also observed in the upstream well, where the concentration peaked in January 2019 and again in September 2019, both times at a concentration level around  $0.1 \mu\text{g L}^{-1}$  in screens situated 2.6-3.6 m and 3.6-4.6 m depth.

From the monitoring results shown in Figure 3.7, it is not possible to discern how much of the detected 1,2,4-triazole relates to the four recent azole applications. However, degradation of accumulated azoles in the plough layer from sprayings and/or sowing of azole coated seeds in the period before the spraying in November 2014, as well as 1,2,4-triazole contributions from upstream fields will likely influence the concentration of 1,2,4-triazole observed in water from the field. To discern between the different azole applications and leaching of 1,2,4-triazole, detailed fate studies of azoles in soils are needed. Possible azole accumulation in the plough layer is mentioned in the EFSA conclusion on tebuconazole (EFSA, 2014) and therefore may cause continuous degradation of azoles into 1,2,4-triazole leading to long-term leaching to the groundwater. Monitoring of 1,2,4-triazole is ongoing.

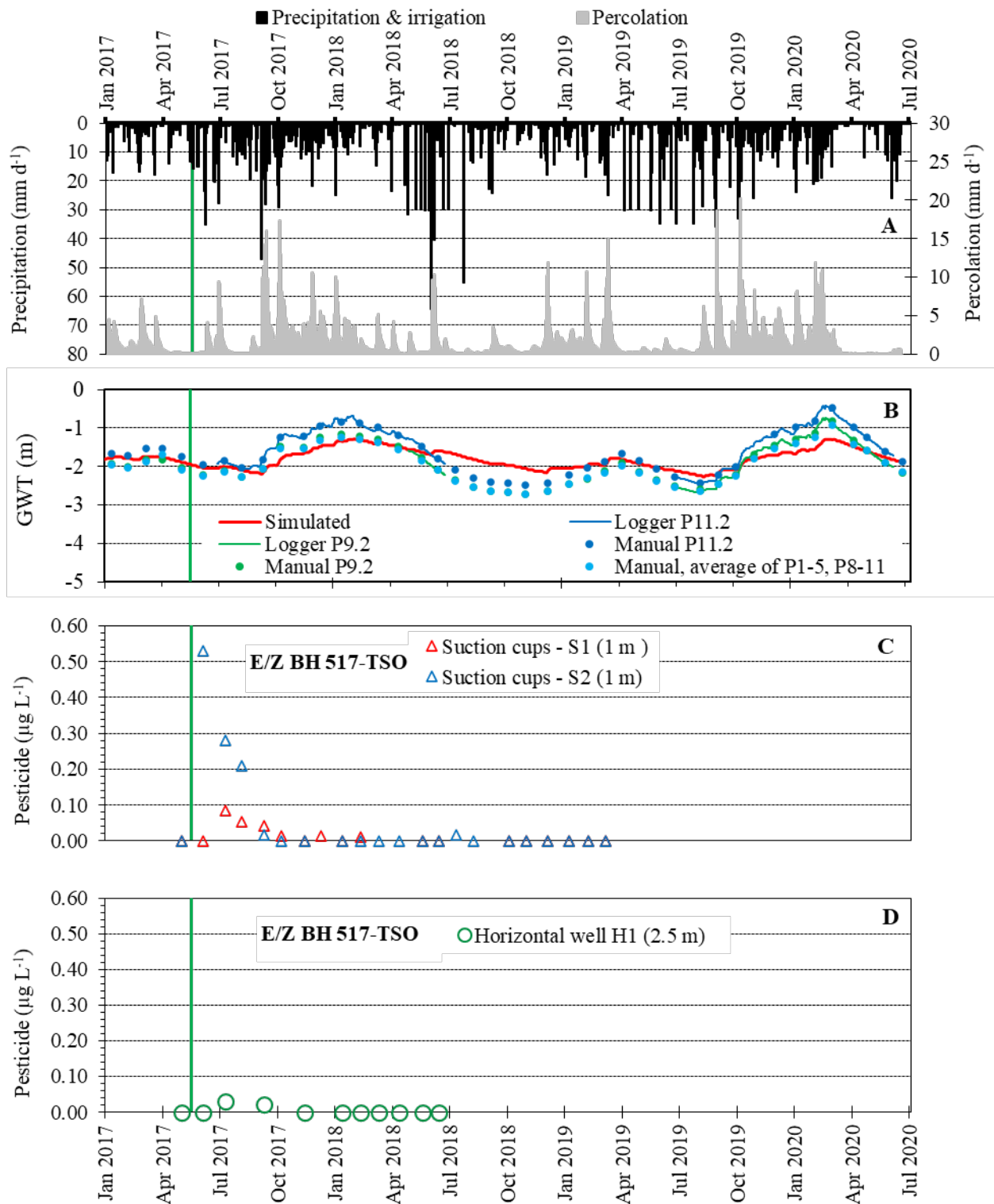
From November 2014 to June 2020, a total of 550 groundwater samples were collected from the vertical wells, 343 contained 1,2,4-triazole (62%), six samples had concentrations  $> 0.1 \mu\text{g L}^{-1}$  (1%), 337 samples had detections  $\leq 0.1 \mu\text{g L}^{-1}$  and 207 (38%) had no detectable amount of 1,2,4-triazole. Out of 57 water samples collected from the horizontal well, 37 (65%) contained 1,2,4-triazole. None of these, however, were  $> 0.1 \mu\text{g L}^{-1}$ . A total of 123 water samples from suction cups were sampled



in the same period. Out of these, 75 (61%) contained 1,2,4-triazole with 9 (7%) having concentrations  $> 0.1 \mu\text{g L}^{-1}$ .

#### **Cycloxydim degradation products, BH 517-T2SO<sub>2</sub> and E/Z BH 517-TSO**

The herbicide cycloxydim was applied in May 2017 to pea and its two degradation products, BH 517-T2SO<sub>2</sub> and E/Z BH 517-TSO, were included in the monitoring programme. E/Z BH 517-TSO was detected in six out of 18 water samples collected from the suction cups at S1. Here, the concentrations ranged from 0.011 to 0.085  $\mu\text{g L}^{-1}$ . At S2 there were five detections in a total of 21 samples, three in a concentration  $> 0.1 \mu\text{g L}^{-1}$ . The maximum detected concentration was 0.53  $\mu\text{g L}^{-1}$  in June 2017, less than one month after the application (Figure 3.8C). In the 12 groundwater samples collected in groundwater from the horizontal well H1 between May 2017 and June 2018, two contained E/Z BH 517-TSO, the highest concentrations being 0.03  $\mu\text{g L}^{-1}$ . Due to the low groundwater table (Figure 3.8B), no samples were collected in the period from June 2018 until monitoring was ended in March 2019 (Figure 3.8C). From October 2017 to June 2018, no detections were obtained for eight consecutive months in water samples from the horizontal well H1. E/Z BH 517-TSO was not detected in a total of 188 groundwater samples taken from the vertical monitoring wells between May 2017 and March 2019. BH 517-T2SO<sub>2</sub> was not detected in any samples during the monitoring period. The monitoring was stopped in March 2019, as no further leaching was observed.



**Figure 3.8.** Results from E/Z BH 517-TSO monitoring at Jydevad. Precipitation, irrigation, and simulated percolation 1 mbgs (A); measured and simulated groundwater level (B); E/Z BH 517-TSO concentration in the variably saturated zone (C) and saturated zone (D). The green vertical line indicates the date of the cycloxydim application. Note, no water was available in the horizontal well H1 from June 2018 to March 2019. Leaching of BH 517-T2SO<sub>2</sub> and E/Z BH 517-TSO was also monitored in the vertical monitoring wells M1, M2, M4, M5, and M7, but there were no detections from May 2017 to March 2019 and therefore this is not shown in the figure.

### **Flupyrsulfuron-methyl degradation products, IN-KC576, IN-JV460, and IN-KY374**

Flupyrsulfuron-methyl was applied to a crop of winter wheat in October 2017 and May 2018. Two of its degradation products not previously included in the monitoring, IN-KF311, and IN-JE127, were included. None of these two new degradation products were detected during the monitoring period from July 2018-June 2020 (181 water samples). IN-JE127 was found unstable in water, and therefore the results are disregarded. To test for the potential presence of another major relevant metabolite of flupyrsulfuron-methyl, all samples collected from Jyndevad on May 7, 2019, were additionally analysed for AE-F092944/IN-J0290. This degradation product was previously tested in PLAP with foramsulfuron applications at Silstrup and Estrup - though without detections in the groundwater. Likewise, no AE-F092944/IN-J0290 was detected after the flupyrsulfuron-methyl application.

Flupyrsulfuron-methyl was previously tested in Jyndevad in October 2014 and March 2015 and flupyrsulfuron-methyl and three of its other degradation products, IN-KC576, IN-JV460, and IN-KY374, were monitored in 259 water samples following these applications. Only the degradation product IN-KY374 was detected, not in the groundwater, but four times in water from the variably saturated zone (both from S1 and S2; max conc.  $0.45 \mu\text{g L}^{-1}$ ) within 5-8 months after the March 2015 application.

Flupyrsulfuron-methyl as an active ingredient was banned by the European Union on 13 September 2017 and subsequently banned in Denmark in December 2018 (Danish EPA, 2017). The monitoring stopped in March 2019.

### **Mesosulfuron-methyl degradation products, AE-F099095, AE-F160459 and AE-F147447**

The herbicide mesosulfuron-methyl-Na was applied to winter wheat in April 2018, and three of its degradation products, AE-F099095, AE-F160459, and AE-F147447, were included in the monitoring programme. When monitoring ended in March 2020 after two years of monitoring, there had been no detections of AE-F099095 or AE-F160459 in 232 water samples. Regarding AE-F147447, 235 water samples were analysed, and the substance was found in two samples from the horizontal well H1. These were collected in December 2019 and January 2020, with concentrations of 0.038 and 0.021  $\mu\text{g L}^{-1}$ , respectively. The monitoring was also stopped in March 2020.

### **Thiophanat-methyl degradation product, carbendazim**

The fungicide thiophanat-methyl was applied to winter wheat in June 2018 and its degradation product, carbendazim, was included in the monitoring. There were no detections of carbendazim in 211 water samples at the end of monitoring in June 2020. As the analytical method was not ready when the monitoring of carbendazim was planned to start, samples were stored ( $-20^{\circ}\text{C}$ ) until ready. As the stability of the compound, when frozen for several months, is unknown, the presence of false-negative results cannot be excluded. Results on carbendazim from the period of May 2018 until October 2018 should therefore be regarded as tentative until further analysis of the effect of freezing is carried out (Chapter 8).

### **Proquinazid degradation products, IN-MM671 and IN-MM991**

Proquinazid was applied in winter rye in April and May 2019, and the two degradation products IN-MM671 and IN-MM991 were included in the monitoring. A total of 149 samples, 30 from suction cups at S1 and S2, 10 from the horizontal well H1, and 109 from vertical wells in the saturated zone did not contain the two compounds. As the analytical method was not ready when the monitoring of IN-MM671 and IN-MM991 was planned to start, samples had to be stored ( $-20^{\circ}\text{C}$ ) until ready. As the stability of the compounds, when frozen for several months, is unknown, the presence of false-

negative results cannot be excluded. Results on IN-MM671 and IN-MM991 from April 2019 until September 2019 should therefore be regarded as tentative until further analysis of the effect of freezing is carried out (Chapter 8).

## 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 approximately 5% but could be as high as 20%.

In September 2011, the monitoring system was extended with a horizontal screen (H3) 2 mbgs in the north-eastern corner of the field (Figure 4.1). One of the screens is located just below the tile drain 1.1 mbgs and two screens between two tile drains. A brief description of the drilling and design of H3 is given in Appendix 8.

The water sampling plan has been revised several times since the beginning of PLAP. During the current monitoring period, water sampling at Silstrup was done monthly from wells M5, M9, H1.2, and H3; with additional samples taken half-yearly from wells M9, M10, and M12. No sampling is done from wells M1-4, M6-8, M11, M13, and H2. Due to earlier budget reduction, only the two uppermost well screens below the groundwater table are sampled. Appendix 2 describes the sampling procedure in more detail.

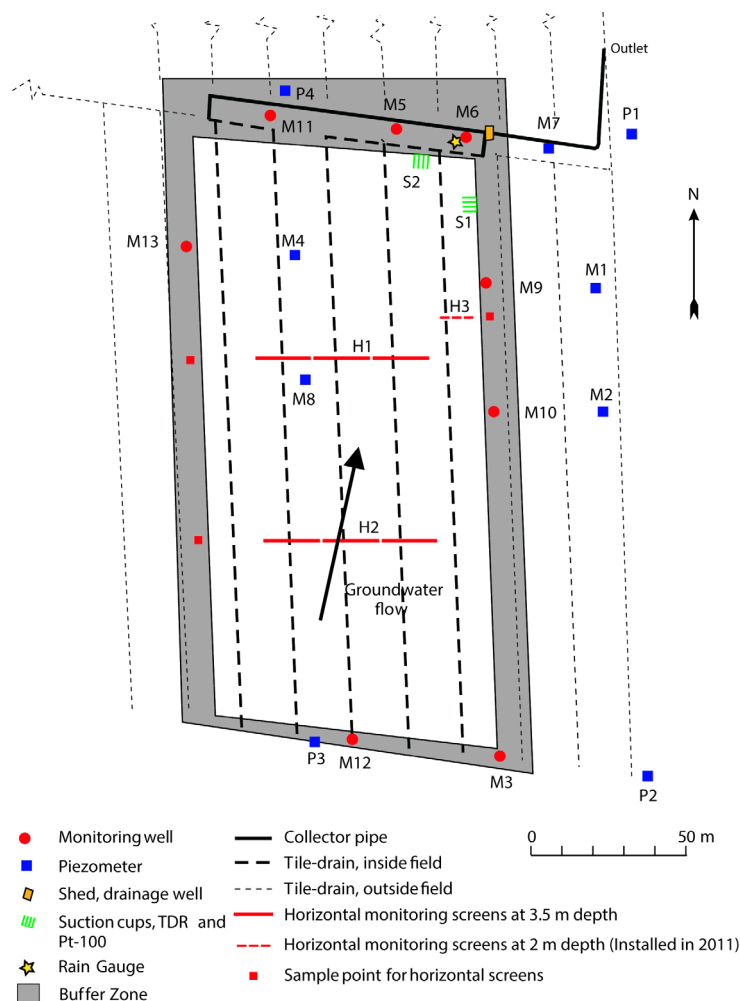
#### 4.1.2 Agricultural management

Agricultural management practice at Silstrup during the 2018-2020 growing seasons is briefly summarised below and detailed in Appendix 3 (Table A3.3). For information about management practice during the past monitoring periods, see previous reports available on [www.plap.dk](http://www.plap.dk).

The 17 August 2018, a crop of winter rape (cv. Exclaim coated with thiram) was sown directly into the barley stubble. Cycloxydim was used against weeds on 17 September and its degradation products, BH 517-T2SO<sub>2</sub> and E/Z BH 517-TSO were included in the monitoring programme. Another spraying of weeds was done with propyzamide on 9 November after which propyzamide was included in the monitoring. Further, the herbicide propaquizifop was applied on 9 April 2019 and its degradation products, CGA 287422, CGA 294972, CGA 290291, and PPA, were subsequently monitored. Harvest of the winter rape was done on August 14, 2019, yielding 44.5 hkg ha<sup>-1</sup> of seeds (91% dry matter). An unknown amount of straw was shredded at the harvest of the rape.

On September 19, 2019, the field was ploughed. On September 21, a winter wheat (cv. Benchmark) coated with fludioxinil was sown and emerging 7 October. Spraying of weeds was done on April 7, 2020, using pyroxsulam and florasulam in a mixture. From pyroxsulam, five degradation products

were included in the monitoring: PSA, 6-Cl-7-OH-XDE-742, 5-OH-XDE-742, 7-OH-XDE-742, and pyridine sulfonamide. From florasulam, four degradation products were monitored TSA, 5OH-florasulam, DFP-ASTCA, and DFP-TSA. Fungicides were sprayed twice using prothioconazole together with azoxystrobin on May 28 and June 16, 2020. From azoxystrobin, the degradation product CyPM was included in the monitoring and 1,2,4-triazole from prothioconazole. On August 13, 2020, 97.0 hkg ha<sup>-1</sup> of grain (85% dry matter) was harvested. The amount of straw shredded at harvest was not determined.



**Figure 4.1.** Overview of the Silstrup field. The innermost white area indicates the cultivated area surrounded by the buffer zone. Pesticide monitoring is conducted weekly from the tile drain system from a drainage well (during periods of continuous drainage) and monthly and half-yearly from selected vertical and horizontal monitoring screens as described in section 4.1.1 and in Appendix 2. At S1 and S2, water content (via TDR) and soil temperature (via Pt100) is measured at four different depths. Additionally, suction cups are installed to collect pore water from the variably saturated matrix for analysis of pH-independent compounds.

### 4.1.3 Model setup and calibration

The one-dimensional numerical model MACRO (version 5.2 Larsbo *et al.*, 2005) represents the treated area of the Silstrup field covering the upper five meters of the soil profile, always including the groundwater table. The model is used to simulate water dynamics in the variably saturated zone during the full monitoring period May 1999-June 2020 and to establish an annual water balance.

Compared to the setup in Rosenbom *et al.* (2021), one year of climate and crop data was added to the MACRO setup. The setup was calibrated for the monitoring period May 1999-June 2004 and subsequently used to compare simulated water balance with monitoring results from July 2004 to June 2020. Daily time series of the groundwater table measured in piezometers located in the buffer zone, soil water content measured at three different depths (0.25, 0.6, and 1.1 mbgs) from the two profiles S1 and S2 (Figure 4.1), and the bromide concentration measured in the suction cups located 1 and 2 mbgs were all used in the calibration process. Data acquisition, model setup, and results related to the simulated bromide transport are described in Barlebo *et al.* (2007).

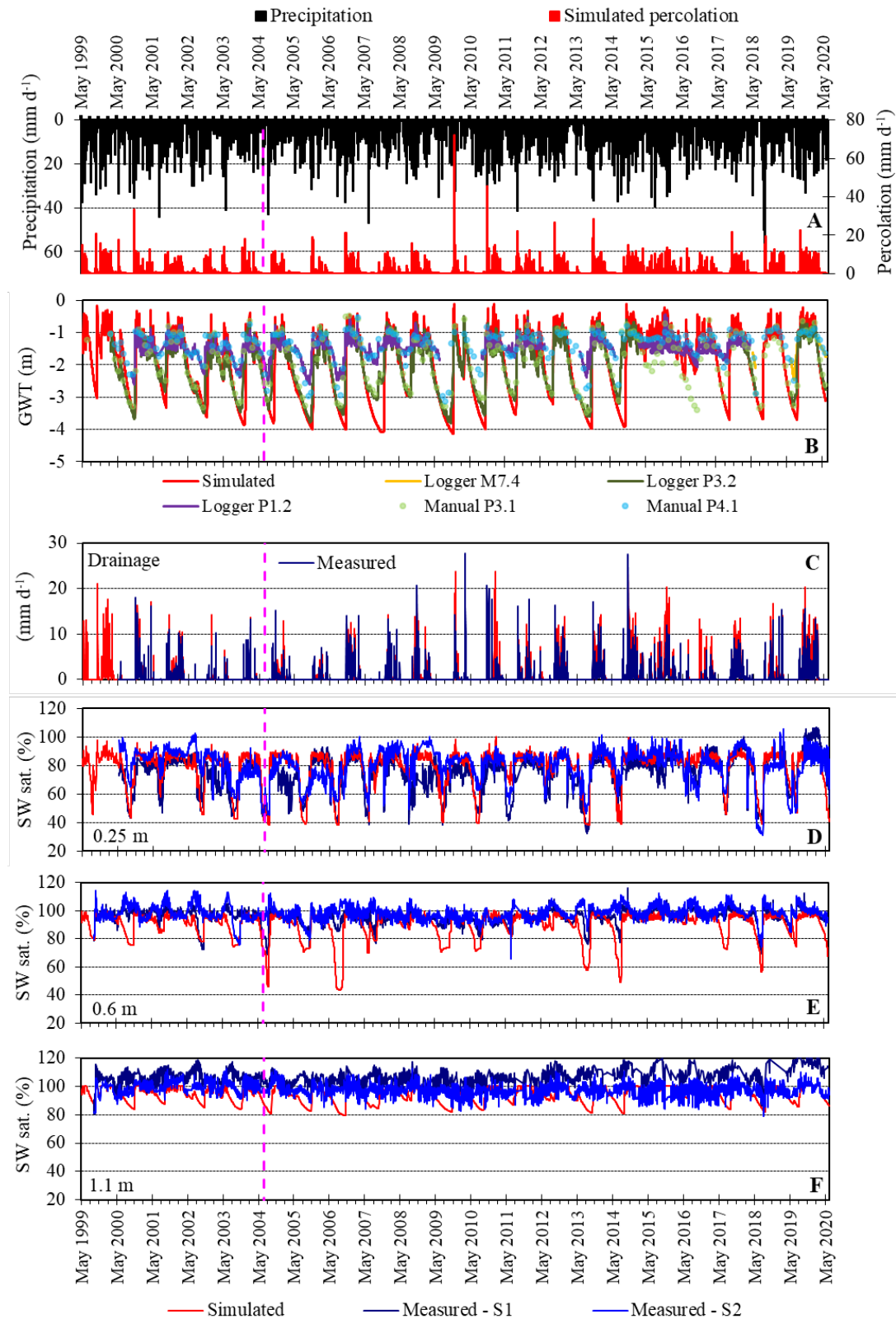
## 4.2 Results and discussion

### 4.2.1 Soil water dynamics and water balances

The model simulation is generally consistent with the measured water balance data (depth to groundwater table; drainage and water saturation) for the recent hydraulic year, July 2019-June 2020, thus indicating a reasonable model description of the overall soil water dynamics in the variably saturated zone (Figure 4.2).

Manually measured groundwater tables at the P3.1 and P4.1 show similar dynamics throughout the years, although offset by ~1 m (Figure 4.2B). The offset is more pronounced during dry seasons and it is noted that the wells, P3.1, and P4.1, are farthest apart at the Silstrup field, and therefore likely to yield the largest difference in depth to the groundwater table. The dynamics of the measured groundwater table in P3.1 and P4.1 follow the automatic loggers, P3.2/P1.2, and M7.4. The simulated groundwater table captures the dynamics of the manual measurements at P3.1 and the automatic logger P3.2. In contrast to the sandy fields, Tylstrup and Jyndevad, the model of Silstrup captures the dynamics throughout 2018 and is thus not affected by the extreme summer of 2018. For the recent hydraulic year, the model continues to capture the groundwater dynamics well. Drainage during the recent two monitoring periods (July 2018-June 2020) was generally well captured by the model (Figure 4.2C).

Similar to previous monitoring periods, the overall trends in soil water saturation were described reasonably well (Figure 4.2D, 4.2E, and 4.2F), although the simulated soil water saturation in 0.6 and 1.1 m depth are underestimated during the summer period (Figure 4.2E and 4.2F). This could be caused by TDR measurements primarily representing the soil matrix conditions and thus deviating from the model that represents both matrix- and preferential transport. In 1.1 m depth, the simulated water saturation seemed to capture the patterns measured in S1. The measurements in S2 differed substantially compared to S1. There seemed to be a pattern of increasing levels of saturation measured in S1 from around 2012 indicating that the TDR is drifting.



**Figure 4.2.** Soil water dynamics at Silstrup: Measured precipitation and simulated percolation 1 mbgs (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 depths (D, E, and F). The measured data in B comprises piezometers located in the buffer zone. The measured data in D, E, and F from TDR probes installed at S1 and S2 (Figure 4.1). The dashed vertical line indicates the calibration period to June 2004.



The water balance for Silstrup for the entire monitoring period of 21 years is shown in Table 4.1. From July 2019 to June 2020, the measured precipitation of 1308 mm yr<sup>-1</sup> and actual evapotranspiration of 518 mm yr<sup>-1</sup> are above the average of 1017 mm yr<sup>-1</sup> and 468 mm yr<sup>-1</sup>, respectively. The precipitation from July 2019 to June 2020 is the highest measured at Silstrup. An overview of the monthly precipitation of the six PLAP fields is presented in Appendix 4.

Compared to the period July 2018-June 2019, the simulated actual evapotranspiration for July 2019-June 2020 increased by 57 mm yr<sup>-1</sup>, whereas the precipitation increased by 205 mm yr<sup>-1</sup>. Hence, with higher precipitation in 2019/2020 compared to 2018/2019, a larger amount of drainage was both measured and estimated, which lead to a decrease in estimated groundwater recharge by 66 mm yr<sup>-1</sup>.

**Table 4.1.** Annual water balance for Silstrup (mm yr<sup>-1</sup>).

	Normal precipitation <sup>2)</sup>	Precipitation <sup>3)</sup>	Actual Evapotranspiration <sup>4)</sup>	Measured drainage	Simulated drainage	Groundwater recharge <sup>5)</sup>
01.07.99–30.06.00 <sup>1)</sup>	976	1175	457	–	443	275 <sup>6)</sup>
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	555
01.07.16–30.06.17	976	869	415	95	228	359
01.07.17–30.06.18	976	985	471	233	293	281
01.07.18–30.06.19	976	1103	461	226	316	416
01.07.19–30.06.20	976	1308	518	440	600	350
Average	976	1017	468	220	294	318

<sup>1)</sup> The monitoring started in April 2000. <sup>2)</sup> Normal values based on time series for 1961–1990 corrected to soil surface (Olesen, 1991).

<sup>3)</sup> Precipitation is corrected to the soil surface according to the method of Allerup and Madsen (1979). <sup>4)</sup> Actual evapotranspiration is estimated by the MACRO-model applying climate data including potential evapotranspiration <sup>5)</sup> Groundwater recharge calculated as precipitation - actual evapotranspiration - measured drainage. <sup>6)</sup> Drainage measurements were lacking - simulated drainage was used to calculate groundwater recharge.

#### 4.2.2 Bromide leaching

As mentioned in Chapter 1, it was decided for the present report to revisit and analyse all bromide data from the fields to possibly improve the fundamental understanding of the hydrogeology at the fields. In the analysis, the time until the maximum concentration of bromide reaches the different depths of water sampling is used to estimate transport times from the surface to the specific filter of interest and allow for comparison between depths. The time of maximum concentration is used in conjunction with the general pattern of breakthrough curves where possible. However, since the number of collected samples differs among the monitored well screens, continuous breakthrough curves are not equally available for all screens. Therefore, the time of maximum concentration is used to achieve transport time ranges within each monitoring depth regardless of the number of samples collected. These transport times are not to be conflated with average transport times. The average transport time (mean breakthrough time) represents when half of the applied mass has passed through the location of measurement which may not necessarily coincide with the breakthrough of maximum

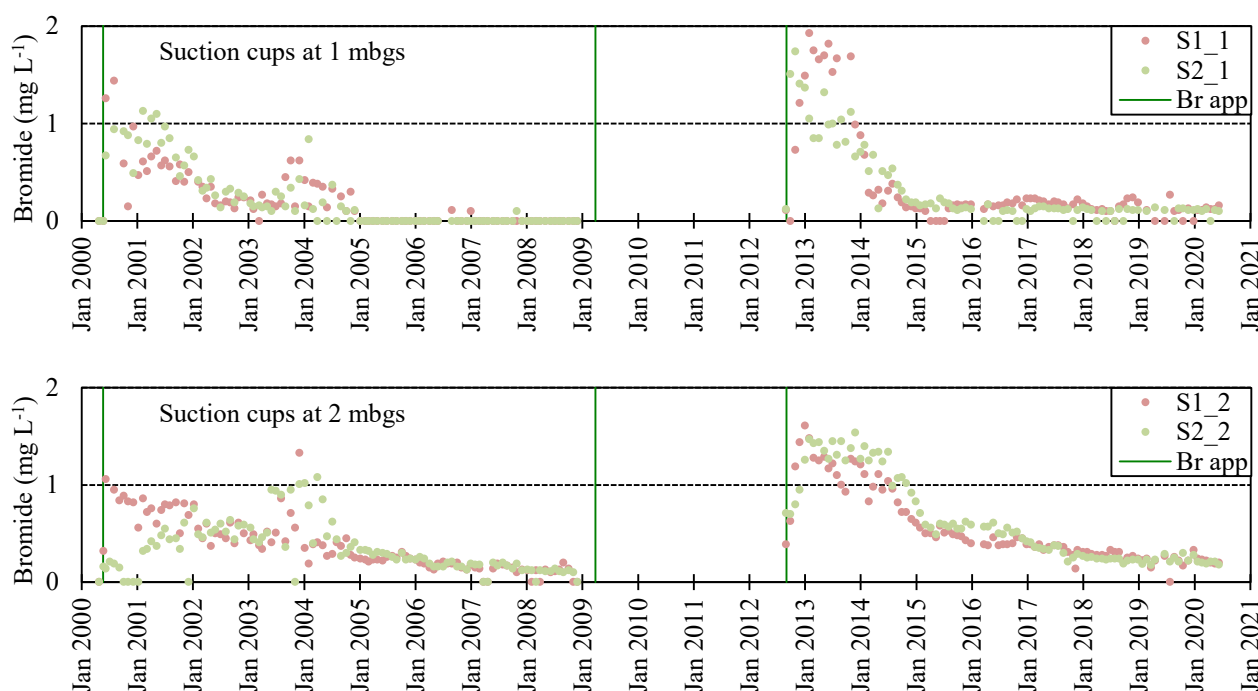
concentration. Consequently, bromide detections are generally occurring both before and after the time of the reported maximum concentration breakthroughs.

At Silstrup, bromide was applied three times (May 2000, April 2009, and September 2012) as 30.0, 31.5, and 30.5 kg ha<sup>-1</sup> potassium bromide, respectively.

In the suction cups, samples were only collected with the May 2000 and September 2012 applications. In the suction cups located 1 mbgs, the maximum bromide concentrations after May 2000 and September 2012 applications are observed within 5-9 and 2-5 months (Figure 4.3). For both applications, it is noted that concentrations are observed immediately after application and that bromide pulses extend up to several years.

In the suction cups located 2 mbgs, the maximum bromide concentrations after May 2000 and September 2012 applications are measured within 39-47 and 4-15 months (Figure 4.3). Again, for both applications, it is noted that concentrations are observed immediately after application and that bromide pulses extend up to several years.

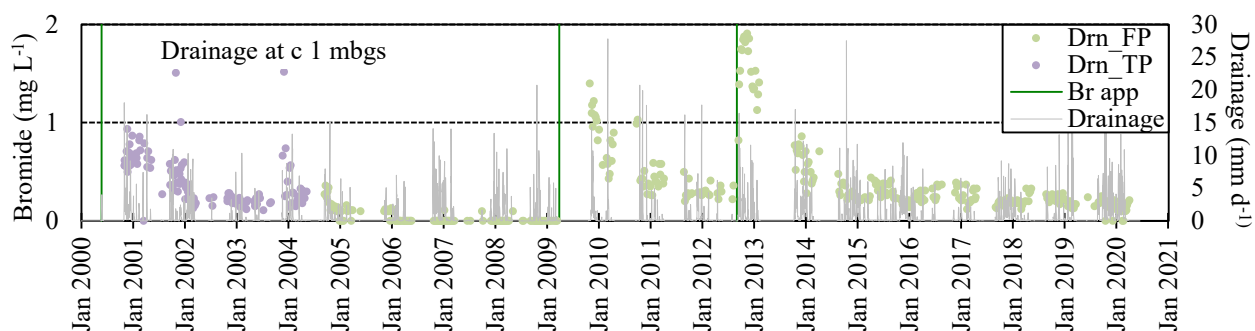
The average breakthrough time for maximum concentration observations in the suction cups at 1 mbgs is overall five months after application. Although the maximum concentration is measured within five months of the May 2000 application in both suction cups, it is evident that another pulse of bromide is measured after around four years (Figure 4.3). In the suction cups at 2 mbgs, the average time for the maximum concentration breakthrough is much longer around 26 months (Figure 4.3). The reason for the overall longer transport times of maximum concentrations at around 2 mbgs is related to a pattern of wider bromide pulses. In fact, the maximum concentration measured at ~2 mbgs after the May 2000 application coincides with the second breakthrough (in January 2004) of bromide at ~1 mbgs. However, though the maximum concentrations are observed quite long after application, it is clear that increased bromide concentrations are occurring immediately after application (Figure 4.3). The results from the suction cups at around 1 mbgs with a bimodal bromide breakthrough pattern together with relatively wide bromide pulses reaching ~2 mbgs contrast with what was observed in the variably saturated zone of the sandy fields. At the sandy fields, the bromide pulses in the variably saturated zone are relatively narrow and patterns of bimodal bromide breakthrough are not observed (Figure 2.3 and Figure 3.3). The Silstrup field is characterized as a clay-till field, and the observed pattern in bromide breakthrough in the variably saturated zone indicates that flow and transport pathways are more heterogeneous compared to the sandy fields.



**Figure 4.3.** Measured bromide concentration at Silstrup.

The samples representing drainage from around 1 mbgs are collected in a drain well collecting drainage from the entire field (Figure 4.1). Therefore, there are no time ranges reported for the drainage samples, and the maximum concentrations in the drainage after May 2000, April 2009, and September 2012 applications are measured after 43, 7, and 3 months, respectively (Figure 4.4). However, it is noted that increased bromide concentrations are detected in drainage samples already in the first event after each application. Though the breakthrough of maximum concentrations varies considerably in this field, it is evident that a fraction of the applied bromide is transported fast to the drains.

Similar to the bimodal breakthrough of bromide in suction cups at around 1 mbgs, the bromide concentrations in drainage samples after the May 2000 application also show a pattern resembling bimodal behavior (Figure 4.4). As such, maximum concentrations around  $1.5 \text{ mg L}^{-1}$  are measured around January 2002 as well as January 2004, which also represented the time of the maximum concentration in suction cups (Figure 4.3). Generally, it is noted that the maximum bromide concentrations are measured after the first drainage event following an application. Although the maximum concentrations are measured relatively fast in drainage samples after bromide applications, detections of bromide are continuous throughout all monitoring periods.



**Figure 4.4.** Measured bromide concentration in drainage at Silstrup. The suffix FP and TP refer to flow- and time proportional sampling, respectively, which are described in Kjær *et al.* (2004) and Appendix 2.

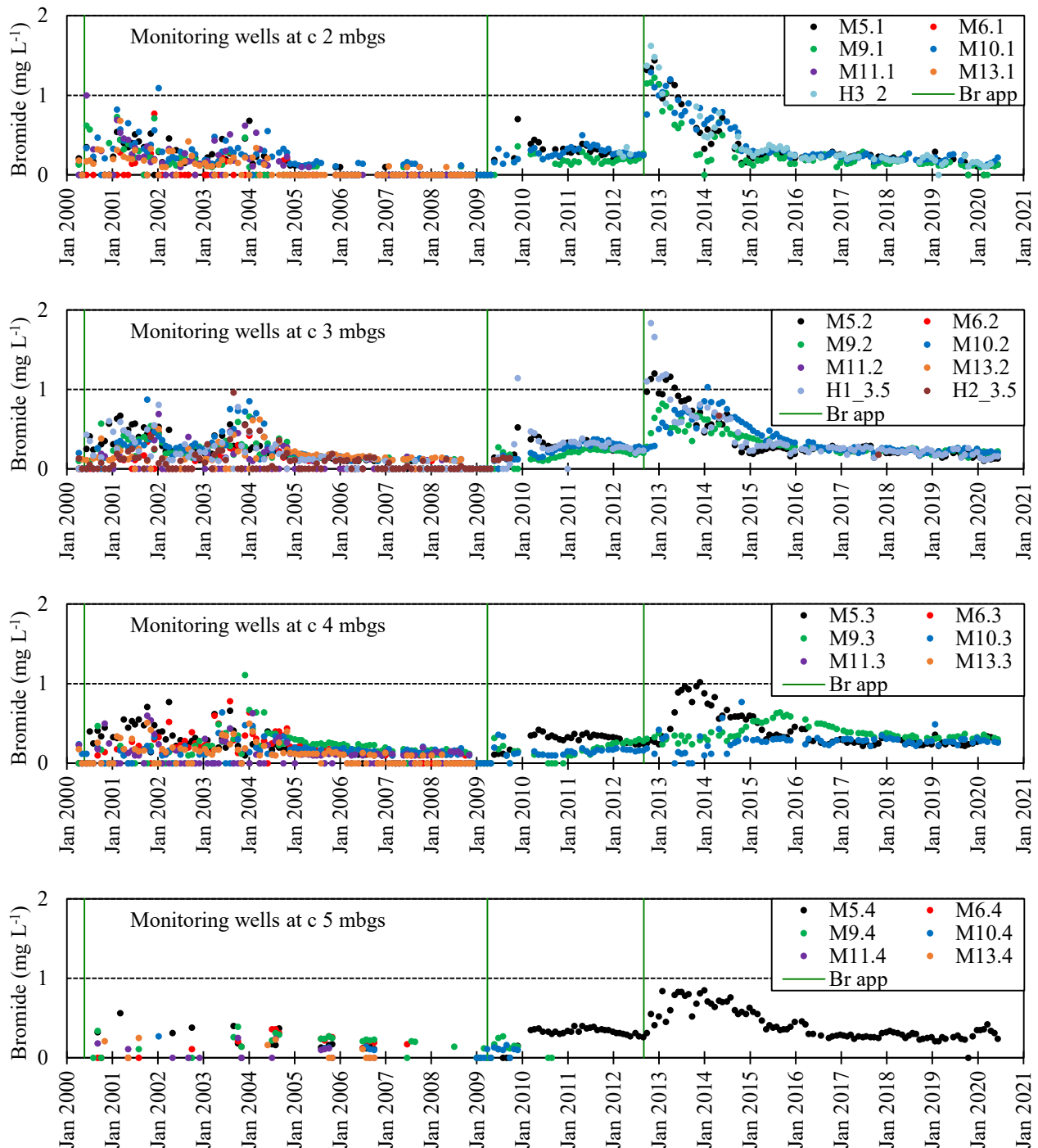
M12 is regarded as an upstream well. However, as bromide is measured in M12, although in low concentration (generally  $< 0.5 \text{ mg L}^{-1}$ ) further analysis of the flow field is needed to fully understand the groundwater flow dynamics across the field. Such analyses are under preparation for all the fields. However, for the sake of simplicity, in the present analysis, M12 is assumed not to part of the flow field represented by the remaining wells. Further, at  $\sim 5$  mbgs, only sampling in a single well, M5 is performed after the application in September 2012.

In the groundwater samples from  $\sim 2$  mbgs, the maximum bromide concentrations after May 2000, April 2009, and September 2012 applications are measured within 1-44, 5-25, and 3 months (Figure 4.5).

In the groundwater samples from  $\sim 3$  mbgs, the maximum bromide concentrations after May 2000, April 2009, and September 2012 applications are measured within 10-46, 2-29, and 2-18 months (Figure 4.5).

In the groundwater samples from  $\sim 4$  mbgs, the maximum bromide concentrations after May 2000, April 2009, and September 2012 applications are measured within 16-45, 1-13, and 15-36 months (Figure 4.5).

In the groundwater samples from  $\sim 5$  mbgs, the maximum bromide concentrations after May 2000, April 2009, and September 2012 applications are measured within 10-50, 4-23, and 16 months (Figure 4.5).



**Figure 4.5.** Measured bromide concentration in the groundwater at Silstrup.

For a specific depth, the average breakthrough time for the maximum bromide concentration is calculated from the time of measured maximum concentration within each of the wells representing that particular depth. Hence, for the May 2000, April 2009, and September 2012 applications, the average time for maximum bromide concentrations reaching depths at around 2, 3, 4, and 5 mbgs are 11, 18, 23, and 23 months, respectively. Although there is a general pattern of longer transport times before reaching maximum concentrations with increasing depths, the intervals in which the maximum concentrations are measured within the different screens have a relatively large range. For instance,

at ~2 mbgs and ~4 mbgs, the maximum concentrations are measured within 1-44 months for the May 2000 application, and 15-36 months for the September 2012 application. From the general pattern of bromide pulses at ~2-3 mbgs, it seems that two breakthroughs are occurring after the May 2000 application: one immediately after and another around three years after application (Figure 4.5). These are likely related to heavy precipitation events enabling fast flow and solute transport. Following the April 2009 application, the bromide pulses are occurring within half a year in all depths. After the September 2012 application, bromide pulses are detected immediately at ~2 mbgs and seem to move further down to ~5 mbgs within 1-1.5 years in M5 while the transport to deeper levels in other wells is less evident.

The intervals in which maximum bromide concentrations are measured at the different depths are specified above and show that maximum bromide concentrations are measured up to around four years after applications depending on the well location. The variation in the time of measured maximum concentrations in the variably saturated zone, drainage, and groundwater samples also indicate that flow and transport of solutes are affected by heterogeneity. It is noted that the breakthrough of maximum concentrations also occurs relatively fast within a few months after application, e.g., at ~2 mbgs, the maximum concentrations are measured within one and three months after the May 2000, and September 2012 applications, respectively (Figure 4.5). Similarly, around 3 and 4 mbgs, maximum concentrations are measured within 2 months after April 2009 and September applications (Figure 4.5). A similar pattern was also seen from the occurrences of bromide pulses in the various depths. These fast occurrences of maximum concentrations or bromide pulses, in general, are not observed at the sandy fields, and with well-known development of preferential flows at the clay-till fields (Lindhardt et al., 2001), the fast maximum breakthroughs are likely caused by preferential transport of solutes. Additionally, the observed fast breakthrough of maximum bromide concentrations in drainage samples within three months of the September 2012 application may be due to preferential flows (Figure 4.4).

Overall, the majority of the maximum bromide concentrations reach the screens at ~2-5 mbgs within 1-2 years after application, but maximum concentration levels are measured up to four years after application. For all the sampled depths, it is noted that increased bromide concentrations above the detection limit are measured before and after the transport times representing maximum concentrations.

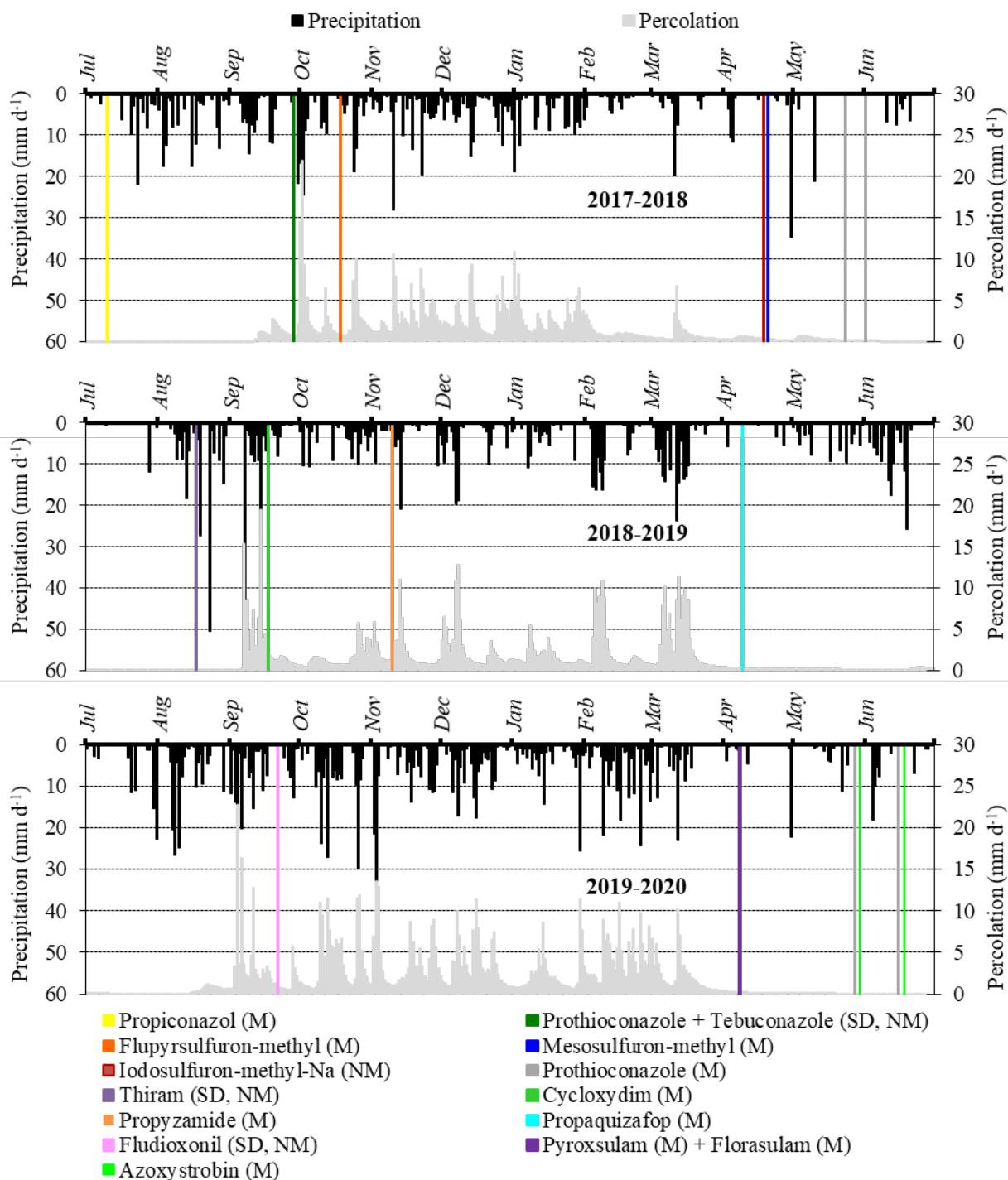
#### **4.2.3 Pesticide leaching**

Monitoring at Silstrup began in May 2000 and a complete list of the monitored pesticides and degradation products before 2017 is provided in Appendix 7. Several azole fungicides have had great focus since the beginning of PLAP, but especially their common degradation product, 1,2,4-triazole, is intensively monitored since it was introduced in 2014. Monitoring of 1,2,4-triazole at Silstrup started in 2017, which is the reason that all pesticide applications from 2017 to 2020 are summarised in Table 4.2, and for the period 2018-2020 shown together with precipitation and simulated percolation in Figure 4.6 It is noted that the precipitation in Table 4.2 is corrected to soil surface according to Allerup and Madsen (1979), whereas percolation (1 m depth) refers to accumulated percolation from July 2019 to June 2020 as simulated with the MACRO model.

**Table 4.2.** Pesticides analysed at Silstrup. Precipitation (precip.) and percolation (percol.) are accumulated within the first year (Y 1<sup>st</sup>), and month (M 1<sup>st</sup>) after application. C<sub>mean</sub> is average leachate concentration at 1 mbgs (drainage). See Appendix 2 for calculation method and Appendix 7 (Table A7.3) for previous applications of pesticides.

Crop – Year of harvest	Applied Product	Analysed Pesticide (P) / Degradation product (M)	Application date	End of monitoring	Y 1 <sup>st</sup> Precip. (mm)	Y 1 <sup>st</sup> Percol. (mm)	M 1 <sup>st</sup> Precip. (mm)	M 1 <sup>st</sup> Percol. (mm)	C <sub>mean</sub> (µg L <sup>-1</sup> )
<b>Spring barley 2017</b> SD: Redigo Pro 170 FS (Prothioconazole + tebuconazole)	Bumper 25 EC Propiconazole(P)	1,2,4-triazole (M)	Jun 17	Jun 20*	520	980	112	0	x
	Zypar Florasulam(P)	TSA (M)	Jun 17	Jun 20*	520	996	30	0	<0.01
	Halauixifen-methyl(P)	X-757 (M)	Jun 17	Sept 19	520	996	30	0	<0.01
<b>Winter barley 2018</b> SD: Redigo Pro 170 FS (Prothioconazole + tebuconazole)	Lexus 50 WG Flupyrsulfuron-methyl (P)	IN-KF311 (M) IN-JE127 <sup>a)</sup> (M)	Oct 17 Oct 17	Mar 19 Mar 19	983 983	623 623	120 120	96 96	<0.01 <0.01
	Hussar Plus OD Mesosulfuron-methyl (P)	AE F099095 (M) AE F160459 (M) AE F147447 (M)	Apr 18 Apr 18 Apr 18	Mar 19 Mar 19 Mar 19	1009 1009 1009	541 541 541	67 67 67	11 11 11	<0.01 <0.01 <0.01
	Proline EC 250 Prothioconazole (P)	1,2,4-triazole (M)	May 18	Jun 20*	990	530	29	1	x
	Focus Ultra Cycloxydim (P)	BH 517-T2SO2 (M) E/Z BH 517-TSO (M)	Sept 18 Sept 18	Jun 20* Jun 20*	1124 1124	560 560	60 60	34 34	<0.01 0.05
	Kerb 400 SC Propyzamide (P)	Propyzamide (P)	Nov 18	Jun 20*	1276	674	124	93	0.03
	Agil 100EC Propaquizifop (P)	CGA 287422 (M) CGA 294972 (M) CGA 290291 (M) PPA (M)	Apr 19 Apr 19 Apr 19 Apr 19	Jun 20* Jun 20* Jun 20* Jun 20*	1390 1390 1390 1390	782 782 782 782	25 25 25 25	4 4 4 4	<0.01 <0.01 <0.01 <0.01
<b>Winter wheat 2020</b> SD: Celest Formula M	Broadway Pyroxsulam (P)	PSA (M)** 6-Cl-7-OH-XDE-742 (M)** 5-OH-XDE-742 (M)** 7-OH-XDE-742 (M)** Pyridine sulfonamide (M)**	Apr 20 Apr 20 Apr 20 Apr 20 Apr 20	Jun 20* Jun 20* Jun 20* Jun 20* Jun 20*	- - - - -	- - - - -	30 30 30 30 30	4 4 4 4 4	- - - - -
	Florasulam (P)	TSA(M) 5OH-florasulam (M)** DFP- ASTCA (M)** DFP-TSA (M)**	Apr 20 Apr 20 Apr 20 Apr 20	Jun 20* Jun 20* Jun 20* Jun 20*	- - - -	- - - -	30 30 30 30	4 4 4 4	- - - -
	Proline 250 EC Prothioconazole (P)	1,2,4-triazole (M)**	May 20	Jun 20*	-	-	28	0	-
	Amistar Azoxystrobin (P)	Azoxystrobin (P)** CyPM (M)**	May 20 May 20	Jun 20* Jun 20*	- -	- -	28 28	0 0	- -

Systematic chemical nomenclature for the analysed pesticides is given in Appendix 1. SD = Seed dressing. \*Monitoring continues the following year. \*\* Parent compound was applied in spring 2020. Data evaluation is not included in this report but will be discussed in next year's report covering 2019-2021. <sup>a)</sup> The degradation product IN-J127 was discontinued due to instability in aqueous solution (Chapter 8). <sup>x</sup> Due to a high background content of 1,2,4-triazole, the results of the analysis cannot be linked directly to the specific application, why C<sub>mean</sub> is not presented.



**Figure 4.6** Application of pesticides at Silstrup in the period 2017-2020. Pesticides are marked (M) if the pesticide and/or its degradation products are included in the monitoring programme, or (NM) if they are not monitored. Pesticides applied as seed dressing are marked SD. Measured precipitation is given on the primary axis and simulated percolation 1 mbgs on the secondary axis.

For all pesticides and degradation products (except 1,2,4-triazole where the full monitoring period is evaluated), this chapter evaluates the monitoring from 2018 to July 2020 at Silstrup. The leaching risk of pesticides evaluated before this period is available in previous monitoring reports (see [www.plap.dk](http://www.plap.dk)). As all seeds sown in the PLAP are purchased from a commercial agribusiness supplier, seeds were likely coated with seed dressing containing pesticides tested in PLAP. Such



information was, however, not registered in PLAP until 2017. Seed dressings used from 2017 and onwards are listed in Table 4.2.

### **Pesticides applied in 2020**

Two pesticides, pyroxsulam, and florasulam were used in winter wheat in April 2020 (Figure 4.6). Five degradation products from pyroxsulam (PSA, 6-Cl-7-OH-XDE-742, 5-OH-XDE-742, 7-OH-XDE-742, and pyridine sulfonamide), and four degradation products from florasulam (TSA, 5OH-florasulam, DFP-ASTCA, and DFP-TSA) were introduced in the monitoring in March 2020. As this present reporting period ends 1 July 2020, the monitoring period for these compounds presently is too short for an evaluation, but the evaluation will be included in next year's report.

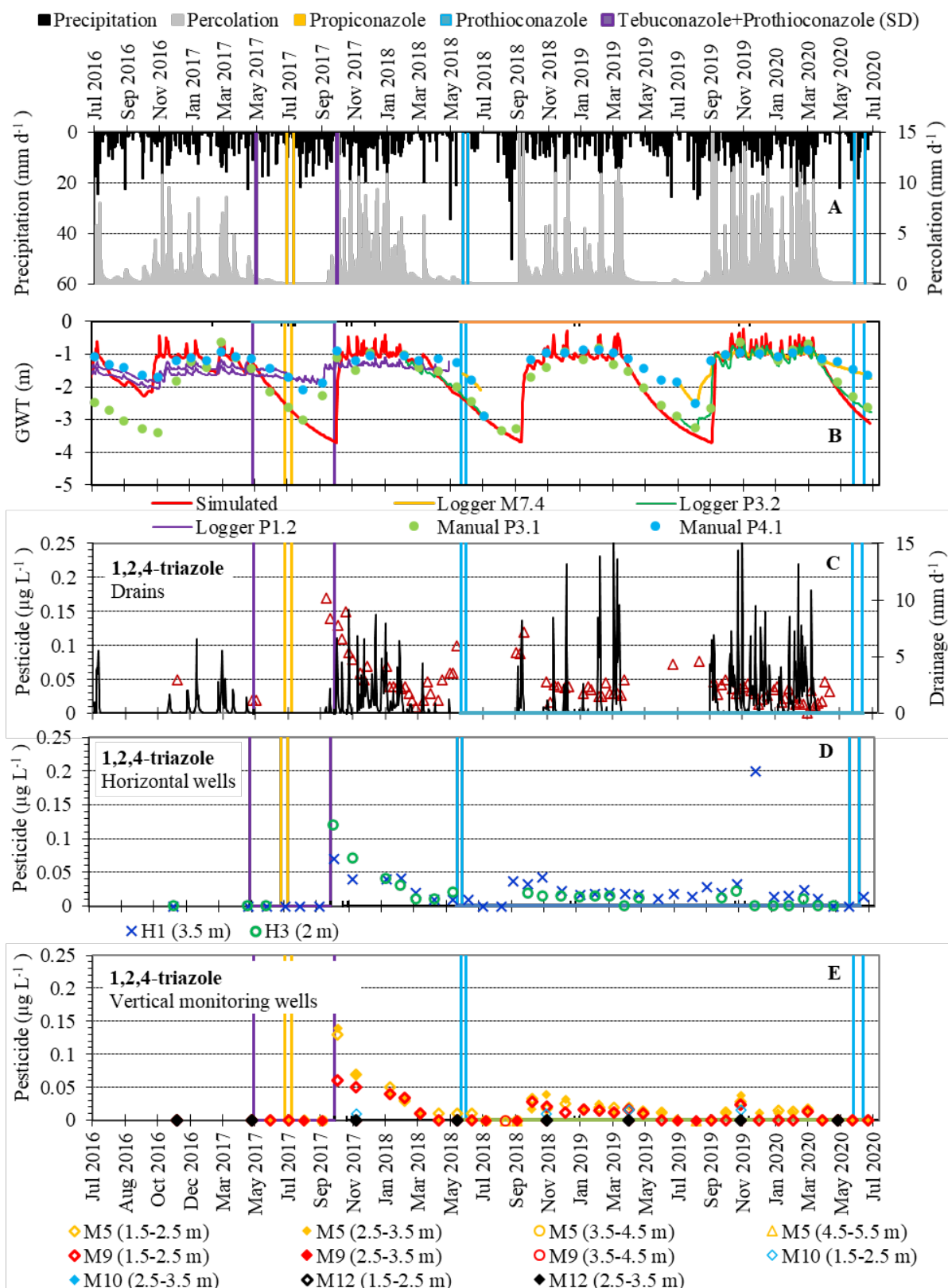
### **Azole fungicides and 1,2,4-triazole monitoring**

Monitoring of 1,2,4-triazole, a common degradation product from azole fungicides, is reported here for the period from December 2016 to July 2020. As previous use of azole-fungicides might contribute to 1,2,4-triazole leaching, it is noted that azoles were used on five occasions in the field before 2017, the most recent was tebuconazole in July 2013. These five previous azole-spraying were twice with tebuconazole and propiconazole, respectively, and once with epoxiconazole, see Table 3.2 and Appendix 3 in previous reports.

In 2017, spring barley coated with prothioconazole and tebuconazole was sown in April and sprayed with propiconazole in June and July. This crop was followed by winter barley also coated with prothioconazole and tebuconazole, which was sown in September. Subsequently, prothioconazole was sprayed on winter barley in May and June 2018, and on winter wheat in May and June 2020.

The 1,2,4-triazole concentrations in drainage seem to follow a trend with high drainage concentrations at the beginning of a draining event after dry periods of no drainage, followed by a decrease in concentration later in the drainage period (Figure 4.7C). A somewhat similar pattern is seen from the bromide analyses, where the maximum bromide concentrations are observed with the first drain event after each application and followed by a decrease in concentration with later drain events (Figure 4.4). Still, 1,2,4-triazole was present in drainage before the first monitored azole spraying in 2017 with propiconazole as a split application (note that no sampling was done from November 2016 to April 2017 although drainage was present). 1,2,4-triazole in relatively high concentrations was also present in drainage in periods with very low drain flow, e.g., in the summer of 2019. The leaching pattern of 1,2,4-triazole in the drainage seems to be correlated with the percolating water rather than a specific azole application. The detection of 1,2,4-triazole in the drainage, whenever percolation was present, likely reflects continuous formation of 1,2,4-triazole from accumulated azoles in the plough layer linked to present and previous azole sprayings and seed coatings. The content of azoles and their degradation rates in the plough layer are currently being studied.

Within the 1,2,4-triazole monitoring period from December 2016 to April 2020, a total of 82 drainage samples were collected. All but one drainage sample (from March 2020) contained 1,2,4-triazole and the highest detected drainage concentration was  $0.17 \mu\text{g L}^{-1}$  in September 2017 (Figure 4.8C). Six of the 82 drainage samples had concentrations  $> 0.1 \mu\text{g L}^{-1}$  (7%).



**Figure 4.7.** 1,2,4-triazole monitoring at Silstrup. Precipitation and simulated percolation 1 mbgs (A); measured and simulated groundwater level (B); 1,2,4-triazole concentration in the variably saturated zone (C) and saturated zone (D-E). It is noted that M12 is regarded as an upstream monitoring well. The vertical lines indicate the date of pesticide application. SD is pesticides applied as seed dressing. Seed dressings used before 2017 were not registered. Note that no sampling was done in the period from November 2016 until April 2017.

None of the groundwater samples collected between December 2016 and September 2017, (Figure 4.7D and 4.7E) contained 1,2,4-triazole. From September 2017 onwards, the groundwater concentration levels generally followed the concentration pattern in drainage with a short time lag and offset in magnitude. Hence, 1,2,4-triazole also seems to be transported rather fast to the groundwater. This rapid transport from the plough layer through a well-connected system of biopores and fractures to the tile drains and shortly thereafter to the groundwater is also evident from the bromide monitoring, where fast occurrences of maximum concentrations after application was also monitored (section 4.2.2). Following the detections of 1,2,4-triazole in the drainage in September 2017, 1,2,4-triazole was also observed in both the horizontal and vertical monitoring wells in October after which concentrations fluctuated between the detection limit ( $0.01 \mu\text{g L}^{-1}$ ) and  $0.05 \mu\text{g L}^{-1}$ . Except for a single detection of  $0.2 \mu\text{g L}^{-1}$  in December 2019 in H1, 1,2,4-triazole concentrations  $> 0.1 \mu\text{g L}^{-1}$  were observed only in October 2017 in the horizontal wells (2-3.5 mbgs), and the downstream vertical wells M5.1 and M5.2 (1.5-3.5 mbgs). In the deeper groundwater (3.5-5.5 mbgs) from M5 and M9, and the upstream well M12 (16 samples collected from 1.5-3.5 mbgs), no 1,2,4-triazole was detected during the monitoring period (Figure 4.7D and Figure 4.7E). This supports the theory that the detected 1,2,4-triazole was formed from the azoles used in the Silstrup field and presumably accumulated in the field rather than stemming from the neighbouring fields. It was, however, not possible to correlate the leaching of 1,2,4-triazole to a specific azole application, although it cannot be ruled out that the split application of propiconazole in summer 2017 contributes to the leaching of 1,2,4 triazole later in 2017. To discern between the different azole applications and leaching of 1,2,4-triazole, detailed fate studies of azoles in soils are needed. Possible azole accumulation in the plough layer is mentioned in the EFSA conclusion on tebuconazole (EFSA, 2014) and could cause continuous degradation of azoles into 1,2,4-triazole leading to long-term leaching to the groundwater. Monitoring of 1,2,4-triazole is ongoing.

A total of 222 groundwater samples were sampled from December 2016 to July 2020. From the vertical well a total of 157 samples were sampled, 61 (39%) contained 1,2,4-triazole, two of these with concentrations  $> 0.1 \mu\text{g L}^{-1}$  (1%). From the horizontal wells, a total of 65 samples were sampled, 46 contained 1,2,4-triazole (71%), two of these with concentration  $> 0.1 \mu\text{g L}^{-1}$  (3%).

#### **Florasulam's degradation product, TSA, and halauxifen-methyl's degradation product X-757**

The herbicides florasulam and halauxifen-methyl were sprayed in combination to the field in June 2017. The degradation products TSA from florasulam and X-757 from halauxifen-methyl were included in the monitoring programme. Monitoring of X-757 ended in September 2019 without any detections in 53 drainage and 150 groundwater samples. In June 2020, the monitoring of TSA was stopped, also without detections in 58 drainage and 181 groundwater samples.

#### **Flupyrsulfuron-methyl degradation products IN-KF311, IN-JE127, and IN-J0290**

The herbicide flupyrsulfuron-methyl was applied to winter barley in October 2017 and its degradation products IN-KF311 and IN-JE127 were included in the monitoring programme. As described in Chapter 8 in (Rosenbom *et al.*, 2021), IN-J127 was found unstable in aqueous solutions, and thus all the monitoring of IN-J127 should be disregarded. The degradation product IN-KF311 was not detected in 69 drainage samples nor 144 groundwater samples. To test for the potential presence of the third major relevant degradation product from flupyrsulfuron-methyl, all samples collected from Silstrup on April 30, 2019, were additionally analysed for AE-F092944/IN-J0290. The degradation product was previously included in PLAP at Silstrup and Estrup with foramsulfuron applications.

AE-F092944/IN-J0290 was not detected in any of the five groundwater samples during the April 30, 2019, sampling. Monitoring of IN-KF311 and IN-JE127 was continued until March 2020, even though flupyr-sulfuron-methyl as an active ingredient was banned by the European Union in September 2017, and subsequently banned in Denmark in December 2018 (Danish EPA, 2017).

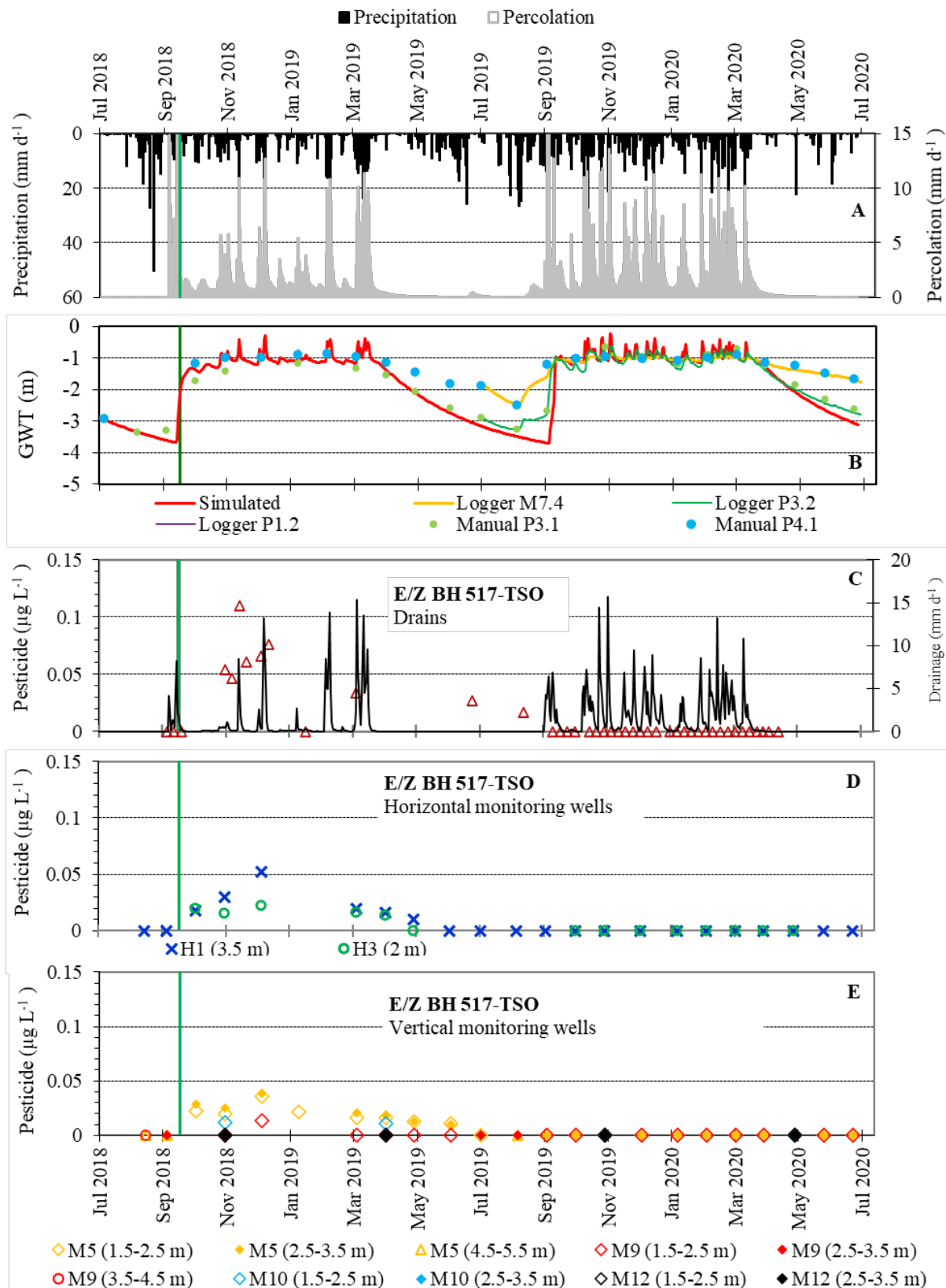
#### **Mesosulfuron-methyl degradation products, AE-F099095, AE-F160459 and AE-F147447**

The herbicide mesosulfuron-methyl (together with iodosulfuron-methyl) was applied to winter barley in April 2018, and its degradation products AE-F099095, AE-F160459, and AE-F147447 were included in the monitoring programme. AE-F147447 was not found in 124 groundwater samples, whereas AE-F099095 and AE-F160459 were not detected in 131 groundwater samples. None of the three compounds were found in 51 drainage samples. Monitoring ended March 2020.

#### **Cycloxydim's degradation products BH 517-T2SO<sub>2</sub> and E/Z BH 517-TSO**

The herbicide cycloxydim was applied to winter rape in September 2018, and two degradation products, BH 517-T2SO<sub>2</sub> and E/Z BH 517-TSO were included in the monitoring programme. Before the cycloxydim application, BH 517-T2SO<sub>2</sub> and E/Z BH 517-TSO were not detected in drainage (two samples) and groundwater (eight samples) (Figure 4.8).

E/Z BH 517-TSO was detected in nine out of 43 drainage samples (21%). Six of the nine detections of E/Z BH 517-TSO were between October and December 2018 in the range of 0.05 to 0.11 µg L<sup>-1</sup>. The remaining three detections were between March and August 2019 in concentrations ranging from 0.02 to 0.03 µg L<sup>-1</sup> (Figure 4.8D and 4.8E). In groundwater, 29 of 122 samples contained E/Z BH 517-TSO (24%), where the highest concentration (0.052 µg L<sup>-1</sup>) was detected in December 2018 in water from the horizontal well H1 (Figure 4.8D). As E/Z BH 517-TSO was not detected in groundwater samples from the upstream well M12, it is evident that the leaching of E/Z BH 517-TSO relates to the cycloxydim applied in the PLAP field. BH 517-T2SO<sub>2</sub> was not detected in any of the 122 groundwater samples and 43 samples of drainage collected from August 2018 to June 2020. Monitoring continues currently until November 2020.

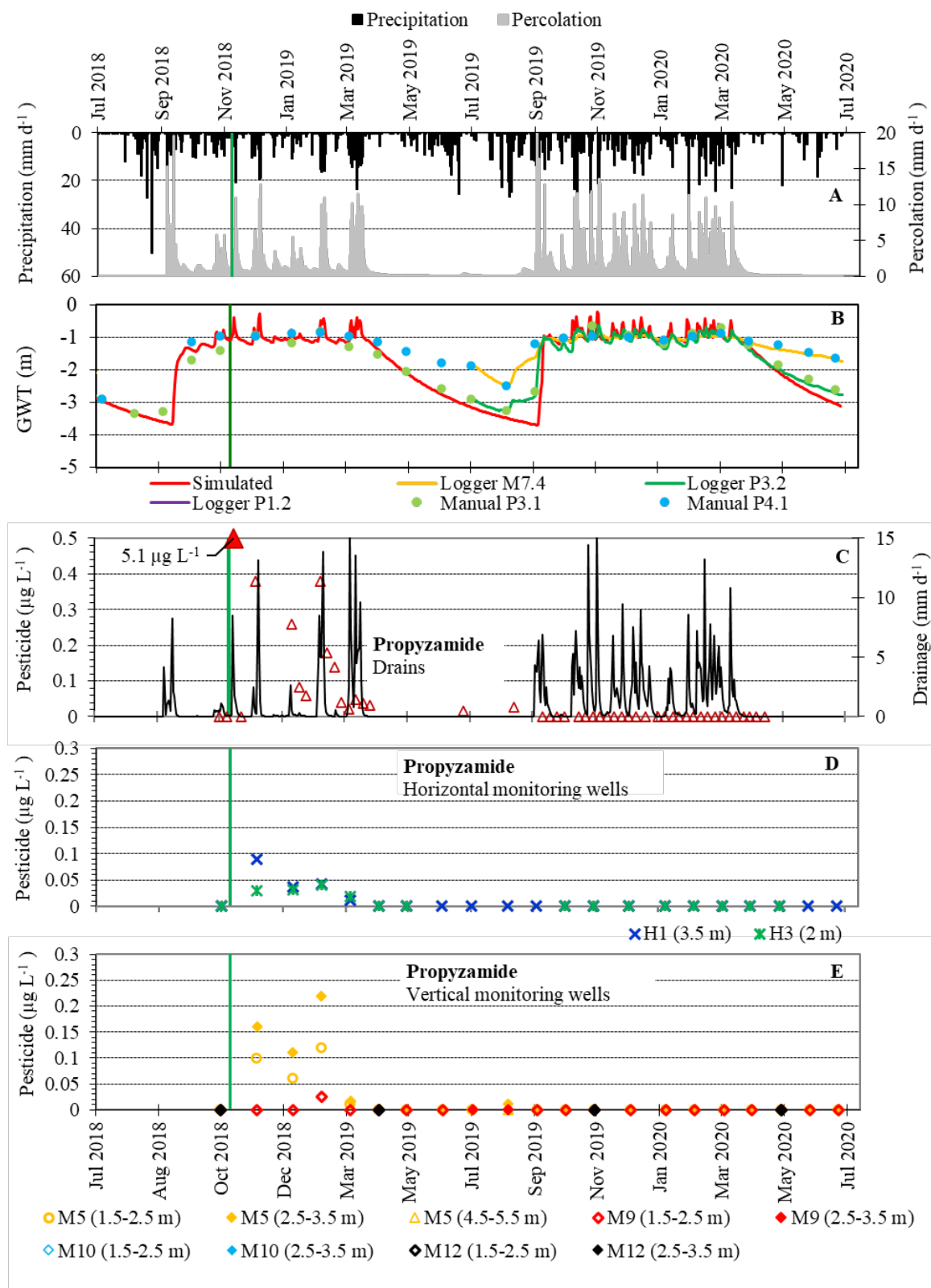


**Figure 4.8.** E/Z BH 517-TSO monitoring at Silstrup. Precipitation and simulated percolation 1 mbgs (A); measured and simulated groundwater level (B); E/Z BH 517-TSO concentration in the variably saturated zone (C) and saturated zone (D-E). It is noted that M12 is regarded as an upstream monitoring well. The green vertical lines indicate the date of cycloxydim application.

## Propyzamide

The herbicide propyzamide was included in the monitoring programme and sprayed on winter rape in November 2018. Just five days after application and in connection with a precipitation event  $> 20 \text{ mm day}^{-1}$ , a drainage concentration of  $5.1 \mu\text{g L}^{-1}$  was detected (Figure 4.9C). This detection seems to be an outcome of the precipitation event resulting in high percolation to the groundwater, a rise in the groundwater table above tile drain level, and the initiation of a drainage event of approximately  $8 \text{ mm day}^{-1}$  (Figure 4.9A-C). One week after the high concentration of propyzamide was detected, a subsequent drainage event was present, but without propyzamide detections. Further, a period with precipitation followed and caused yet another drainage event. In this drainage sample, collected in December 2018, the propyzamide concentration was  $0.38 \mu\text{g L}^{-1}$ . Thereafter concentrations declined gradually, except in one sample from February 2019, where a new drainage flow event resulted in a concentration of  $0.38 \mu\text{g L}^{-1}$ . Between February and August 2019 concentrations fluctuated in concentrations  $< 0.05 \mu\text{g L}^{-1}$ , and from September 2019 until April 2020 there were no further detections in drainage. Between the application of propyzamide in November 2018 and until the drainage period stopped in April 2020, a total of 48 drainage samples were collected, 15 contained propyzamide (31%), and six with a concentration  $> 0.1 \mu\text{g L}^{-1}$  (13%).

Propyzamide was also detected in the groundwater (Figures 4.9D-E), both from the horizontal wells (H1 and H3) and from downstream monitoring wells (M5, M9, and M10). Detections in the groundwater coincide with detections in drainage, but at lower concentration levels. In total, 75 groundwater samples were collected from M5, M9, and M10, where 10 samples (13%) contained propyzamide, four (5%) had concentrations  $> 0.1 \mu\text{g L}^{-1}$  with the highest concentration ( $0.22 \mu\text{g L}^{-1}$ ) detected in February 2019. 36 groundwater samples were collected from the horizontal wells (H1 and H3), and here eight (22 %) contained propyzamide, but none with concentrations  $> 0.1 \mu\text{g L}^{-1}$ . Propyzamide was not detected in any of the eight groundwater samples from the upstream well M12. This supports that the propyzamide used in the field caused the detections in both drainage and groundwater. In summary, the propyzamide application on winter rape in November 2018 led to detections in 18 out of 119 groundwater samples (15%), four in concentrations  $> 0.1 \mu\text{g L}^{-1}$  (3%). Monitoring continues until January 2021.



**Figure 4.9.** Propyzamide monitoring at Silstrup. Precipitation and simulated percolation 1 mbgs (A); measured and simulated groundwater level (B); propyzamide concentration in the variably saturated zone (C) and saturated zone (D-E). It is noted that M12 is regarded as an upstream monitoring well. The vertical lines indicate the date of propyzamide application. Note that the propyzamide concentration on 14 November 2018 is 5.1 µg L<sup>-1</sup>. This concentration is higher than the plot range in (C) and thus the data point is represented as a solid red triangle at 0.5 µg L<sup>-1</sup>.

**Propaquizafop's degradation products, CGA 287422, CGA 294972, CGA 290291, and PPA**

The herbicide propaquizafop was sprayed on winter rape in April 2019 and four of its degradation products (CGA 287422, CGA 294972, CGA 290291, and PPA) were included in the monitoring. None of the degradation products have been detected in drainage (32 samples) nor groundwater (84 samples) up until July 2020. As the analytical methods were not ready when the monitoring of the four degradation products was planned to start, samples were stored (-20°C) until ready. As the stability of the compounds, when frozen for several months, is unknown, the presence of false-negative results may be possible. Results on CGA 287422, CGA 294972, CGA 290291, and PPA from April 2019 until December 2019 should therefore be regarded as tentative (Chapter 8). Monitoring continues until April 2021, and the influence of freezing on the quality of analyses is currently investigated.



## 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 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  $10^{-8} \text{ m s}^{-1}$ , which is about two orders of magnitude lower than at the other clayey till fields (Table 5.1). The geological structure is complex comprising clayey till core with deposits of different ages and compositions including freshwater peat in the southwestern part of the field (Lindhardt *et al.*, 2001).

In September 2011, the monitoring system was extended with three horizontal screens (H2) 2 mbgs in the northeastern part of the field (Figure 5.1). With maps of tile drain systems always being uncertain, one of the screens should be located just below a tile drain 1.1 mbgs, whereas two should be located between two tile drains. A brief description of the drilling and design of H2 is given in Appendix 8.

The water sampling plan has been revised several times since the beginning of PLAP. During the current monitoring period, water sampling at Estrup was done monthly from wells M4, H1.2, and H2 (and from M6 until 1/1 2019), with additional samples taken half-yearly from wells M1, M5, and M6. No sampling is done from wells M2, M3, and M7. Due to earlier budget reduction, only the two uppermost well screens below the groundwater table are sampled. Appendix 2 describes the sampling procedure in more detail.

#### 5.1.2 Agricultural management

Management practice at Estrup during the 2018-20 growing seasons is briefly summarized below and detailed in Appendix 3 (Table A3.4). For information about management practice in the previous monitoring periods, see the monitoring reports available on [www.plap.dk](http://www.plap.dk).

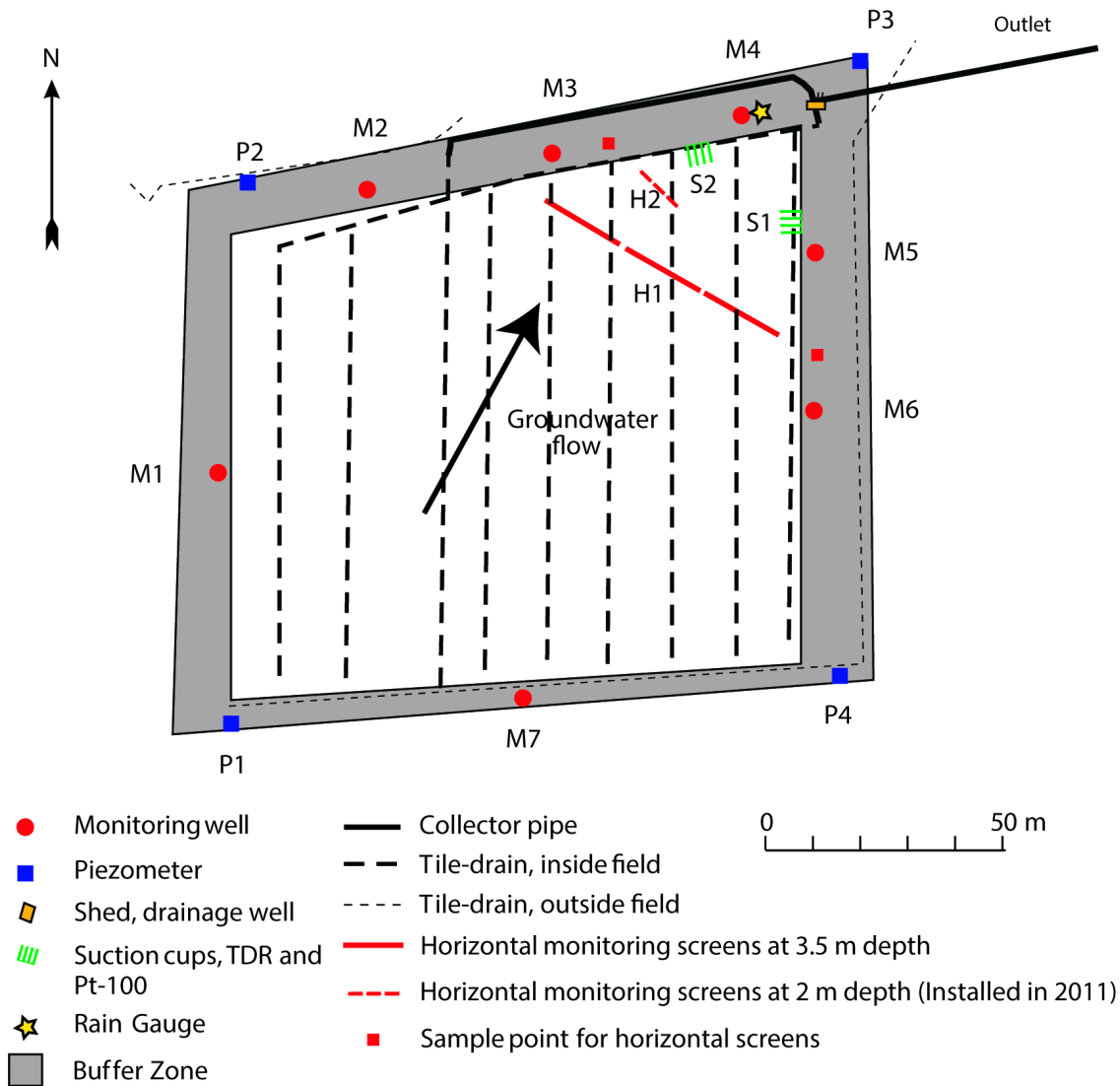
Due to an error in the previous report, Rosenbom *et al.* 2021 covering the monitoring period 2017-2019, the following includes corrections regarding the agricultural management.

On September 22, 2017, the field was ploughed and a winter wheat (cv. Sheriff coated with prothioconazole and tebuconazole) sown. The winter wheat emerged on October 5. The herbicide flupyr-sulfuron-methyl was applied on October 16, though not included in the monitoring. On April 20, 2018 weeds were sprayed, this time using a product containing mesosulfuron-methyl and

iodosulfuron-methyl-Na, the latter not monitored. Three degradation products of mesosulfuron-methyl (AE F099095, AE F160459, and AE F147447) were included in the monitoring. Another spraying of weeds, using flupyr-sulfuron (not monitored) was done on May 3. The fungicide thiophanate-methyl was applied on June 6, 2018 and the degradation product carbendazim was included in the monitoring. The insecticide lambda-cyhalothrin was used on June 21, though not monitored. At harvest on June 27, 2018 the grain yield of the winter wheat was 75.2 hkg ha<sup>-1</sup> (85 % dry matter). An amount of 37.9 hkg ha<sup>-1</sup> (100% dry matter) of straw was shredded on the day of harvest.

Ploughing of the field took place November 5, 2018 and on April 8, 2019 a spring barley (cv. Flair) coated with a mixture of prothioconazole and tebuconazole was sown. On April 17, 2019, the barley emerged. The herbicides fluroxypyr and halauxifen-methyl were sprayed on May 22, 2019. Only X-729 (halauxifen or X11393729), a degradation product from halauxifen-methyl, was included in the monitoring program. A split application of metconazole against fungi was done on May 22 and June 13, and the compound, as well as 1,2,4-triazole, was subsequently monitored. Harvest of the spring barley took place on August 11, 2019 yielding 70.4 hkg ha<sup>-1</sup> of grain (85% dry matter), whereas 23.3 hkg ha<sup>-1</sup> of straw (100 % dry matter) was shredded.

Ploughing as well as sowing of winter wheat (cv. Sheriff) coated with prothioconazole and tebuconazole was done on September 16, 2019. The winter wheat emerged on September 26, 2019 and was sprayed with the herbicide pendimethalin on October 7, 2019 (no monitoring). Further spraying of weeds was done on May 3, 2020 using a mixture of pyroxsulam and florasulam. From pyroxsulam five degradation products were included in the monitoring: PSA, 6-Cl-7-OH-XDE-742, 5-OH-XDE-742, 7-OH-XDE-742, and pyridine sulfonamide. Additionally, four degradation products from florasulam were monitored: TSA, 5-OH-florasulam, DFP-ASTCA, and DFP-TSA. None of these nine compounds included in the monitoring have yet been monitored for a sufficient period to be evaluated regarding their leaching. Harvest of the winter wheat on August 11, 2020, yielded 71.4 hkg ha<sup>-1</sup> of grain (85% dry matter) and 38.4 hkg ha<sup>-1</sup> of straw (fresh weight; shredded at harvest).



**Figure 5.1.** Overview of the Estrup field. The innermost white area indicates the cultivated area surrounded by the buffer zone. Pesticide monitoring is conducted weekly from the tile drain system in a drainage well (during periods of continuous drainage) and monthly and half-yearly from selected vertical and horizontal monitoring screens as described in section 5.1.1 and Table A2.1 in Appendix 2. At S1, water content (via TDR) and soil temperature (via Pt100) are measured at four different depths. Additionally, suction cups are installed at both S1 and S2 to collect pore water from the variably saturated matrix for analysis of pH-independent compounds.

### 5.1.3 Model setup and calibration

The one-dimensional numerical model MACRO (version 5.2 Larsbo *et al.*, 2005) represents the treated area of the Estrup field covering the upper five meters of the soil profile, always including the groundwater table. The model is used to simulate water dynamics in the variably saturated zone during the full monitoring period May 1999–June 2020 and to establish an annual water balance.

Compared to the setup in Rosenbom *et al.* (2021), one year of climate and crop data was added to the MACRO setup. The setup was calibrated for the monitoring period May 1999–June 2004 and subsequently used to compare simulated water balance with monitoring results from July 2004 to June 2020. Daily time series of the groundwater table measured in piezometers located in the buffer zone, soil water content measured at three different depths (0.25, 0.6, and 1.1 mbgs) from the two profiles S1 and S2 (Figure 5.1), and the bromide concentration measured in the suction cups located

1 and 2 mbgs were all used in the calibration process. Data acquisition, model setup, and results related to the modelling are described in Barlebo *et al.* (2007).

## 5.2 Results and discussion

### 5.2.1 Soil water dynamics and water balances

For the monitoring period 1999-June 2019, the model simulation is generally consistent with the measured water balance data (depth to groundwater table, drainage, and water saturation) for the recent hydraulic year July 2019-June 2020 indicating a good model description of the overall soil water dynamics in the variably saturated zone (Figure 5.2).

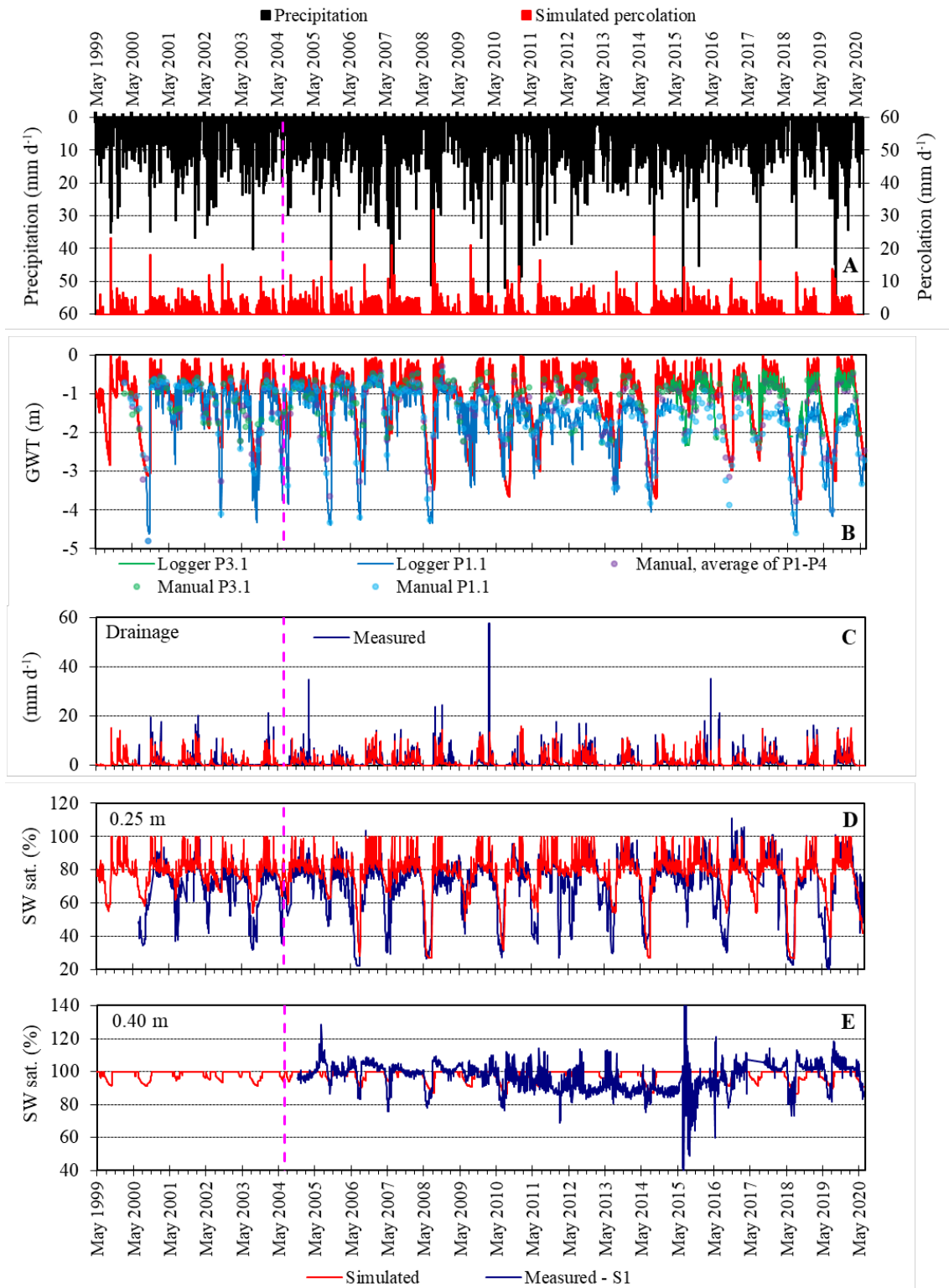
Similar to the previous years, the seasonal dynamics in groundwater levels (Figure 5.2B) of this year are captured by the model, except during a measured groundwater level decline during summer 2019, which is underestimated by approximately one meter. Nevertheless, the initiation of the decline in water level from March to June 2020 is captured quite well by the model.

The simulated groundwater levels were similar to the measured levels of the automatic data logger P3.1 situated downstream, whereas the simulated levels were up to a meter higher compared to those logged with an automatic data logger installed in P1.1 situated upstream of the field. This difference between the groundwater levels in P1.1 and P3.1 is also observed in the manually measured groundwater levels and has been present since approximately 2010.

For the recent year, the simulated pattern and level of drainage are comparable to the measured drainage and thus, capture the dynamics of the measured drainage (Figure 5.2C) except for the initiation of the drainage in September 2019. This discrepancy between measured and simulated drainage was also observed in 2018 and could be caused by the inability of the model to describe i) the extent of the decline in groundwater level during summer 2019 and ii) the degree of measured drainage due to the simulated groundwater level being below the depth of the tile drain system (1.1 m depth) for short periods compared to the measured. However, the general drainage dynamics are well captured by the model. Drainage was high during the whole monitoring period compared to that of the other three clayey till fields. At Estrup, the average yearly drainage amount was measured to 428 mm, whereas it was 220 mm at Silstrup (Table 4.1), 90 mm at Faardrup (Table 6.1), and 85 mm at Lund (Table 7.1). This seems to be due to a significantly lower permeability of the C-horizon than of the overlying A and B horizons at Estrup (see Kjær *et al.* 2005c for details).

The simulated water saturation captures the measured water saturation at 0.25 mbgs and 0.40 mbgs to some extent (Figure 5.2D-E). In 0.25 m depth, the simulated soil water saturation generally follows the measurements. During the summer of 2019, the decrease in soil water saturation is not captured, and simulated saturations are overestimated. Though the measured lows are not fully captured by the model, the overall pattern of decline is captured. As noted in Rosenbom *et al.* (2020), TDR probes do not always have sufficient contact to the surrounding soil matrix, which could be the case at 0.25 m depth where the TDR probes are re-installed after ploughing. In 0.4 m depth, the simulated soil water saturation is 100% in the periods between summers (Figure 5.2E). The reason is that the simulated groundwater table is relatively high in these periods yielding high soil water saturation in 0.4 m depth. In longer periods, the measured data, however, shows water saturations > 100% indicating that (i) fully saturated conditions are encountered and/or (ii) the TDR at 0.4 m depth is showing deviating

measurements. The groundwater table is often above 0.4 m depth supporting the fully saturated condition that is simulated at 0.4 m depth. Still, the model is not able to capture the decline in water saturation following the decline in water table level during summer periods.



**Figure 5.2.** Soil water dynamics at Estrup: Measured precipitation and simulated percolation 1 mbgs (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 comprises piezometers located in the buffer zone. The measured data in D and E are from TDR probes installed at S1 (Figure 5.1). The dashed vertical line indicates the calibration period to June 2004.

The resulting water balance for Estrup for the entire monitoring period of 21 years is shown in Table 5.1. The measured precipitation (1389 mm yr<sup>-1</sup>) and actual evapotranspiration (506 mm yr<sup>-1</sup>) in the recent year lie above average (1096 mm yr<sup>-1</sup> and 477 mm yr<sup>-1</sup>) since monitoring started. Overview of the monthly precipitation of the six PLAP fields is presented in Appendix 4.

Compared to the previous period from July 2018 to June 2019, the actual evapotranspiration for July 2019 – June 2020 increased by 100 mm yr<sup>-1</sup>, whereas the precipitation increased by 471 mm yr<sup>-1</sup>. Hence, with substantially higher precipitation in 2019/2020 compared to 2018/2019, a higher degree of drainage was both measured and estimated and apparently increasing the estimated groundwater recharge of 35 mm yr<sup>-1</sup> (Table 5.1).

**Table 5.1.** Annual water balance for Estrup (mm yr<sup>-1</sup>).

	Normal precipitation <sup>2)</sup>	Precipitation <sup>3)</sup>	Actual Evapo- transpiration <sup>4)</sup>	Measured drainage	Simulated drainage	Groundwater recharge <sup>5)</sup>
01.07.99–30.06.00 <sup>1)</sup>	968	1173	466	—	553	154 <sup>6)</sup>
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
01.07.17–30.06.18	968	1098	533	546	536	19
01.07.18–30.06.19	968	918	406	284	307	228
01.07.19–30.06.20	968	1389	506	620	709	263
Average	968	1096	477	428	464	187

<sup>1)</sup> The monitoring regarding water sampling started in April 2000. <sup>2)</sup> Normal values based on time series for 1961–1990 corrected to the soil surface (Olesen, 1991). <sup>3)</sup> Precipitation is corrected to the soil surface according to the method of Allerup and Madsen (1979).

<sup>4)</sup> Actual evapotranspiration is estimated by the MACRO-model applying climate data including potential evapotranspiration <sup>5)</sup> Groundwater recharge calculated as precipitation - actual evapotranspiration - measured drainage. <sup>6)</sup> Drainage measurements were lacking - simulated drainage was used to calculate groundwater recharge.

### 5.2.2 Bromide leaching

As mentioned in Chapter 1, it was decided for the present report to revisit and analyse all bromide data from the fields to possibly improve the fundamental understanding of the hydrogeology at the fields. In the analysis, the time until the maximum concentration of bromide reaches the different depths of water sampling is used to estimate transport times from the surface to the specific filter of interest and allow for comparison between depths. The time of maximum concentration is used in conjunction with the general pattern of breakthrough curves where possible. However, since the number of collected samples differs among the monitored well screens, continuous breakthrough curves are not equally available for all screens. Therefore, the time of maximum concentration is used to achieve transport time ranges within each monitoring depth regardless of the number of samples

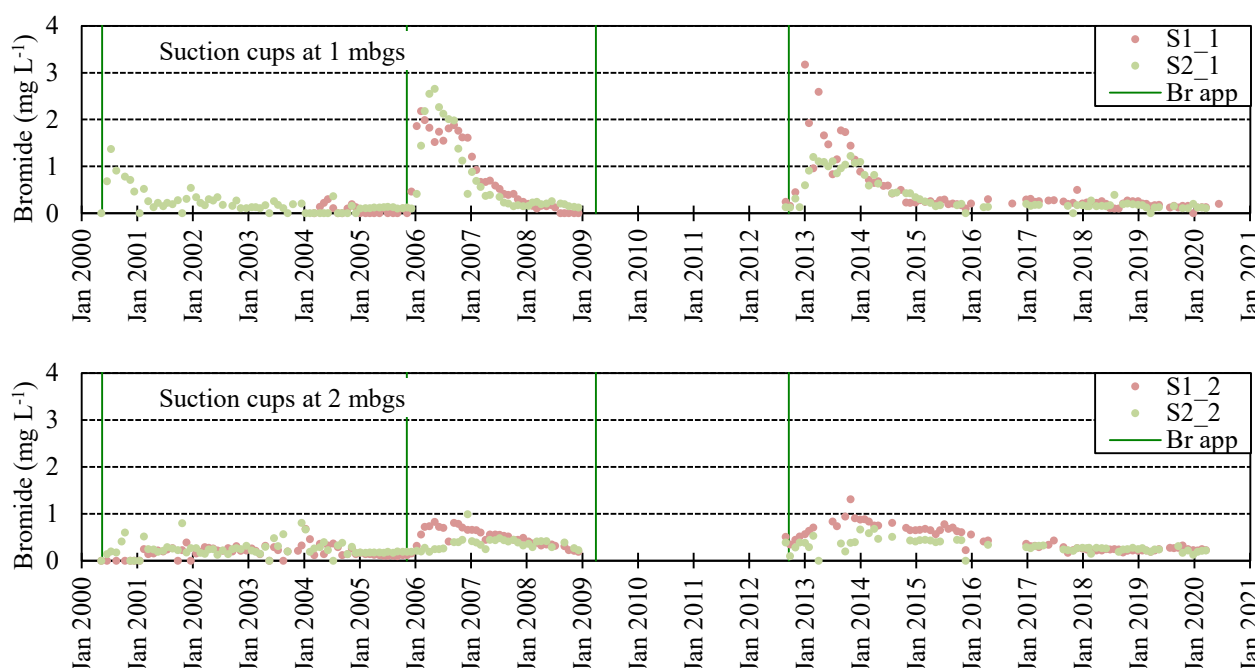
collected. These transport times are not to be conflated with average transport times. The average transport time (mean breakthrough time) represents when half of the applied mass has passed through the location of measurement which may not necessarily coincide with the breakthrough of maximum concentration. Consequently, bromide detections are generally occurring both before and after the time of the reported maximum concentration breakthroughs.

At Estrup, bromide was applied four times (May 2000, November 2005, April 2009, and September 2012) as 30 kg ha<sup>-1</sup> potassium bromide.

In the suction cups, samples were only collected with the May 2000, November 2005, and September 2012 applications. In the suction cups located 1 mbgs, the maximum bromide concentrations after May 2000, November 2005, and September 2012 applications are measured within 2, 3-6, and 4-14 months (Figure 5.3). For all applications, it is noted that increased concentrations are observed more or less immediately after application and that bromide pulses extend up to several years.

In the suction cups located 2 mbgs, the maximum bromide concentrations after May 2000, November 2005, and September 2012 applications are measured within 43-44, 6-13, 14-19 months, respectively (Figure 5.3). Again, it is noted that concentrations are observed shortly after application and that bromide pulses extend up to several years.

In general, at 1 mbgs, the maximum concentrations are measured six months after application. At 2 mbgs, the average breakthrough time for the maximum concentration is much longer, around 23 months (Figure 5.3). The patterns of wide bromide pulses and immediate occurrence of increased bromide concentrations just after application in the variably saturated zone are similar to what is observed at Silstrup. As such both Silstrup and Estrup are characterized as clay-till fields and the low permeable properties of the sediment matrix are likely causing the relatively slow passing of maximum bromide pulses (and the wider pulses) as well as fast occurrence of increased concentrations related to preferential flows.



**Figure 5.3.** Measured bromide concentration at Estrup.

The samples representing drainage from around 1 mbgs are collected in a drain well collecting drainage from the entire field (Figure 5.4). Therefore, no ranges are reported for the drainage samples. The maximum concentrations in the drainage after May 2000, November 2005, and September 2012 applications are measured after 5, 0, 5, and 1 month, respectively (Figure 5.4). After the November 2005 application, the maximum concentration is measured within the same month of application and therefore reported as zero. Generally, it is noted that the maximum bromide concentrations are measured after the first drainage event following an application. Although the maximum concentrations are measured relatively fast in drainage samples after bromide applications, detections of bromide are continuous throughout all monitoring periods.

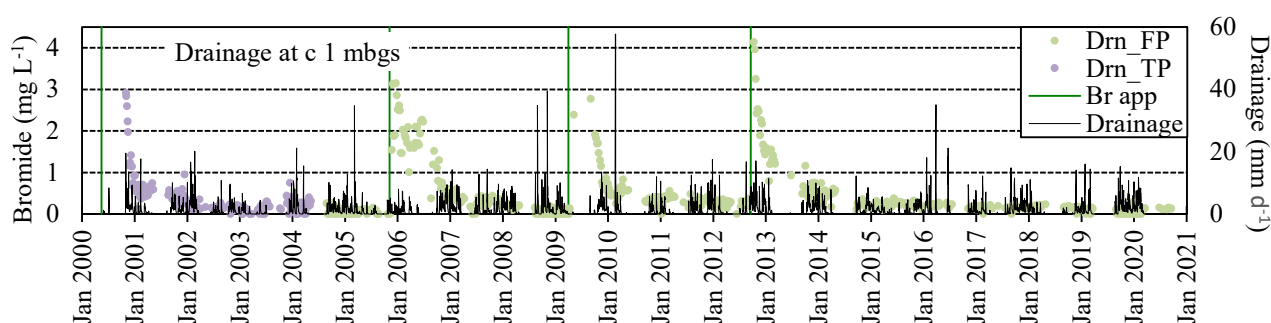


Figure 5.4. Measured bromide concentration in drainage at Estrup. The suffix FP and TP refer to flow- and time proportional sampling, respectively, which are described in Kjær *et al.* (2004) and Appendix 2.

In groundwater, sampling results are based on measured bromide concentrations in wells M1-M6 and the horizontal monitoring wells (Figure 5.1). M7 is regarded as an upstream well. However, as bromide is measured in M7, although in low concentrations (generally  $< 0.5 \text{ mg L}^{-1}$ ), further analysis of the flow field is needed to fully understand the groundwater flow dynamics across the field. Such analyses are under preparation for all the fields. However, for the sake of simplicity, in the present analysis, M7 is assumed not to be part of the flow field represented by the remaining wells.

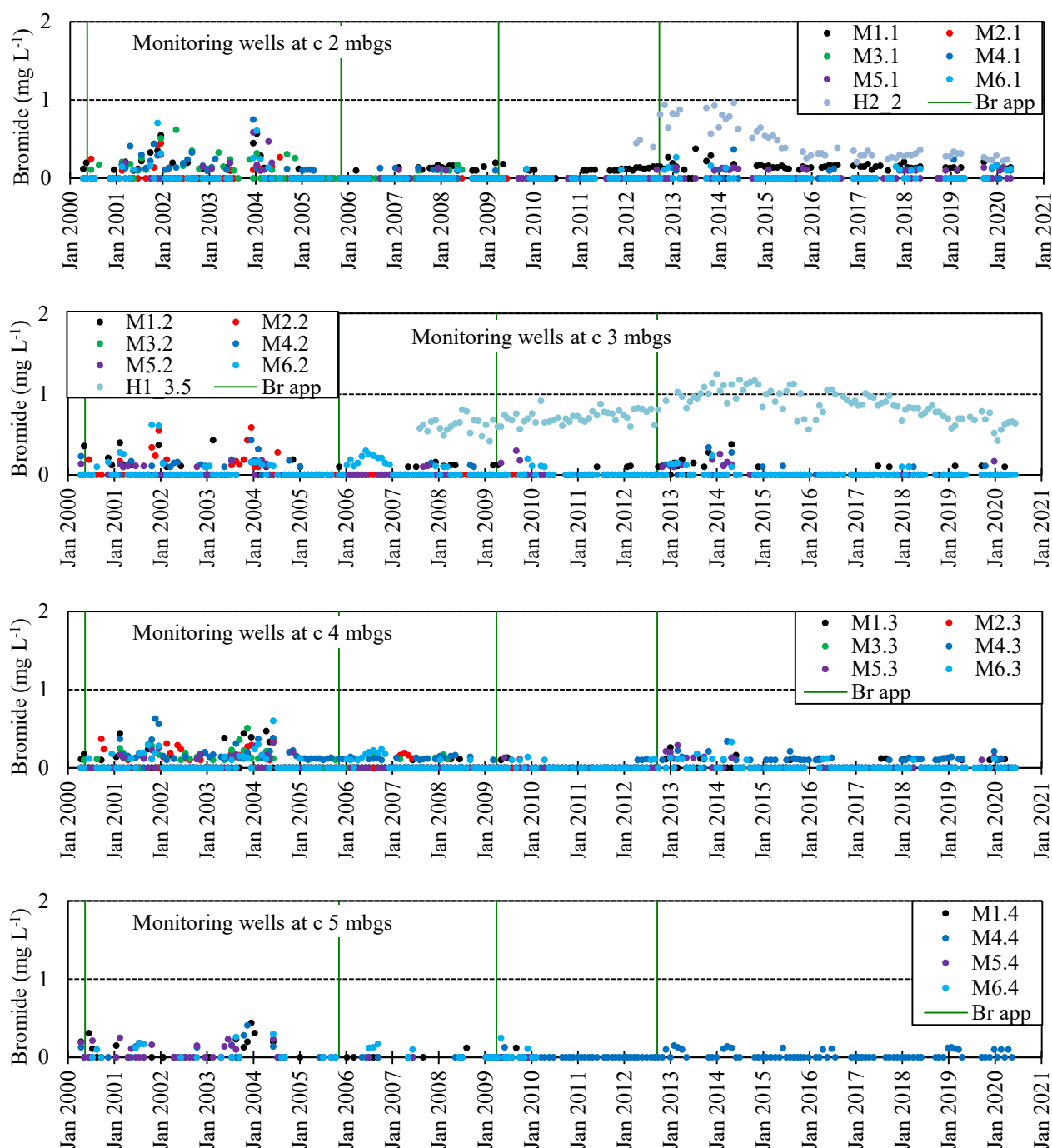
In the groundwater samples from  $\sim 2$  mbgs, the maximum bromide concentrations after May 2000, November 2005, and September 2012 applications are measured within 18-44, 10-40, 1-41, and 5-88 months (Figure 5.5).

In the groundwater samples from  $\sim 3$  mbgs, the maximum bromide concentrations after May 2000, November 2005, and September 2012 applications are measured within 9-46, 7-25, 5-34, and 5-20 months (Figure 5.5).

In the groundwater samples from  $\sim 4$  mbgs, the maximum bromide concentrations after May 2000, November 2005, and September 2012 applications are measured within 4-49, 2-30, 2-39, and 4-20 months (Figure 5.5).

In the groundwater samples from  $\sim 5$  mbgs, the maximum bromide concentrations in May 2000, November 2005, and September 2012 applications are measured within 9-49, 10-33, 2, and 5 months (Figure 5.5).





**Figure 5.5.** Measured bromide concentrations in the groundwater at Estrup.

For each depth, the average breakthrough time for maximum bromide concentrations is calculated from the time of measured maximum concentration within each of the wells representing that particular depth. Thus, for the May 2000, November 2005, April 2009, and September 2012 applications, the average breakthrough time for maximum bromide concentrations reaching depths at around 2, 3, 4, and 5 mbgs are 27, 21, 20, and 24 months, respectively. However, in general, continuous data series are scarce and therefore challenging to interpret overall bromide breakthrough patterns.

After the May 2000 application, there seems to be a pattern of bimodal breakthrough (Figure 5.5) which was also seen at Silstrup (Figure 4.5) and also the timing of the breakthroughs is similar. This indicates that the breakthroughs are governed by precipitation events generating fast flows. In general, there are no clear patterns in the average breakthrough time for the maximum concentrations reaching the different screen depths, although increasing transport time with increasing depth would be expected in a homogeneous setting. Also, the sampling is not sufficient to achieve a general pattern of the bromide pulse breakthroughs within the different depths. After the April 2009 and September 2012 applications, the fast occurrences in some well locations are lowering the average breakthrough time for maximum concentration. However, these fast occurrences immediately after an application may not represent the actual application. E.g., in M1 at ~2 mbgs, the maximum concentration is observed within a month from the April 2009 application, while the maximum concentration of the previous application is measured within a month before the April 2009 application (Figure 5.5). Hence, it is difficult to discern which application the maximum concentration following the April 2009 application represents. Nevertheless, the fast breakthrough of maximum bromide concentrations in drainage samples affirms that preferential flow paths are present in the variably saturated zone. Further, the range in which the maximum bromide concentrations are measured vary substantially from a few months to several years and supports that the flow and transport field is affected by heterogeneity related to clay-till settings comprising preferential flow paths as well as low permeable sediments.

In general, the majority of the maximum bromide concentrations reach the screens at ~2-5 mbgs within ~2 years after application, but maximum concentration levels are measured up to several years after application. For all the sampled depths, it is noted that bromide concentrations above the detection limit are measured before and after the transport times representing maximum concentrations.

### **5.2.3 Pesticide leaching**

Monitoring at Estrup began in May 2000. Pesticides and degradation products monitored from 2000 to 2020 are shown in Table 5.2 (2014-2020) and Table A7.4 in Appendix 7 (2000-2014). Several azole fungicides have had great focus since the beginning of the programme, but especially their common degradation product 1,2,4-triazole is intensively monitored since it was introduced in 2014. Monitoring of 1,2,4-triazole at Estrup started in 2014, therefore, all pesticide applications from 2014 to 2020 are summarised in Table 5.2, and for 2018-2020 shown together with precipitation and simulated percolation in Figure 5.6. It is noted that precipitation is corrected to the soil surface according to Allerup and Madsen (1979), whereas percolation refers to accumulated percolation simulated with the MACRO model (Section 5.2.1). Moreover, due to the very short monitoring period and therefore few data points, pesticides applied after 1 April 2020 are not evaluated in the chapter, although presented in Table 5.2 and Figure 5.6.

For all pesticides and degradation products (except 1,2,4-triazole where the full monitoring period is evaluated), this chapter evaluates the monitoring from 2018 to July 2020 at Estrup. The leaching risk of pesticides evaluated before this period is available in previous monitoring reports (see <http://www.plap.dk/>). All seeds sown in PLAP are purchased from a commercial agribusiness supplier, seeds were likely coated with seed dressing containing pesticides included for testing in PLAP. Such information was, however, not registered in PLAP until 2017. Seed dressings used from 2017 and onwards are listed in Table 5.2.

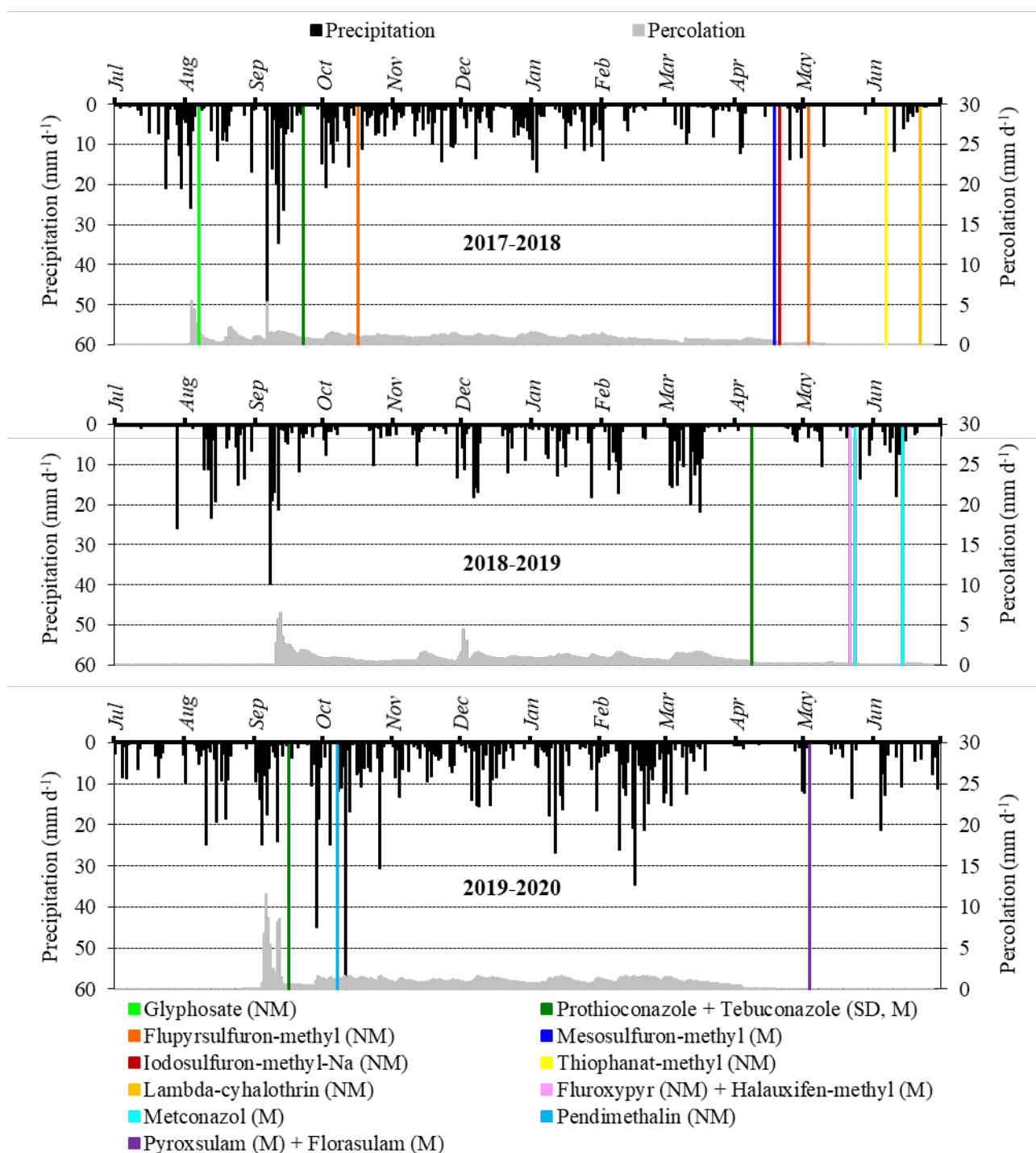
**Table 5.2** Pesticides analysed at Estrup. Precipitation (precip.) and percolation (percol.) are accumulated within the first year (Y 1<sup>st</sup>), and month (M 1<sup>st</sup>) after application. C<sub>mean</sub> is average leachate concentration at 1 mbgs. See Appendix 2 for the calculation method and Appendix 7 (Table A7.4) for previous applications of pesticides.

Crop – Year of harvest	Applied product	Analysed Pesticide (P) / Degradation product (M)	Application date	End of monitoring	Y 1 <sup>st</sup> Precip. (mm)	Y 1 <sup>st</sup> Percol. (mm)	M 1 <sup>st</sup> Precip. (mm)	M 1 <sup>st</sup> Percol. (mm)	C <sub>mean</sub> (µg L <sup>-1</sup> )
<b>Winter wheat 2014</b>	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	1,2,4-triazole(M)	May 14	Jun 20*	1152	249	51	0.4	x
	Tebuconazole (P)	Azoxystrobin(P)	Jun 14	Apr 16	1176	257	49	0	0.02
		CyPM(M)	Jun 14	Apr 17	1176	257	49	0	0.38
	Amistar	Glyphosate(P)	Jul 14	May 16	1219	305	117	0	0.06
		AMPA(M)	Jul 14	May 16	1219	305	117	0	0.1
<b>Maize 2015</b>	Callisto	Mesotrione(P)	May 15	May 18	1196	299	91	23	0.11
	Mesotrione (P)	AMBA(M)	May 15	May 18	1196	299	91	23	<0.01
		MNBA(M)	May 15	May 18	1196	299	91	23	<0.01
		Foramsulfuron(P)	May 15	May 18	1196	299	91	23	<0.01
	Foramsulfuron-methyl (P)	AE-F130619(M)	May 15	May 18	1196	299	91	23	<0.01
	Iodosulfuron-methyl (P)	AE-F092944(M)	May 15	May 18	1196	299	91	23	<0.01
<b>Maize 2016</b>	Callisto	Mesotrione(P)	Jun 16	May 18	870	209	148	19	<0.01
		AMBA(M)	Jun 16	May 18	870	209	148	19	<0.01
		MNBA(M)	Jun 16	May 18	870	209	148	19	<0.01
		Triazinamine(M)	Jun 16	May 18	870	209	148	19	<0.01
	Harmony SX	Foramsulfuron(P)	Jun 16	May 18	936	204	201	28	<0.01
	MaisTer	AE-F130619(M)	Jun 16	May 18	936	204	201	28	<0.01
	Foramsulfuron-methyl (P)	AE-F092944(M)	Jun 16	May 18	936	204	201	28	<0.01
	Iodosulfuron-methyl (P)		Jun 16	May 18	936	204	201	28	<0.01
<b>Pea 2017</b>									
<b>Winter wheat 2018</b> SD: Redigo Pro 170 FS (Prothioconazole + tebuconazole)	Hussar Plus OD	AE-F099095 (M)	Apr 18	Mar 20	876	231	45	13	<0.01
	Mesosulfuron-methyl (P)	AE-F160459 (M)	Apr 18	Mar 20	876	231	45	13	<0.01
		AE-F147447 (M)	Apr 18	Mar 19	876	231	45	13	<0.01
	Topsin WG	Carbendazim (M)	Jun 18	Jun 20*	898	187	32	2	<0.01
<b>Spring barley 2019</b> SD: Redigo Pro 170 FS (Prothioconazole + tebuconazole)	Pixxaro EC	X-729 (M)	May 19	Jun 20*	1365	257	81	0	<0.01
	Halauxifen-methyl (P)								
	Fluroxypyr (P)								
	Juventus 90	Metconazole (P)	May 19	Jun 20*	1365	257	81	0	<0.01 <sup>x</sup>
<b>Winter wheat 2020</b> SD: Redigo Pro 170 FS (Prothioconazole + tebuconazole)	Broadway	1,2,4-triazole (M)	May 19	Jun 20*	1365	257	81	0	
		Amitrol (M)	May 20	Jun 20*	-	-	-6	25	-
		PSA (M)**							
		6-Cl-7-OH-XDE-742 (M)**							
	Pyroxulam (P)	5-OH-XDE-742 (M)**							
		7-OH-XDE-742 (M)**							
		Pyridine sulfonamide (M)**							
		TSA (M)**							
	Florasulam (P)	5OH-florasulam (M)**	May 20	Jun 20*	-	-	-6	25	-
		DFF-ASTCA (M)**							
		DFF-TSA (M)**							

Systematic chemical nomenclature for the analysed pesticides is given in Appendix 1. SD = Seed dressing.

\*Monitoring continues the following year. \*\* Parent compound was applied in spring 2020. Data evaluation is not included in this report but will be discussed in next year's report covering 2019-2021.

<sup>x</sup> Due to a high background content of 1,2,4-triazole, the results of the analysis cannot be linked directly to the specific application, why C<sub>mean</sub> is not presented.



**Figure 5.6.** Application of pesticides at Estrup in the period 2017-2020. Pesticides are marked (M) if the pesticide and/or its degradation products are included in the monitoring programme, or (NM) if they are not monitored. Pesticides applied as seed dressing are marked SD. Measured precipitation is given on the primary axis and simulated percolation 1 mbgs on the secondary axis.

### Pesticides applied in 2020

Two pesticides, pyroxsulam, and florasulam were applied in winter wheat in May 2020. Five degradation products from pyroxsulam (PSA, 6-Cl-7-OH-XDE-742, 5-OH-XDE-742, 7-OH-XDE-742, and pyridine sulfonamide), and four degradation products from florasulam (TSA, 5OH-florasulam, DFP-ASTCA, and DFP-TSA) were introduced in the monitoring in April 2020. As this

present reporting period ends 1 July 2020 the monitoring period for these compounds is too short for an evaluation, but the evaluation will be included in next year's report.

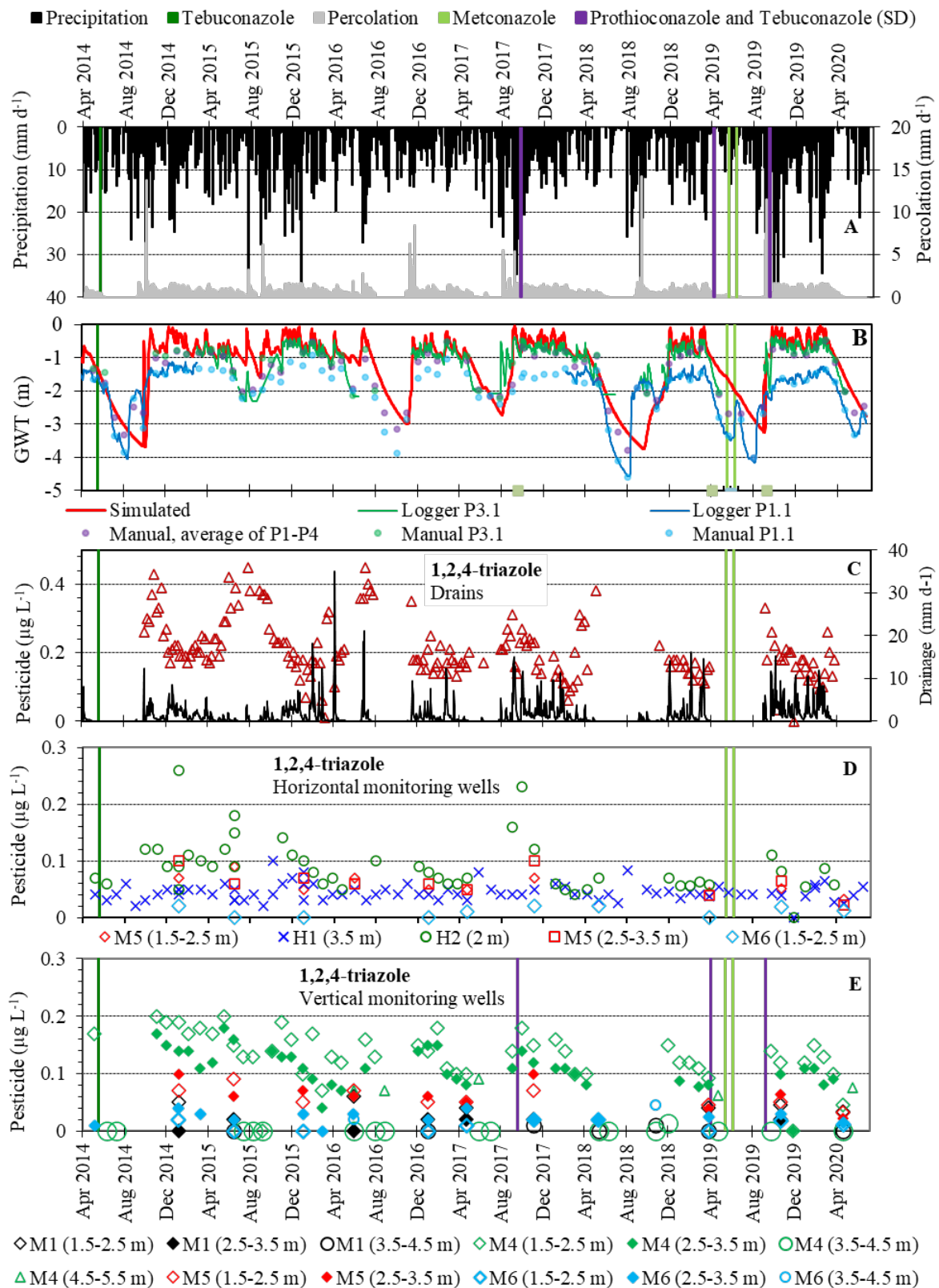
### **Azole fungicides and 1,2,4-triazole monitoring**

Monitoring of 1,2,4-triazole (a common degradation product from several azole fungicides) at Estrup started in 2014 after application of tebuconazole on winter wheat in May and is still ongoing. The monitoring results of 1,2,4-triazole is therefore reported from March 2014 to July 2020 (Figure 5.7), but as use of azole-fungicides before 2014 might contribute to 1,2,4-triazole leaching, it is noted that the azoles were sprayed three times in Estrup before 2014, the most recent was tebuconazole in July 2008. The former two sprayings were with propiconazole, epoxiconazole, respectively (see Table 3.2 and Appendix 3 in previous reports). In addition to the previous azole sprayings, the use of azole coated seeds might also contribute to the azole soil content and potentially 1,2,4-triazole leaching (Albers *et al.*, 2022). The use of azole-coated seeds was registered from 2017, but they were most likely used before this. The known use of azole-coated seeds is presented together with the azole sprayings in Figures 5.6 and 5.7.

Due to a very dry spring in 2014, and consequently lack of drainage, background samples could only be collected from groundwater before the spraying with tebuconazole. Therefore, no drainage background samples are presented in Figure 5.7C. The first collected drainage sample after the application of tebuconazole in April 2014 was in October the same year, where 1,2,4-triazole was detected in a concentration of  $0.26 \mu\text{g L}^{-1}$  (Figure 5.7C). The 1,2,4-triazole concentration peaked during the winter of 2014/2015 followed by a decrease, and a new peak occurrence during summer 2015. This fluctuating trend with pronounced 1,2,4-triazole concentration peaks in drainage continued throughout the monitoring period. The highest concentration in drainage samples was  $0.45 \mu\text{g L}^{-1}$  observed in a sample collected in July 2015 and 2016. 1,2,4-triazole leaching to drainage cannot be linked to any specific application but seems to correlate with precipitation and percolation. Hence, increases in 1,2,4-triazole concentrations in drainage ( $> 0.1 \mu\text{g L}^{-1}$ ) generally coincide with rainfall events (Figure 5.7A and Figure 5.7C). However, whether the pattern in drainage sample concentrations is seasonal needs further evaluation. Looking at the entire monitoring period since 2014, the concentration magnitude of 1,2,4-triazole in drainage seems to follow an overall decreasing trend.

186 drainage samples were collected from October 2014 to March 2020 (there was no drainage in April-July 2020) and all but one (detected in December 2019) contained 1,2,4-triazole. 175 samples had concentrations  $> 0.1 \mu\text{g L}^{-1}$  and in 10 samples concentrations were  $\leq 0.1 \mu\text{g L}^{-1}$ . This is equivalent to 94% of the drainage samples having concentrations  $> 0.1 \mu\text{g L}^{-1}$ .

Leaching of 1,2,4-triazole to groundwater is presented in Figure 5.7D and E. Before tebuconazole is applied in 2014, 1,2,4-triazole was present in groundwater from both horizontal wells and the vertical well, M4, located downstream of the field, and even in concentrations  $> 0.1 \mu\text{g L}^{-1}$ . As mentioned above, likely sources for 1,2,4-triazole could be previous azole sprayings or sowing of azole-coated seeds.



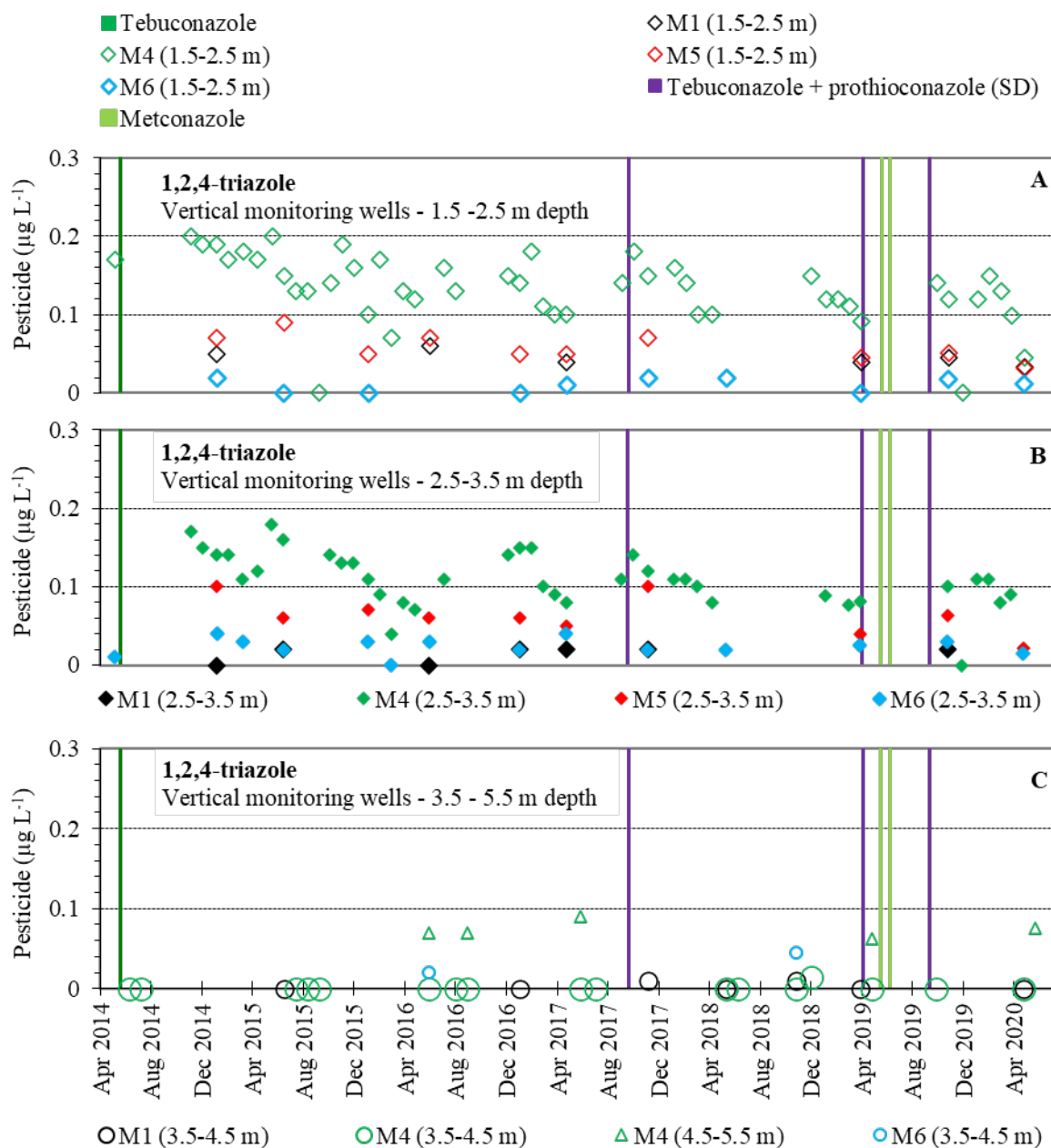
**Figure 5.7.** 1,2,4-triazole monitoring at Estrup: Precipitation and simulated percolation 1 mbgs (A); measured and simulated groundwater level (B); 1,2,4-triazole concentration in the variably saturated zone (C) and saturated zone (D-E). It is noted that M1 is regarded as an upstream monitoring well. The coloured vertical lines indicate the date of pesticide application. SD is pesticides applied as seed dressing. Seed dressings used before 2017 were not registered.

In groundwater monitoring from May 2014 to July 2020, 1,2,4-triazole was detected in all samples from the horizontal wells (Figure 5.7D), except samples collected in December 2019. In H1 at 3.5 m depth, there seem to be consistent 1,2,4-triazole concentrations fluctuating around  $0.04 \mu\text{g L}^{-1}$ . In groundwater from H2 at 2 m depth, the concentration variations are greater than in H1, with concentrations ranging from 0.02 to  $> 0.1 \mu\text{g L}^{-1}$  (the two non-detects excluded) indicating that H2 is more susceptible to temporal fluctuations compared to H1.

In the horizontal wells H1 and H2, 1,2,4-triazole was detected in 126 out of 128 groundwater samples (98.4%), and 13 samples (10%) with concentrations  $> 0.1 \mu\text{g L}^{-1}$  (Figure 5.7D).

Figure 5.7E and Figure 5.8 (Figure 5.7E divided in screen depth for a better overview), show similar to drainage, an overall decreasing trend in leaching of 1,2,4-triazole to groundwater during the entire monitoring period. The 1,2,4-triazole concentrations in the individual wells decrease with depth (Figure 5.8A-C). Comparing the four vertical monitoring wells (M1, M4, M5, and M6), 1,2,4-triazole concentrations  $> 0.1 \mu\text{g L}^{-1}$  are solely observed in M4 in both depth intervals, 1.5-2.5 m and 2.5-3.5 m. The samples collected in these depth intervals (1.5-2.5 m and 2.5-3.5) from M4 also show that concentration levels decrease with depth in this well (Figure 5.8A and Figure 5.8B). A similar pattern of decreased concentration with depth is observed for the measured concentrations in M1. In groundwater from well M5 and M6, the measured concentration levels remain similar in the two depths. In terms of concentration magnitude, it seems that groundwater collected from wells M1 and M5 have comparable concentration levels around  $0.05 \mu\text{g L}^{-1}$  in the depth interval 1.5-2.5 m, while the levels in M6 are slightly lower around  $0.03 \mu\text{g L}^{-1}$  (Figure 5.8A). In the groundwater from the three wells M1, M4, and M6, where sampling was conducted in the depth interval 3.5-4.5 m, concentration levels were low, or no 1,2,4-triazole was detected (Figure 5.8C). It is noted that sampling is conducted at the depth interval 4.5-5.5 m from M4 and shows relatively high concentration levels ( $> 0.06 \mu\text{g L}^{-1}$ ) compared to the overlaying depth interval 3.5-4.5 m, where 1,2,4-triazole was only detected in low concentration ( $0.014 \mu\text{g L}^{-1}$ ) in one sample. Based on the concentration levels measured in the different depth intervals, it appears that M4 differs substantially from M1, M5, and M6. In relation to the general groundwater flow direction, M4 is located directly downstream of the field, and M1, M5, and M6 are located on the sides of the field, almost parallel to the flow direction (Figure 5.1), which might explain the differences. Hence, M4 may better represent the leaching from the field to the groundwater compared to the remaining vertical wells. Similar to the location of M4, both horizontal wells are also located directly downstream from the groundwater flow direction. Thus, there seem to be similarities in the concentration magnitude pattern of well M4 and H2, where concentrations decrease with depth. As such, wells likely located in the groundwater flow fields are prone to temporal fluctuations with larger leaching concentrations ( $> 0.1 \mu\text{g L}^{-1}$ ) in most surface-near screens. This could indicate that the source is primarily from the azole applications in the field rather than upstream sources. This also corroborates with the relatively high concentrations and temporal fluctuations in the drainage samples. However, it is not possible to link specific groundwater concentrations to specific applications in the field.

In total 175 groundwater samples were collected from the vertical wells. 1,2,4-triazole was detected in 144 samples (82%), 60 of these contained concentrations  $> 0.1 \mu\text{g L}^{-1}$ . 1,2,4-triazole was not detected in 31 samples (18%). Thus, 1,2,4-triazole concentrations  $> 0.1 \mu\text{g L}^{-1}$  are present in 34% of all groundwater samples collected from vertical wells at Estrup.



**Figure 5.8.** 1,2,4-triazole monitoring in groundwater from vertical monitoring wells at Estrup at different depths; 1.5-2.5 mbgs (A), 2.5-3.5 mbgs (B), and 3.5-5.5 mbgs (C). It is noted that M1 is regarded as an upstream monitoring well. The green vertical lines represent tebuconazole (2014) and metconazole (2019) application. The purple vertical lines represent seed dressing, which was not registered before 2017. The data are also presented in Figure 5.7E.

The omnipresent background concentrations of 1,2,4-triazole in groundwater collected from most of the monitoring wells both before the 2014 tebuconazole application and in the subsequent 1,2,4-triazole monitoring in PLAP, indicate other sources of 1,2,4-triazole in addition to the specific applications of azole-fungicides since 2014. These other sources are likely from the degradation of accumulated azoles from previous azole applications and sowing with seeds coated with azoles at the field, and possible contribution from upstream sources. As mentioned, the patterns of higher concentrations in drainage and water from the uppermost well screens – compared to the concentrations in deeper well screens – could indicate that the primary source of the relatively high 1,2,4-triazole concentrations at Estrup is related to the azole applications in the field, rather than



upstream sources. Still, the leaching of 1,2,4-triazole cannot be coupled to current sprayings and application of azole-dressed sowing seeds or directly related to past applications of azoles. To discern between the different azole applications and leaching of 1,2,4-triazole, detailed fate studies of azoles in soil are needed. Possible azole accumulation in the plough layer is mentioned in the EFSA conclusion on tebuconazole (EFSA, 2014) and therefore may cause continuous degradation of azoles into 1,2,4-triazole leading to long-term leaching to the groundwater. Monitoring of 1,2,4-triazole is ongoing.

### **Metconazole**

A split application of metconazole against fungi was conducted in May and June 2019 and subsequently monitored together with 1,2,4-triazole (as shown in Figure 5.6-5.8). Metconazole is not detected in any of the 30 drainage samples, 39 groundwater samples collected from vertical wells, or 23 groundwater samples collected from horizontal wells. As there was no detection of metconazole, only the application time of metconazole is shown in the figures. As the analytical method was not ready by the time of monitoring of metconazole, samples were stored (-20°C) until ready. The stability of the compound, when frozen for several months, is currently unknown, which is why the presence of false-negative results may be possible. Results on metconazole from April 2019 to September 2019 should therefore be regarded as tentative (Chapter 8). Monitoring of metconazole is ongoing and the influence of freezing on the quality of analyses is currently investigated.

### **Mesosulfuron-methyl degradation products, AE-F099095, AE-F160459 and AE-F147447**

Mesosulfuron-methyl-Na was applied to winter wheat in April 2018, and neither of its three degradation products AE-F099095, AE-F160459, and AE-F147447 are detected in any of the collected samples. AE-F099095 and AE-F160459 measurements were done in 48 drainage samples, 50 vertical well samples, and 37 horizontal well samples. AE-F147447 measurements were done in 19 drainage samples, 19 vertical well samples, and 16 horizontal well samples. Monitoring ended 30 March 2020.

### **Thiophanat-methyl degradation product, carbendazim**

Thiophanat-methyl was applied to winter wheat in June 2018 and the degradation product carbendazim was included in the monitoring programme. Until July 2020, only three detections in 54 drainage samples (max. conc. 0.015 µg L<sup>-1</sup>) are observed, while no detections are monitored in any of the 60 samples collected from the vertical wells and 36 samples from the horizontal wells. As the analytical method was not ready, when the monitoring of carbendazim was planned to start, samples were stored (-20°C) until ready. As the stability of the compound, when frozen for several months, is unknown, the presence of false-negative results may be possible. Results on carbendazim from May 2018 to October 2018 should therefore be regarded as tentative (Chapter 8). Monitoring is ongoing and the influence of freezing on the quality of analyses is currently investigated.

### **Halauxifen-methyl degradation product, X-729**

The herbicide halauxifen-methyl and fluroxypyr (not monitored) were sprayed on the field on 22 May 2019. The halauxifen-methyl degradation product X-729 was not detected in any of the 30 drainage samples, 39 vertical well samples, or 23 horizontal well samples. As the analytical method was not ready, when the monitoring of X-729 was planned to start, samples were stored (-20°C) until ready. As the stability of the compound, when frozen for several months, is unknown, the presence of false-negative results may be possible. Results on X-729 from the period of April 2019 until September 2019 should therefore be regarded as tentative (Chapter 8). Monitoring is ongoing and the influence of freezing on the quality of analyses is currently investigated.



## 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 1.1) and the test field covers a cultivated area of 2.3 ha (150 x 160 m, Figure 6.1). The terrain slopes gently ( $1-3^\circ$ ) to the west. 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 meltwater 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 mbgs, respectively.

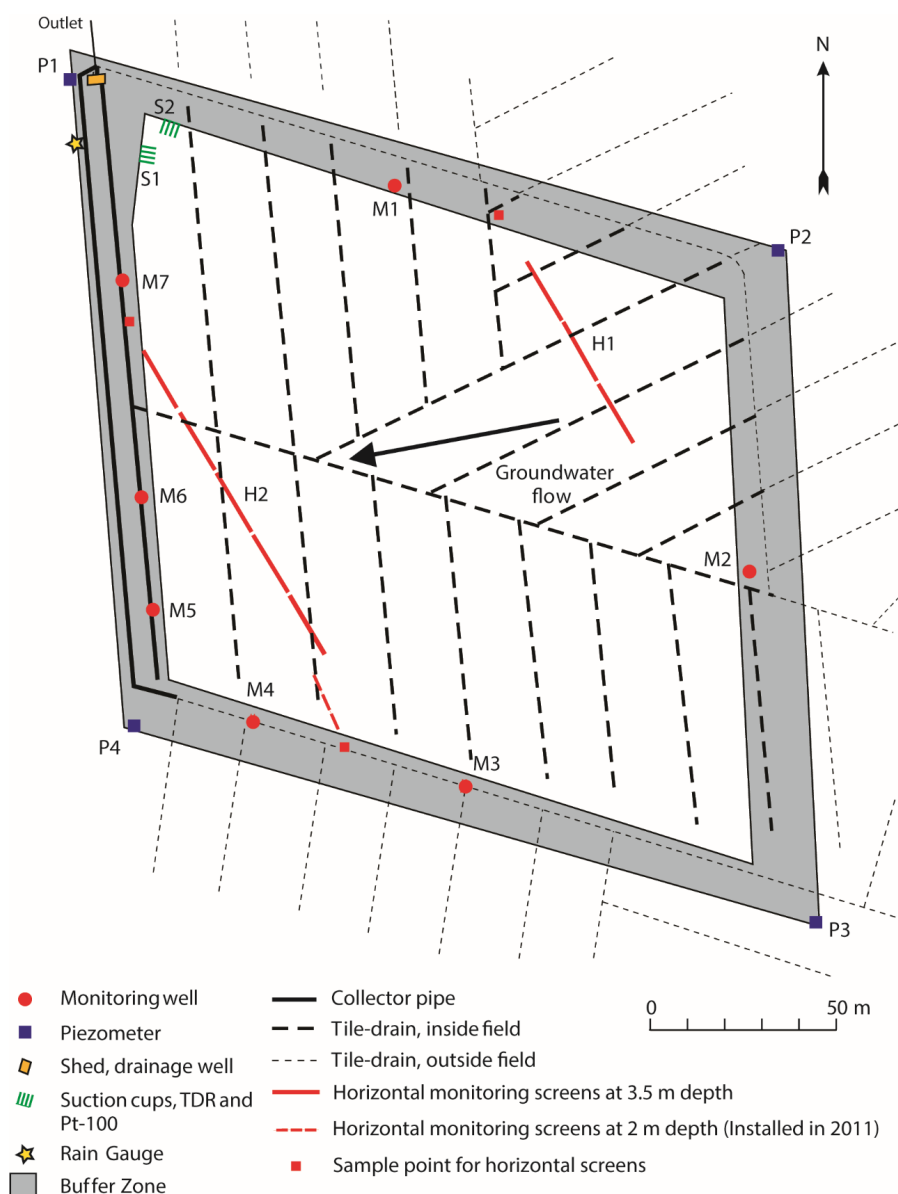
The dominant direction of groundwater flow is towards the west in the upper part of the aquifer (Figure 6.1). During the whole monitoring period 1999-2020, the groundwater table was located 1-3 mbgs. During fieldwork within a 5 m deep test pit dug nearby the field, it was observed that most of the water 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.

In March 2008, the monitoring programme was revised and optimised. Hereafter, water sampling at Faardrup is done monthly from well screen M4, M5, and H2, and half-yearly from well screen M6, H2.1, and H2.5. No sampling is done from wells M1-3, M7, and H1. Appendix 2 describes the sampling procedure in more detail.

Due to budget reduction at the initiation of 2010, only the two uppermost well screens below the groundwater table in downstream wells were included in the monitoring programme.

In September 2011, the monitoring system was extended with three horizontal screens (H3) 2 mbgs in the southwestern corner of the field (Figure 6.1). One of the screens was located just below the drain 1.2 mbgs. A brief description of the drilling and design of H3 is given in Appendix 8.

Due to errors in the programme of the new data logger installed at Faardrup on October 25, 2019, TDR-data were erroneous. As the old logger was uninstalled on October 22, 2019, no TDR-data were added to the plots after this date (Figure 6.2D-F).



**Figure 6.1.** Overview of the Faardrup 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 (arrow). Pesticide monitoring is conducted weekly from the tile drain system via a drainage well underneath the shed (during periods of continuous drainage), and monthly and half-yearly from selected vertical and horizontal monitoring screens as described in section 5.1.1 and Appendix 2. At S1 and S2, water content (via TDR) and soil temperature (via Pt100) is measured at four different depths as at the other PLAP-fields. Additionally, suction cups are installed to collect pore water from the variably saturated matrix for analysis of pH-independent compounds.

### 6.1.2 Agricultural management

Management practice at Faardrup during the 2018-2020 growing seasons is briefly summarised 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 [www.plap.dk](http://www.plap.dk).

On April 20, 2018, sugar beets (cv. Smart Jannika coated with imidacloprid and hymexazol – neither monitored) were sown. The beets emerged on May 7, 2018. The first spraying of weeds took place on May 29, 2018, where the following five pesticides were used: phenmedipham, ethofumesate,

foramsulfuron-methyl, metamitron, and thien carbazon-methyl. Phenmedipham, ethofumesate, and foramsulfuron-methyl were not monitored. Metamitron and its two degradation products desamino-metamitron and MTM-126-ATM were monitored. From thien carbazon-methyl, only the degradation product AE1394083 (BYH 18636-carboxylic acid) was monitored. As weeds at the time of the first spraying had developed well beyond the stage of cotyledon, the treatment was not sufficient and consequently, mechanical weeding was done on June 8. The second and third spraying of weeds was carried out on June 12 and 27, using metamitron, phenmedipham, and ethofumesate. At the spraying on June 27, the substance lambda-cyhalothrin (not monitored) was used against aphids. Harvest of the sugar beets took place on September 28, 2018, yielding 79.8 hkg ha<sup>-1</sup> of beet root (100% dry matter) and 32.0 hkg ha<sup>-1</sup> of beet top (leaves) (100 % dry matter).

On April 8, 2019, a spring barley (cv. IKWS Irina coated with prothioconazole and tebuconazole, 1,2,4-triazole monitored) was sown. On April 15, 2019, the barley emerged. Spraying of weeds with diflufenican was done on April 26, 2019 (not monitored). Applications of proquinazid against fungi were done on June 3 and 17, 2019 and its degradation products IN-MM671 and IN-MM991 were included in the monitoring. Harvest of the spring barley was done on August 12, 2019, where yields of grain were 82.0 hkg ha<sup>-1</sup> (85 % dry matter). The amount of straw shredded and left in the field was 35.5 hkg ha<sup>-1</sup> fresh weight.

Ploughing of the field was done on November 15, 2019. Spring wheat (cv. Cornette coated with fludioxonil, not monitored) was sown on March 26, 2020, and emerged on April 6. Spraying of fungi was done with proquinazid on April 20, 2020, and its degradation products IN-MM671 and IN-MM991 were continuously monitored. At harvest August 14, 2020, yields of grain were 56.5 hkg ha<sup>-1</sup> (85% of dry matter) and 43.1 hkg ha<sup>-1</sup> of straw was shredded (100% dry matter).

### **6.1.3 Model setup and calibration**

The one-dimensional numerical model MACRO (version 5.2 Larsbo *et al.*, 2005) represents the treated area of the Faardrup field covering the upper five meters of the soil profile, always including the groundwater table. The model is used to simulate water dynamics in the variably saturated zone during the full monitoring period May 1999–June 2020 and to establish an annual water balance.

Compared to the setup in Rosenbom *et al.* (2021), one year of climate and crop data was added to the MACRO setup. The setup was calibrated for the monitoring period May 1999-June 2004 and subsequently used to compare simulated water balance with monitoring results from July 2004 to June 2020. Daily time series of the groundwater table measured in piezometers located in the buffer zone, soil water content measured at three different depths (0.25, 0.6, and 1.1 mbgs) from the two profiles S1 and S2 (Figure 6.1), and the bromide concentration measured in the suction cups located 1 and 2 mbgs were all used in the calibration process. Data acquisition, model setup, and results related to the modelling are described in Barlebo *et al.* (2007).

## 6.2 Results and discussion

### 6.2.1 Soil water dynamics and water balance

Similar to the monitoring period 1999-June 2019, the model simulations are generally consistent with the measured water balance data (depth to groundwater table, drainage, and water saturation) for the recent hydraulic years July 2019-June 2020 indicating a good model description of the overall soil water dynamics in the variably saturated zone (Figure 6.2).

Like the previous years, the seasonal dynamics in groundwater levels (Figure 6.2B) of this year are captured by the model except for the level of decline during summer 2019, where the simulated groundwater level is underestimated by around two meters. Nevertheless, the approximate timing but not the magnitude of the measured decline in groundwater level from March to October 2019 is captured with the model. Due to heavy rain events in the middle of October resulting in simulation of high percolation ( $21 \text{ mm d}^{-1}$  in October 2019) through the soil to 1 m depth (Figure 6.2A), the simulated groundwater level rises abruptly to nearly 1 mbgs. This rise is delayed in the measurements. Not until December 2019, with around 1.5 months delay, does the model capture the manually measured groundwater level at the depth. This discrepancy seems to relate to the fact that the model did not simulate the full extent of the decline in the measured groundwater level. Thereby, the simulated rise in groundwater level started two meters above the measured groundwater table.

As was the case in the previous periods with drainage, the simulated drainage of the recent year is overestimated compared to measured drainage (Figure 6.2C, Table 6.1). This overestimation is because the model simulates groundwater levels above the drainage level at 1 mbgs with the heavy rain events in the middle of October 2019. Generally, the model is capturing the main trends in seasonality throughout the entire monitoring period.

The simulated water saturation in all three horizons from July 2019 to June 2020 was generally described by the model (Figure 6.2D, 6.2E, and 6.2F) even though the decline in water saturation during summer 2019 is underestimated by the model.

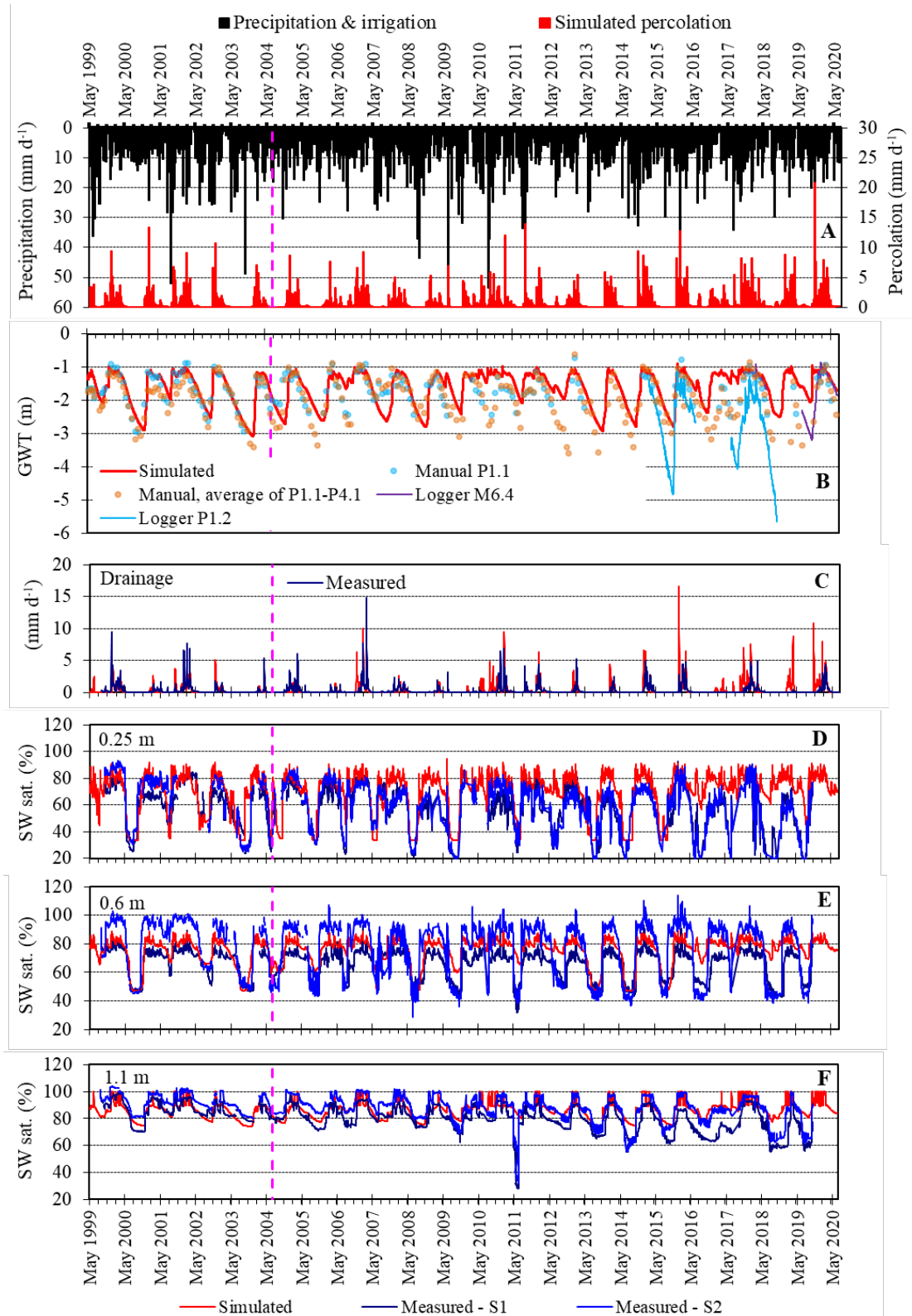
The resulting water balance for Faardrup covering the entire monitoring period of 21 years is shown in Table 6.1. Comparing the recent year with the total monitoring period of Faardrup, the measured precipitation ( $737 \text{ mm yr}^{-1}$ ) is above the average of  $690 \text{ mm yr}^{-1}$  and actual evapotranspiration ( $338 \text{ mm yr}^{-1}$ ) is below the average of  $446 \text{ mm yr}^{-1}$  and represents the minimum actual evapotranspiration for a hydrological year (July-June) in the whole monitoring period. Overview of the monthly precipitation of the six PLAP fields is presented in Appendix 4.

**Table 6.1.** Annual water balance for Faardrup (mm yr<sup>-1</sup>).

	Normal Precipitation <sup>1)</sup>	Precipitation <sup>2)</sup>	Actual Evapotranspiration <sup>3)</sup>	Measured drainage	Simulated drainage	Groundwater Recharge <sup>4)</sup>
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
01.07.17–30.06.18	626	789	378	169	287	242
01.07.18–30.06.19	626	667	386	5	144	277
01.07.19–30.06.20	626	737	338	33	273	366
Average	626	690	446	90	116	154

<sup>1)</sup> Normal values based on time series for 1961–1990 (Olesen, 1991). <sup>2)</sup> 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). Precipitation is corrected to the soil surface according to the method of Allerup and Madsen (1979). <sup>3)</sup> Actual evapotranspiration is estimated by the MACRO-model applying climate data including potential evapotranspiration

<sup>4)</sup> Groundwater recharge calculated as precipitation - actual evapotranspiration - measured drainage.



**Figure 6.2.** Soil water dynamics at Faardrup. Measured precipitation and simulated percolation 1 mbgs (A); simulated and measured groundwater table in m above the soil surface, 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 derives 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). No water saturation measurements from 23 October 2019 to 30 June 2020. The dashed vertical line indicates the beginning of the validation period (July 2004-June 2020).



### 6.2.2 Bromide leaching

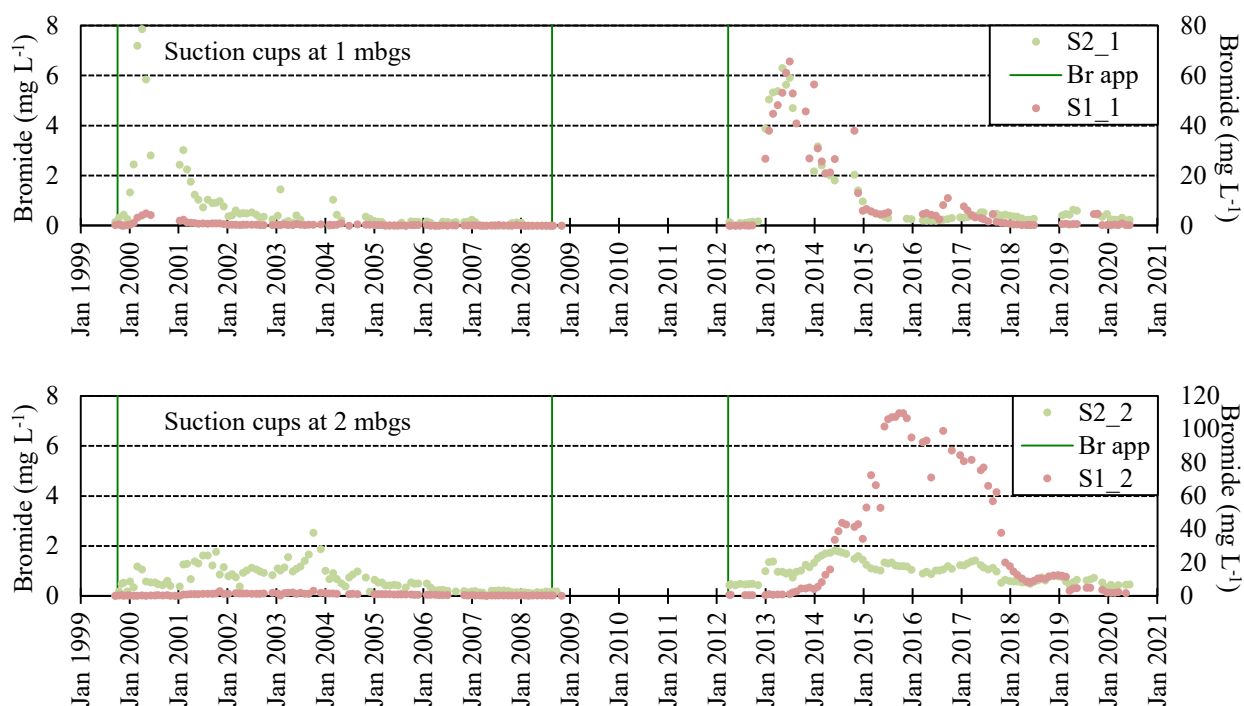
As mentioned in Chapter 1, it was decided for the present report to revisit and analyse all bromide data from the fields to possibly improve the fundamental understanding of the hydrogeology at the fields. In the analysis, the time until the maximum concentration of bromide reaches the different depths of water sampling is used to estimate transport times from the surface to the specific filter of interest and allow for comparison between depths. The time of maximum concentration is used in conjunction with the general pattern of breakthrough curves where possible. However, since the number of collected samples differs among the monitored well screens, continuous breakthrough curves are not equally available for all screens. Therefore, the time of maximum concentration is used to achieve transport time ranges within each monitoring depth regardless of the number of samples collected. These transport times are not to be conflated with average transport times. The average transport time (mean breakthrough time) represents when half of the applied mass has passed through the location of measurement which may not necessarily coincide with the breakthrough of maximum concentration. Consequently, bromide detections are generally occurring both before and after the time of the reported maximum concentration breakthroughs.

At Faardrup, bromide was applied three times (October 1999, August 2008, and April 2012) as 30 kg ha<sup>-1</sup> potassium bromide.

In the suction cups, samples were only collected with the October 1999 and April 2012 applications. In the suction cups located 1 mbgs, the maximum bromide concentrations after October 1999 and April 2012 applications are measured within 6-15 and 13-15 months (Figure 6.3).

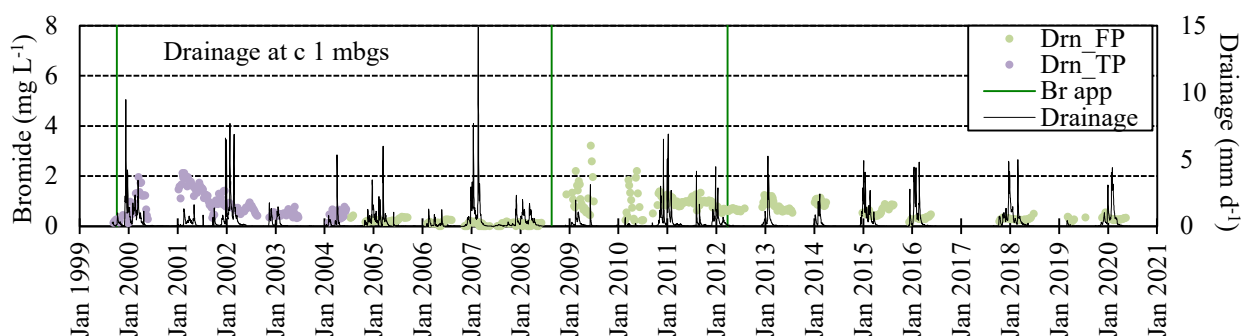
In the suction cups located 2 mbgs, the maximum bromide concentrations after October 1999 and April 2012 applications are measured within 48 and 26-43 months (Figure 6.3).

The time range in which the maximum concentrations are measured in the suction cups at 1 mbgs is overall 12 months after application, while at 2 mbgs, the average time for the breakthrough of maximum concentrations is much slower around 41 months (Figure 6.3). After the April 2012 application, it is noted that at suction cups in the S1 nest the measured concentrations are substantially higher compared to those measured at nest S2. Here, concentrations are up to a factor of 20 higher in nest S1 compared to S2. The reason for this is unknown and not readily explained. Despite the difference in concentration magnitude, the pattern of the measured breakthrough curve at 1 mbgs of S1 and S2 is similar. Generally, the pulse of breakthrough curves in the variably saturated zone is wider compared to those observed at the sandy fields (Figure 2.3 and 3.3) and coincident with those observed at the other clay-till fields (Fig 4.3 and 5.3).



**Figure 6.3.** Measured bromide concentrations at Faardrup. The measured concentrations in the S1 nest are substantially larger than those measured in the nest S2. Therefore, the S1 measurements are denoted on the right y-axis.

The samples representing drainage from around 1 mbgs are collected in a drain well collecting drainage from the entire field (Figure 6.1). Therefore, no ranges are reported for the drainage samples. The maximum concentrations in the drainage after October 1999, August 2008, and April 2012 applications are measured after 16, 10, and 9 months, respectively (Figure 6.4). Compared to the other clay-till fields (Silstrup and Estrup), where the maximum bromide concentrations are measured after the first drainage event following an application, Faardrup seems to differ. Here, maximum concentrations are not necessarily coincident with the first drainage event. Still, detections of bromide during drainage events are continuous throughout all monitoring periods.



**Figure 6.4.** Measured bromide concentrations in the groundwater at Faardrup. The suffix FP and TP refer to flow- and time proportional sampling, respectively, which are described in Kjær *et al.* (2004) and Appendix 2.

In the groundwater sampling, results are based on measured bromide concentrations in all wells except M2 (Figure 6.1). M2 is regarded as an upstream well. However, as bromide is measured in M2, although in low concentrations (generally  $< 0.5 \text{ mg L}^{-1}$ ), further analysis is needed to fully understand the groundwater flow dynamics across the field. Such analyses are under preparation for

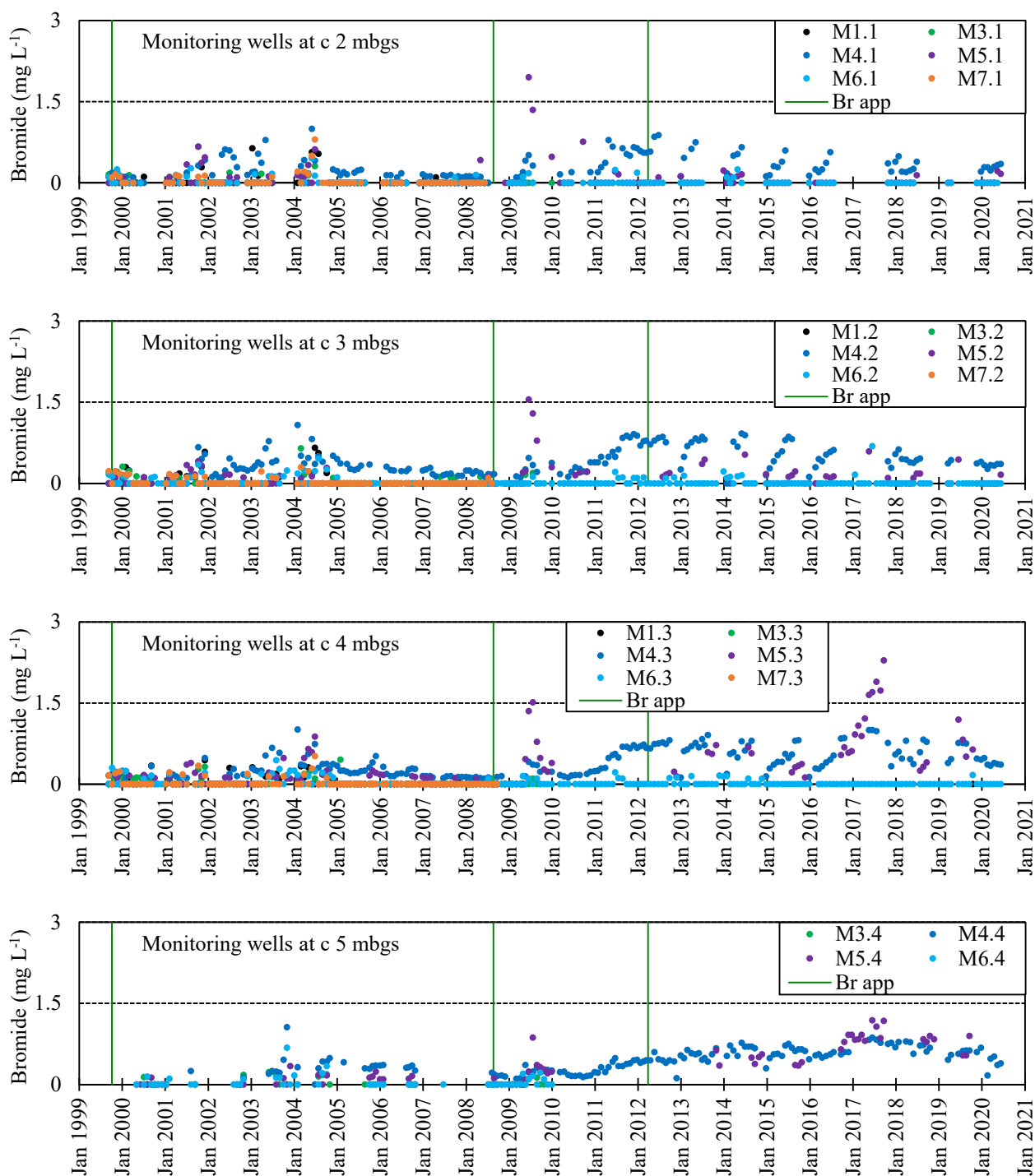
all the fields. However, for the sake of simplicity, in the present analysis, M2 is assumed not to be part of the flow field represented by the remaining wells.

In the groundwater samples from ~2 mbgs, the maximum bromide concentrations after October 1999, August 2008, and April 2012 applications are measured within 24-56, 10-34, and 3-25 months (Figure 6.5).

In the groundwater samples from ~3 mbgs, the maximum bromide concentrations after October 1999, August 2008, and April 2012 applications are measured within 24-57, 10-40, and 26-62 months (Figure 6.5).

In the groundwater samples from ~4 mbgs, the maximum bromide concentrations after October 1999, August 2008, and April 2012 applications are measured within 26-67, 11-42, and 61-90 months (Figure 6.5).

In the groundwater samples from ~5 mbgs, the maximum bromide concentrations in October 1999, August 2008, and April 2012 applications are measured within 49-55, 11-34, and 62-63 months (Figure 6.5).



**Figure 6.5.** Measured bromide concentrations in the groundwater at Faardrup.

The average breakthrough time for maximum bromide concentrations is calculated from the time of measured maximum concentration within each of the wells representing a particular depth. Thus, for the October 1999, August 2008, and April 2012 applications, the average time for maximum bromide concentrations reaching depths at around 2, 3, 4, and 5 mbgs are 31, 44, 51, and 47 months, respectively. However, especially in the case of Faardrup the average breakthrough time for the maximum concentration is difficult to use as a proxy for transport to the well screens. Hence, the

sampling is not sufficiently detailed to achieve a general pattern of the bromide breakthroughs within the different depths. But from the depth interval around 2 to 4 mbgs, the average breakthrough times for maximum concentrations reaching the screens are increasing with depth from around 12 months to 51 months. From the depth interval around 4 to 5 mbgs, the average breakthrough time for the maximum concentration decreases from 51 to 47 months. This could be an artifact of having samples from fewer screens at ~5 mbgs, where the number of screens used to compute the average maximum concentration times is based on the average of eight screens compared to an average of 12-13 screens at the other depths.

Compared to the other clay-till fields (Silstrup and Estrup), the average breakthrough time for maximum concentrations to reach the different monitoring depths is longer at Faardrup. In the variably saturated zone in Faardrup, the average breakthrough time for maximum concentration to reach 1 mbgs is one year compared to half a year or less at the other clay-till fields. Similarly, at 2 mbgs at Faardrup, the maximum concentrations arrive after more than three years compared to around two years at the other clay-till fields. In the groundwater monitoring wells at Faardrup, the average breakthrough time for maximum concentrations at depths of ~2-5 mbgs vary between ~3-4 years, whereas the average breakthrough time at similar depths at the other clay-till sites varies between ~1-2 years. Based on these results, it seems that there is a general pattern of slower transport of bromide at Faardrup compared to the other clay-till fields.

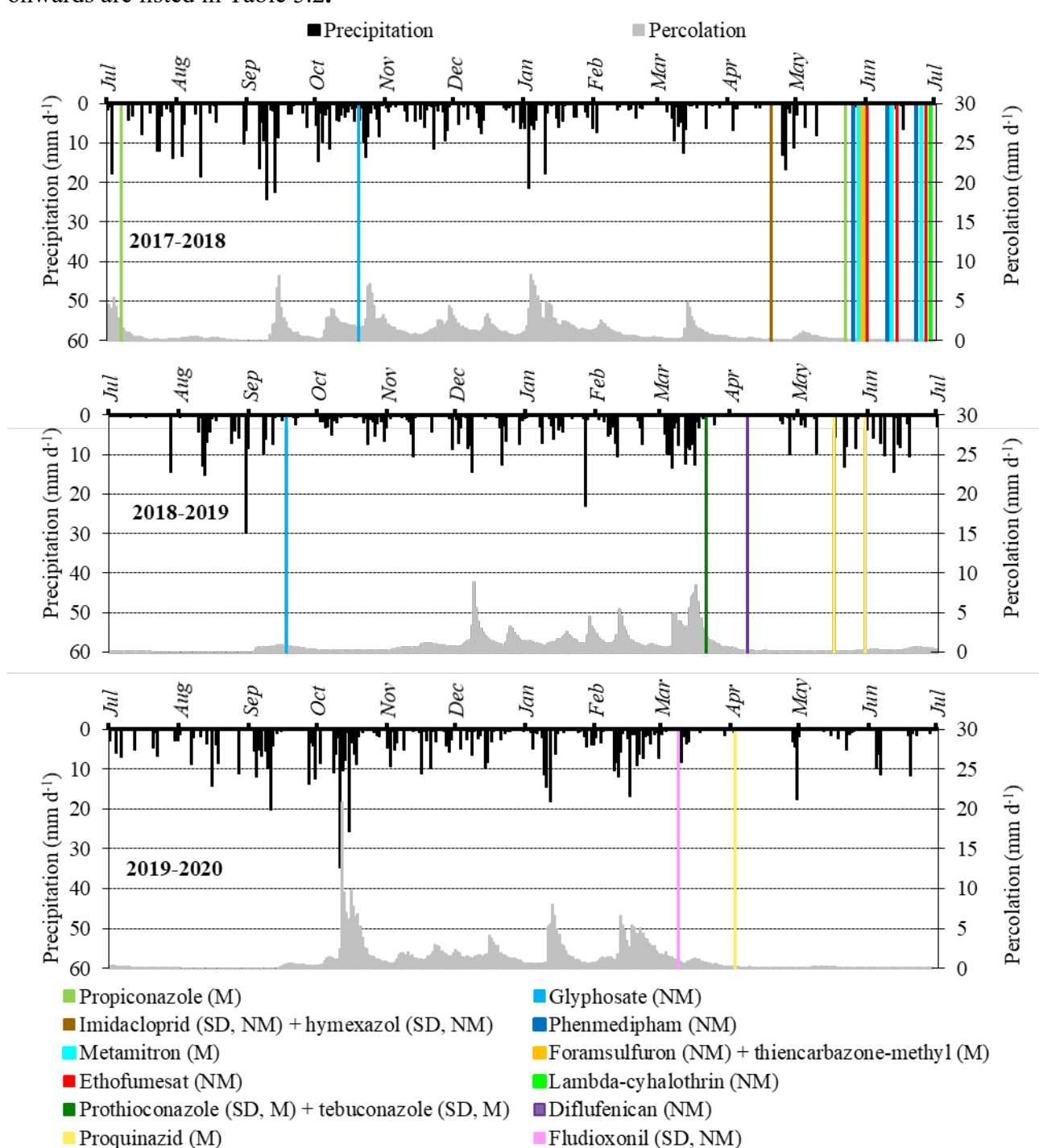
In general, the majority of the breakthroughs for maximum bromide concentrations reach the screens at ~2-5 mbgs within 3.5 years after application, but bromide is detected in concentrations similar to the maximum concentration levels up to several years after application. For all the sampled depths, it is noted that bromide concentrations above the detection limit are measured before and after the transport times representing maximum concentrations.

### **6.2.3 Pesticide leaching**

Monitoring at Faardrup began in September 1999. Pesticides and degradation products monitored from 1999 to 2020 are shown in Table 6.2 (2014-2020) and Table A7.5 in Appendix 7 (2000-2014). Several azole fungicides have had great focus since the beginning of the programme, but especially their common degradation product 1,2,4-triazole is intensively monitored since it was introduced in 2014. Monitoring of 1,2,4-triazole at Faardrup was started in 2014, why all pesticide applications from 2014 to 2020 is summarised in Table 6.2, and for 2018-2020 shown together with precipitation and simulated percolation in Figure 6.6. It is noted that the precipitation is corrected to the soil surface according to Allerup and Madsen (1979), whereas percolation (1 mbgs) refers to accumulated values as simulated with the MACRO model. Moreover, due to the very short monitoring period and therefore few data points, pesticides applied after 1 April 2020 are not evaluated in this chapter, although presented in Table 6.2 and Figure 6.6. As all seeds sown in PLAP are purchased from a commercial agribusiness supplier, seeds were most likely coated with seed dressing, containing one or more pesticides included for testing in PLAP. Such information was, however, first registered in PLAP in 2017. Seed dressings used from 2017 and onwards are also listed in Table 6.2.

For all pesticides and degradation products (except 1,2,4-triazole where the full monitoring period is evaluated), this chapter evaluates the monitoring from 2018 to July 2020 at Faardrup. The leaching risk of pesticides evaluated before this period is available in previous monitoring reports (see <http://www.plap.dk/>). All seeds sown in PLAP are purchased from a commercial agribusiness supplier, seeds were likely coated with seed dressing containing pesticides included for testing in PLAP. Such

information was, however, not registered in PLAP until 2017. Seed dressings used from 2017 and onwards are listed in Table 5.2.



**Figure 6.6.** Application of pesticides at Faardrup in the period 2017-2020. Pesticides are marked (M) if the pesticide and/or its degradation products are included in the monitoring programme, or (NM) if they are not monitored. Substances applied as seed dressing are marked SD. Measured precipitation is given on the primary axis and simulated percolation 1 mbgs on the secondary axis.

Due to too high costs on analyses, the monitoring of the degradation product 1,2,4-triazole originating from azole fungicides (e.g. tebuconazole and prothioconazole) was temporarily suspended from September 2015 until May 2016. In addition, the economic constraints were also the reason that no other new compounds were added to the monitoring at Faardrup until May 2016.

**Table 6.2.** Pesticides analysed at Faardrup. Precipitation (precip.) and percolation (percol.) are accumulated within the first year (Y 1<sup>st</sup>), and month (M 1<sup>st</sup>) after application. C<sub>mean</sub> is average leachate concentration at 1 mbgs. See Appendix 2 for the calculation method and Appendix 7 (Table A7.5) for previous applications of pesticides.

Crop– Year of harvest	Applied Product	Analysed Pesticide (P) / Degradation product (M)	Application date	End of Monitoring	Y 1 <sup>st</sup> Precip. (mm)	Y 1 <sup>st</sup> Percol. (mm)	M 1 <sup>st</sup> Precip. (mm)	M 1 <sup>st</sup> Percol. (mm)	C <sub>mean</sub> (µg L <sup>-1</sup> )
<b>Winter wheat 2014</b>	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)	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
<b>Spring Barley 2016</b>	Starane 180S Fluroxypyr-meptyl (P)	Fluroxypyr methoxy-pyridine(M)	May 15	May 18	785	286	46	0	<0.01
		Fluroxypyr pyrdinol(M)	May 15	May 18	785	286	46	0	<0.01
	Bumper 25 EC Propiconazole(P) <sup>1)</sup>	1,2,4-triazole(M)	Jun 16	Jun 20*	621	204	129	23	x
<b>Spring Barley 2017</b> SD: Fungazil A (Imazalil)	Zypar Florasulam(P)	TSA (M)	Jun 17	Mar 19	1176	271	110	0	<0.01
	Halauxifen-methyl (P)	X-757 (M)	Jun 17	Mar 19	1176	271	110	0	<0.01
	Bumper 25 EC Propiconazole(P) <sup>2)</sup>	1,2,4-triazole (M)	Jun 17	Jun 20*	1176	271	110	0	x
<b>Sugar Beet 2018</b> SD: Gaucho WS70 (Imidacloprid) + Tachigaren WP (Hymexazol)	Conviso One Thiencarbazone-methyl (P)	AE1394083 (M)	May 18	Mar 20	607	234	31	0	<0.01
	Foramsulfuron (P)								
	Goltix SC 700 Metamitron (P)	Metamitron (P)	May 18	Mar 20	607	234	31	0	<0.01
		Desamino-metamitron (M)	May 18	Mar 20	607	234	31	0	<0.01
<b>Spring barley 2019</b> SD: Redigo Pro 170 FS (prothioconazole and tebuconazole)	Talius Proquinazid (P) <sup>3)</sup>	IN-MM671 (M)	Jun 19	Jun 20*	758	407	69	10	<0.01
		IN-MM991 (M)	Jun 19	Jun 20*	758	407	69	10	<0.01
<b>Spring wheat 2020</b> SD: Celest Formula M (Fludioxinil)	Talius Proquinazid (P)	IN-MM671 (M)	Apr 20	Jun 20*	-	-	32	3	-
		IN-MM991 (M)	Apr 20	Jun 20*	-	-	32	3	-

Systematic chemical nomenclature for the analysed pesticides is given in Appendix 1. SD = Seed dressing.

<sup>1)</sup> Propiconazole only applied in half of the maximum allowed dose.

<sup>2)</sup> Propiconazole applied twice 19 June and 7 July.

<sup>3)</sup> Proquinazid applied twice on 3 and 17 June.

\*Monitoring continues the following year.

\*\*Monitoring started in May 2014.

x Due to a high background content of 1,2,4-triazole, the results of the analysis cannot be linked directly to the specific application, why C<sub>mean</sub> is not presented.

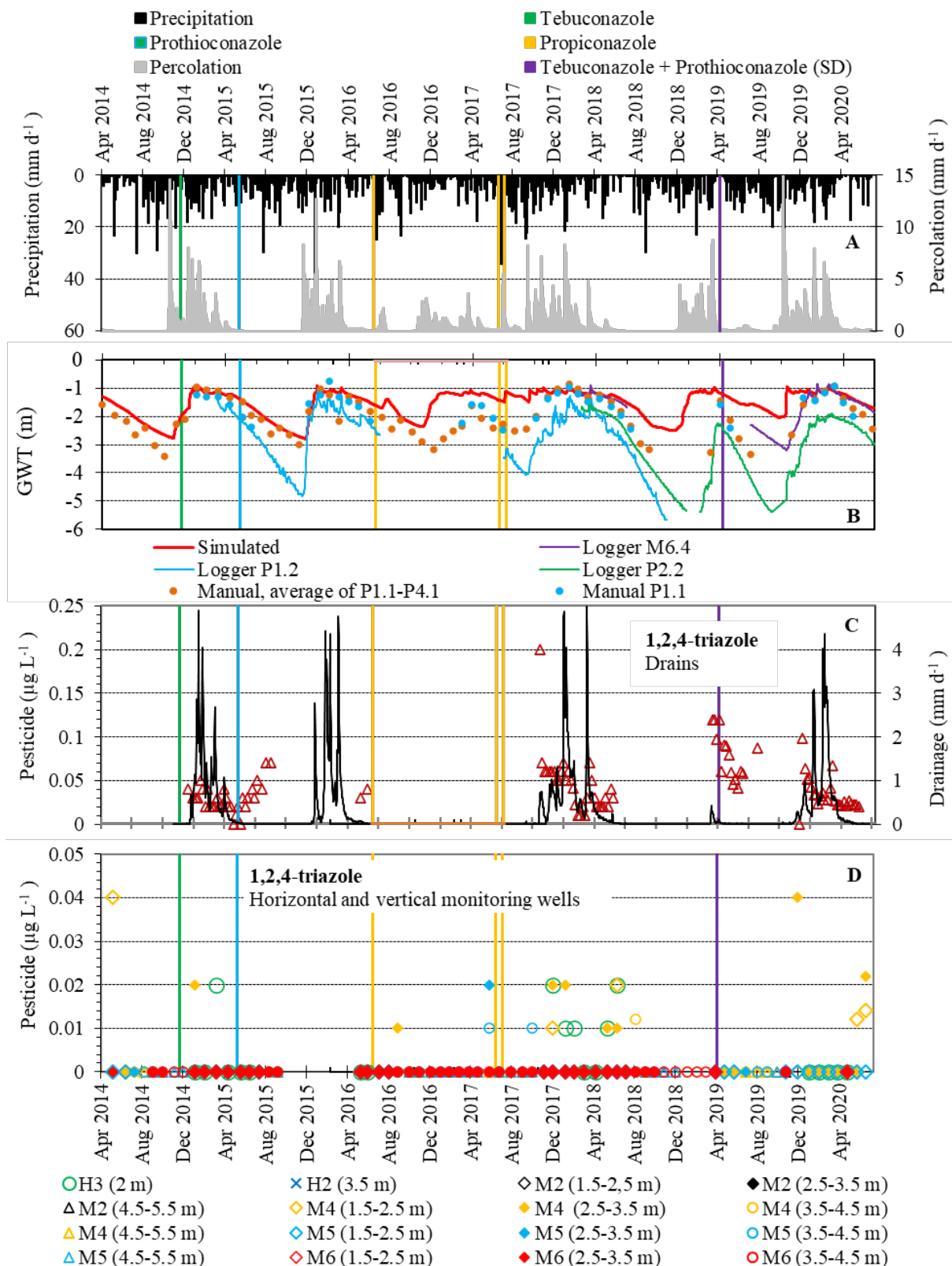
## Azole fungicides and 1,2,4-triazole monitoring

Tebuconazole was applied on winter wheat in November 2014 to test the leaching potential of its degradation product 1,2,4-triazole. 1,2,4-triazole monitoring started half a year before in May 2014 and has been ongoing (except between August 2015 and May 2016 given economic constraints). Thus, the 1,2,4-triazole monitoring results are reported from May 2014 to July 2020 (Figure 6.7). However, since the use of azole-fungicides before 2014 may contribute to 1,2,4-triazole leaching, it is noted that the azoles were sprayed on four occasions in Faardrup before 2014, most recent was

tebuconazole in November 2007. The former three azole-sprays comprised propiconazole twice, and epoxiconazole once, respectively (see Table 3.2 and Appendix 3 in previous reports). In addition to the previous azole sprays, the use of azole-coated seeds may also contribute to the azole soil content and thus, 1,2,4-triazole leaching (Albers *et al.*, 2022). The use of azole-coated seeds was registered from 2017, but coated seeds were most likely used before this date. The registered use of azole-coated seeds is presented together with the azole sprays in Figure 6.7.

It is noted that from May to December 2014 there was no drainage and consequently no collection of drainage samples for measuring 1,2,4-triazole background concentrations before the tebuconazole application in November 2014. Before the tebuconazole application, no detections of 1,2,4-triazole were made in the groundwater, except in one sample. This sample was collected from the upper screen in the vertical well M4 (depth 1.5-2.5 m), and the concentration of 1,2,4-triazole was the highest concentration measured in the groundwater ( $0.04 \mu\text{g L}^{-1}$ ; Figure 6.7D). In May 2015, another azole fungicide, prothioconazole, was applied to spring barley to evaluate its contribution to 1,2,4-triazole under field conditions. Prothioconazole is specified in the EFSA conclusion (2007) not to form major amounts of 1,2,4-triazole in soil. Following the May 2015 application, an increase in the concentration of 1,2,4-triazole was detected in samples collected from drainage (Figure 6.7C). It is, however, uncertain whether the increase is caused by leaching of 1,2,4-triazole from the May 2015 application, or a consequence of continuous production and presence of 1,2,4-triazole from accumulated azoles in the plough layer coupled to relatively low drainage volume. Low drainage volume could result in a concentration build-up of 1,2,4-triazole in the samples. This theory is supported by the general pattern in drainage concentrations of 1,2,4-triazole, where the highest concentrations are measured in periods with low drainage flow, and the fact that 1,2,4-triazole is detected in the uppermost groundwater before the first 2014 application. As previously mentioned, no sampling was made from August 2015 to May 2016, which makes it difficult to evaluate if an increase in drainage concentration occurs after the May 2015 application. After resuming the monitoring in May 2016, two drainage samples were collected before the end of the drainage period. Both samples contained 1,2,4-triazole. Drainage was initiated again in late autumn 2017 approximately five months after the split application with propiconazole in June 2017, and  $0.2 \mu\text{g L}^{-1}$  1,2,4-triazole was detected in the first collected drainage sample. Hereafter, the concentration level in the drainage samples declines. Between this drainage event, terminating in May 2018, and a minor drainage event starting in March 2019, no water was running in the drains. The two drainage samples collected five days prior to and two days after sowing with azole coated seeds in April 2019, both contained 1,2,4-triazole ( $0.097 \mu\text{g L}^{-1}$  and  $0.12 \mu\text{g L}^{-1}$ , respectively). The fact that 1,2,4-triazole is detected in drainage in a continuous fluctuating pattern, indicates a surface-near source wherefrom 1,2,4-triazole is formed. Hitherto, nearly all drainage samples (103 of 106 samples, that is 97%) showed detections of 1,2,4-triazole, whereof four (4%) had concentrations  $> 0.1 \mu\text{g L}^{-1}$  (Figure 6.7C).





**Figure 6.7.** 1,2,4-triazole monitoring at Faardrup. Precipitation and simulated percolation 1 mbgs (A); measured and simulated groundwater level (B); concentration of 1,2,4-triazole in the variably saturated zone (C) and saturated zone (D). It is noted that M2 is regarded as an upstream monitoring well. The coloured vertical lines indicate the date of pesticide application. SD is pesticides applied as seed dressing. Seed dressings used before 2017 were not registered. Note that no samples were analysed for 1,2,4-triazole between August 2015 and May 2016 given economic constraints.

In the vertical monitoring wells, 18 of 313 (6%) groundwater samples contained 1,2,4-triazole concentrations  $\leq 0.1 \mu\text{g L}^{-1}$ . In the horizontal monitoring wells, 17 of 93 (18%) groundwater samples contained 1,2,4-triazole concentrations  $\leq 0.1 \mu\text{g L}^{-1}$ . Note that, since all detected concentrations are  $< 0.05 \mu\text{g L}^{-1}$  in groundwater from both the vertical monitoring wells and the horizontal wells, measured concentrations are plotted in the same figure (Figure 6.7D). In periods without drainage, 1,2,4-triazole is still detected in groundwater samples (Figure 6.7B and 6.7C). When the groundwater table was lower than the screen depth around 4.5 mbgs, no sampling was done. As 1,2,4-triazole is detected in 97% of the drainage samples and present in the groundwater in the upper-most screen (depth 1.5-2.5 m) of well M4, located downstream (Figure 6.1), before the 2014 tebuconazole application, the source for 1,2,4-triazole leaching is likely continuous degradation of azoles accumulated in the plough layer from previous and present applications. Monitoring of 1,2,4-triazole is continued.

#### **Metamitron and the degradation products, metamitron-desamino, MTM-126-ATM, and thiencarbazone-methyl degradation product, AE1394083**

The two herbicides metamitron and thiencarbazone-methyl were applied together on sugar beets in May 2018. Hereafter, metamitron itself plus its two degradation products, metamitron-desamino and MTM-126-ATM, as well as the thiencarbazone-methyl degradation product AE1394083 (BYH 18636-carboxylic acid) were included in the monitoring programme. Since May 2018, none of the compounds were found in any of the 36 drainage samples, 90 vertical well samples, or 22 horizontal well samples collected. As the analytical method was not ready, when the monitoring of AE1394083 was planned to start, samples were stored ( $-20^{\circ}\text{C}$ ) until ready. As the stability of the compound, when frozen for several months, is currently unknown, the presence of false-negative results may be possible. Results on AE1394083 from the period of May 2018 until January 2019 should therefore be regarded as tentative (Chapter 8). Monitoring ended in April 2020, but the influence of freezing on the quality of analyses is currently investigated.

#### **Proquinazid degradation products, IN-MM671 and IN-MM991**

The fungicide proquinazid was applied on spring barley in June 2019 and its two degradation products IN-MM671 and IN-MM991 were included in the monitoring programme. None of the two degradation products were found in any of the 39 drainage samples, 59 vertical well samples, and 18 horizontal well samples. As the analytical methods were not ready, when the monitoring of IN-MM671 and IN-MM991 was planned to start, samples were stored ( $-20^{\circ}\text{C}$ ) until ready. As the stability of the compounds, when frozen for several months, is currently unknown, the presence of false-negative results may be possible. Results on IN-MM671 and IN-MM991 from the period of April 2019 until September 2019 should therefore be regarded as tentative (Chapter 8). Monitoring continues, and the influence of freezing on the quality of analyses is currently investigated.

## 7 Pesticide leaching at Lund

### 7.1 Materials and methods

#### 7.1.1 Field description and monitoring design

Lund is located in the southern part of the Stevns peninsula in the eastern part of Zealand 500 m west of the village Lund (Figure 7.1). The entire area is a glacial till plain formed during the Weichselian glaciation, and the topographic map shows that mega-lineations are trending southeast-northwest across the landscape. These are formed subglacially and indicate the ice movement direction (Houmark-Nielsen, 2011). The soil types in the area are classified as clayey till overlying bryozoan limestone of Danien age. The field is located south of the road Lundeledsvej, approximately 500 m north of the shoreline at an elevation of 7-10 m a.s.l. It covers an area of 2.76 ha, of which the cultivated area makes up 2.1 ha (Figure 7.1). Here, the total thickness of clay till is approximately 8-10 m. Based on two profiles excavated in the buffer zone bordering the field the soil was classified as Anthric Luvisol and Anthric Stagnic Luvisol. The topsoil is characterised as sandy loam with a clay content of 13.7–16.7% and organic carbon content of 0.9–1.7%.

The monitoring design for Lund is, as described in Haarder *et al.* (2021), similar to the other tile-drained clay till fields (Silstrup, Estrup, and Faardrup) that are described in detail in Lindhardt *et al.* (2001). Unlike the other clay till fields, no horizontal wells are installed yet, as this requires knowledge of the groundwater fluctuation to assess the optimal installation depths of such wells.

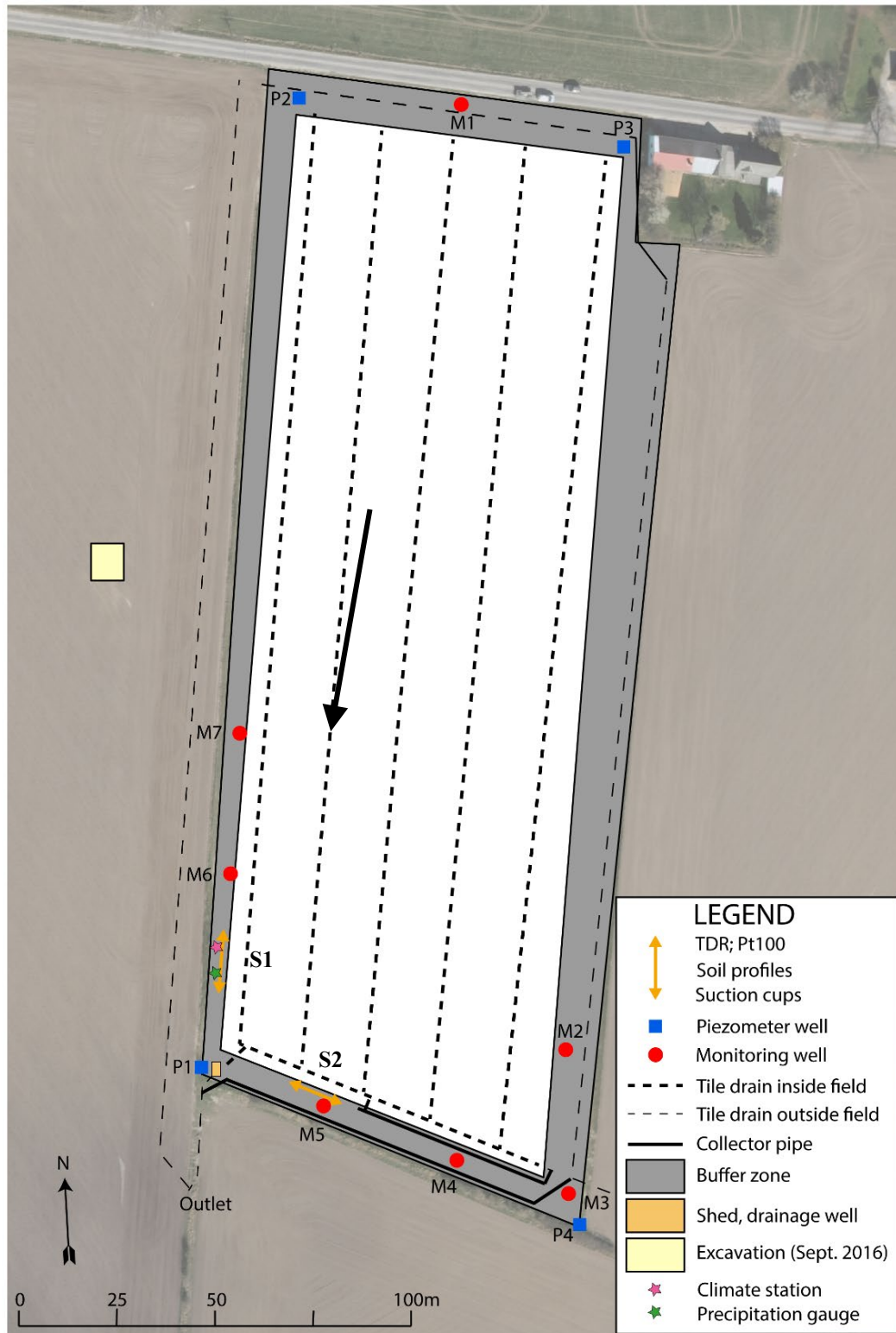
The monitoring period was initiated at Lund in April 2017. However, due to initial installation errors and lag in device installation, not all measurements were initiated. For example, precipitation measurements were obtained from February 25, 2018.

As no existing climate station was found in the vicinity of the field, an automatic climate station from Campbell Scientific (UK) was installed (Haarder *et al.*, 2021). The climate station ensures local measurements of precipitation, barometric pressure, global radiation, air temperature, relative humidity, wind speed, and direction. The precipitation measured with the Pluvio2 rain gauge (OTT Hydromet, Germany) was found to generally overestimate the precipitation when compared with the MACRO modelling for Lund. The overestimation was confirmed by comparison to i) precipitation obtained from the 10 km x 10 km grid (no. 10570) of Denmark (provided by The Danish Meteorological Institute, DMI), ii) Flakkebjerg, situated 60 km from Lund (provided by DMI), and iii) Tokkerup, situated 11 km from Lund (provided by Aarhus University, AU). It was not possible to correct the precipitation measured locally at Lund and therefore precipitation data from July 1, 2018 to June 30, 2020 were obtained from a research project at Tokkerup conducted by The Department of Agroecology, AU. It is noted that the Tokkerup rain gauge only measures liquid precipitation, and it is located further away from the sea than Lund. In the modelling, the precipitation data applied from February 25, to June 30, 2018 is the locally measured precipitation and can potentially be overestimated. Similarly, the precipitation data applied from July 1, 2018 to June 30, 2020 is from Tokkerup and can potentially be underestimated since these data do not account for periods with snow or the closeness to the sea. However, whether there are problems related to over/underestimation of applied precipitation in the modelling needs further evaluation.

Groundwater level monitoring was initiated in April 2017 in both piezometers, P, and monitoring wells, M (Figure 7.1). These data indicate that the screens in multiple wells do not respond hydraulically to seasonal fluctuations in the groundwater table. However, after pumping of the wells before sampling in October 2017 some well screens (M1.3, M3.2, M3.3, M4.3, and M6.2) started showing hydraulic response with fluctuations from ~4.9 mbgs to the drainage depth of ~1.1 mbgs (Figure 7.2B). To improve the hydraulic response to groundwater fluctuations in the remaining well screens, these well screens were pumped clean up to six times in the autumn of 2019. It seems that the cleaning improved the hydraulic response in P1.1 (Figure 7.2B), which clogged during October 2018 showing a groundwater table decline of ~four meters. An additional investigation was initiated to examine hydraulic contact between the hydraulically active system in selected screens. In-situ loggers were installed, and continuous measurements of the groundwater fluctuations are collected. The results will be analysed for the selection of screens to be included in future monitoring. Pesticide monitoring data for this field should thus, be interpreted with caution.

During the period June 2018-April 2019, wells M1, M4, M5, and M6 were sampled monthly, with additional samples taken half-yearly from wells M2, M3, and M7. From May 2019- to July 2020 wells M1, M4 and M5 were sampled monthly, with additional samples taken half-yearly from well M6. See Appendix 2 for details.

Monitoring of the drainage was initiated in July 2017 via a Thomson weir 30 V-notch. In March 2018, in a period of snowmelt, free flow of the drainage was obstructed, and water was retained in the drainage monitoring well thereby causing erroneous measurements. Hereafter, a pump was installed in the well preventing drainage water from damming up at the downstream side of the V-notch. The V-notch was repaired in June 2019, since it was not properly installed. Consequently, the measurement of the high-intensity drainage may have been underestimated until June 2019. Sampling of drainage for pesticide analyses was started in November 2017.



**Figure 7.1.** Overview of the Lund 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 (arrow). Pesticide monitoring is conducted weekly from the tile drain system via a drainage well located underneath the shed (during periods of continuous drainage) and monthly from selected vertical monitoring well screens as described in section 7.1.1 and in Appendix 2. At S1 and S2, water content (via TDR) and soil temperature (via Pt100) is measured at four different depths. Additionally, suction cups are installed to collect pore water from the variably saturated matrix for analysis of pH-independent compounds.

The water content in 1.1 m depth at S1 was monitored since September 1, 2017, whereas the TDR measurements from the three depths (0.25 m, 0.60 m, and 1.1 m depth) at S2 and the two other depths (0.25 m and 0.60 m depth) at S1 were initiated June 30, 2018.

### 7.1.2 *Agricultural management*

Management practice at Lund during the 2018-2020 growing seasons is briefly summarised below and detailed in Appendix 3 (Table A3.6).

Ploughing of the field was done on January 4, 2018. Spring barley (cv. Quench coated with prothioconazole and tebuconazole) was sown on April 20, 2018. A mixture of the fungicide prothioconazole and the herbicides halauxifen-methyl and florasulam was sprayed in the field on May 30, 2018. The degradation products, TSA from florasulam and 1,2,4-triazole from prothioconazole, were included in the monitoring. Second spraying with prothioconazole against fungi was done on June 12, 2018. The spring barley was harvested on August 6, yielding 55.5 hkg ha<sup>-1</sup> of grain (85% dry matter) and 22.4 hkg ha<sup>-1</sup> of straw (100 % dry matter).

The field was ploughed on September 18, 2018 and sown with winter barley (cv. Memento coated with prothioconazole and tebuconazole) the following day. On September 28, 2018, the winter barley had emerged. Diflufenican together with prosulfocarb was used against weeds November 8, 2018, neither were monitored. The herbicide fluroxypyr was applied on May 9, 2019 and was not monitored. On May 11, 2019, the field was sprayed with halauxifen-methyl and florasulam. The degradation product TSA from florasulam was continuously monitored (since May 2018) and degradation product X-729 from halauxifen-methyl was included in the monitoring. Harvest of winter barley was done July 13, 2019 where the grain yield was 66.4 hkg ha<sup>-1</sup> (85% dry matter) and that of straw 35.9 hkg ha<sup>-1</sup> (fresh weight).

On August 25, 2019, the field was power harrowed and subsequently sown with winter rape (cv. InVigor 1030). On August 28, glyphosate and clomazone were used against weeds but not included in the monitoring programme. The winter rape emerged on August 30. On December 17, the substances propyzamid, picloram, and halauxifen-methyl were used against weeds. The degradation product from halauxifen-methyl, X-729 was continuously monitored. Propyzamid and the two degradation products, RH-24644 and RH-24580, and picloram were included in the monitoring. Harvest of the winter rape was done August 1, 2020 yielding 49.2 hkg ha<sup>-1</sup> of seeds (fresh weight). The straw yield was not measured before being shredded at harvest.

### 7.1.3 *Model setup and calibration*

The one-dimensional numerical model MACRO (version 5.2 Larsbo *et al.*, 2005) represents the treated area of the Lund field covering the upper five meters of the soil profile, always including the groundwater table. The model is used to simulate water dynamics in the variably saturated zone from 25 February 2018- 30 June 2020 and to establish an annual water balance. The model was set up based on the hydrogeological description of the field presented in Haarder *et al.* (2021), climate data (daily values of corrected precipitation and Makkink's evapotranspiration estimates added with maximum and minimum air temperature), and the registered crop development (Appendix 3). To calibrate the model, the following time series were used: observed groundwater table measured in selected wells and piezometers installed in the buffer zone, water content measured at three depths (0.25, 0.6, and 1.1 mbgs) from the two profiles S1 and S2 (Figure 7.1), and measured drainage (Figure

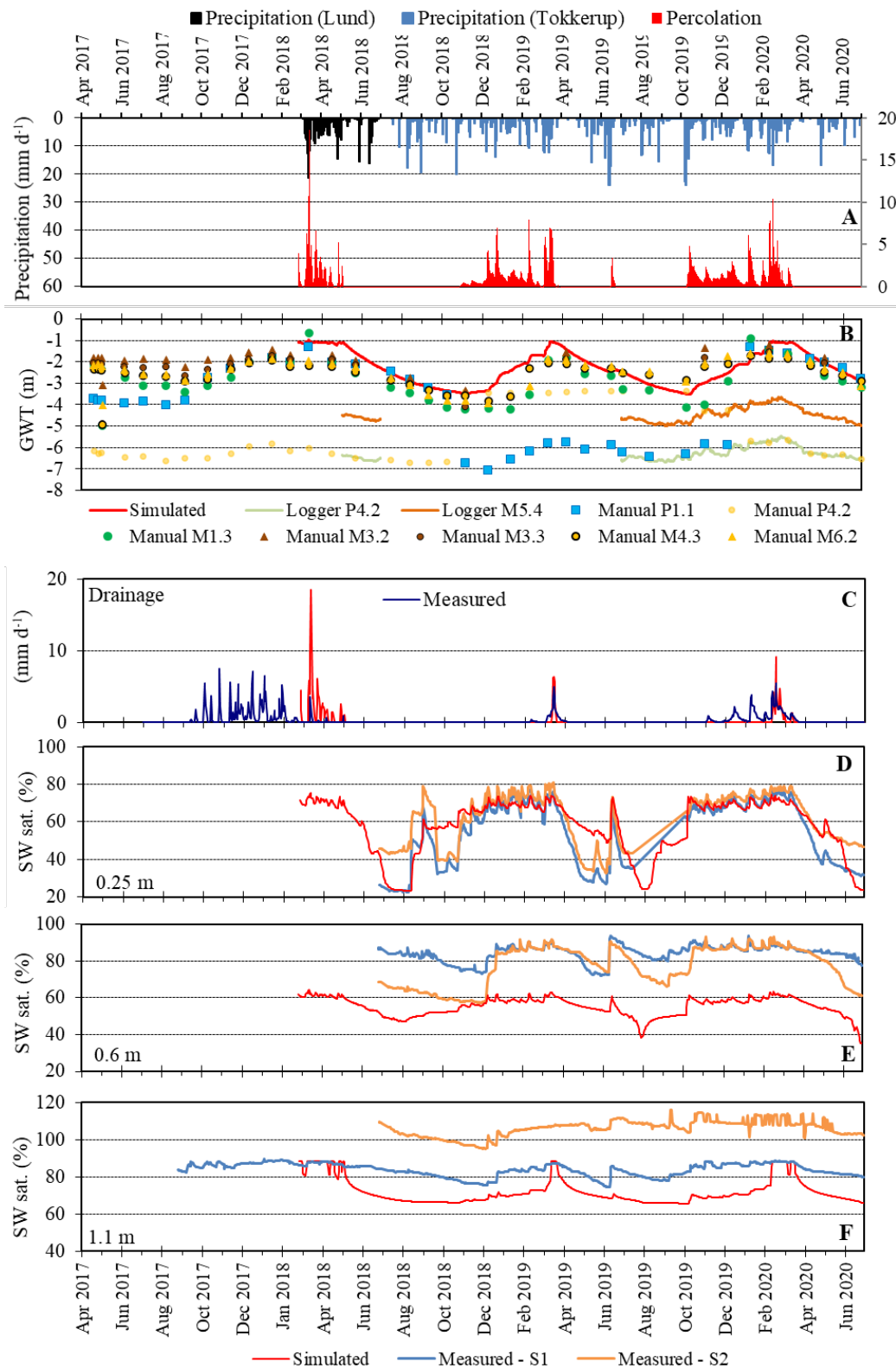
7.2). There seemed to be some inconsistencies between measured and simulated groundwater levels when applying precipitation measured at the Lund field from February 25, 2018 to June 30, 2020, and therefore precipitation data from Tokkerup was applied in this period (see Chapter 7.1.1).

## **7.2 Results and discussion**

### **7.2.1 Soil water dynamics and water balance**

Groundwater levels measured manually in selected well screens of different depths at Lund showed a groundwater table fluctuating between 0.5 - 4.5 m depth (Figure 7.2B), which supports drainage occurring when the groundwater table is at tile drain depth (1.1 m depth; Figure 7.2C). However, Figure 7.2B also shows measurements of the groundwater level in other well screens like P4.2 (measured both manually and with a logger) and M5.4 (measured with a logger) being up to 4 m below this level. This is also the case for P1.1 (measured manually) from October 2018 to December 2019. Here, the sudden offset in the groundwater table in October 2018, possibly caused by clogging of the well screen, disappeared after the well screen was flushed (September 10, 2019, October 8, 10 and 17, 2019, and November 5, 2019) in the autumn 2019. P4.2 and M5.4 were also flushed at the time of P1.1 but the measured groundwater levels obtained from these two well screens were still offset. The reason for these offsets and damping in amplitude is not readily explained but will be investigated further.

The model simulation is generally consistent with the manually measured groundwater level as presented in Figure 7.2B. Thus, for these monitoring wells, the seasonal dynamics in terms of highs/lows in measured groundwater levels are captured well with the model (Figure 7.2B). In general, the simulated groundwater table also compares with P1.1 except for the period October 2018 to December 2019, where the mentioned offset of approximately 4 m appears in the measurements. Such an offset is generally measured in M5.4 and P4.2 (Figure 7.2B), indicating minimal contact between the well screen and the hydraulically active soil system, as also inferred by the reduced amplitude.



**Figure 7.2.** Soil water dynamics at Lund: Measured precipitation and simulated percolation 1 mbgs (A); simulated and measured groundwater table in m above the soil surface, GWT (B); simulated and measured drainage (C); and simulated and measured soil saturation (SW sat.) at three different soil depths (D, E, and F). The measured data in B derives from piezometers (P) and wells (M) located in the buffer zone. The measured data in D, E, and F were derived from TDR probes installed at S1 and S2 (Figure 7.1).



The simulated drainage corresponded with the measured drainage except for spring of 2018, maybe because the overestimated measured precipitation from the Lund field is applied. Also, in autumn 2019, the initiation of simulated drainage was delayed compared to the measured. Here, the precipitation from Tokkerup was applied, but this precipitation might be underestimated compared to the actual precipitation at Lund (Figure 7.2C).

For the water saturation, the dynamics are in general captured by the model in the upper 0.60 m of the clayey till. However, only in the depth of 0.25 m, the measured saturation is approximated by the simulated water saturation (Figure 7.2D). In 0.6 mbgs, the simulated water saturation is underestimated, while still capturing the measured dynamics (Figure 7.2E). In 1.1 mbgs, the model does not capture the dynamic or the measured water saturation (Figure 7.2F). This could be due to the higher uncertainty in the measured water saturation as the soil matrix could be closer to saturation.

The water balance for Lund from July 2018 to June 2020 is shown in Table 7.1. The measured precipitation between July 2019 - June 2020 (588 mm yr<sup>-1</sup>) is 14 mm lower than the previous period (July 2018 - June 2019) and estimated actual evapotranspiration (518 mm yr<sup>-1</sup>) is 52 mm higher (Table 7.1). This should leave less water to percolate to drainage or groundwater in the recent period (July 2019 - June 2020). Following the model predictions, the contribution to drainage should be 56 mm yr<sup>-1</sup> this year leaving 14 mm yr<sup>-1</sup> to percolate to the groundwater. The measured drainage being 131 mm yr<sup>-1</sup> leaves a deficit of water percolating to the groundwater of 61 mm yr<sup>-1</sup>. This estimated deficit could be an indication of the applied (in the model) precipitation from Tokkerup underrepresenting the actual yearly precipitation at the field. Overview of the monthly precipitation of the six PLAP fields is presented in Appendix 4.

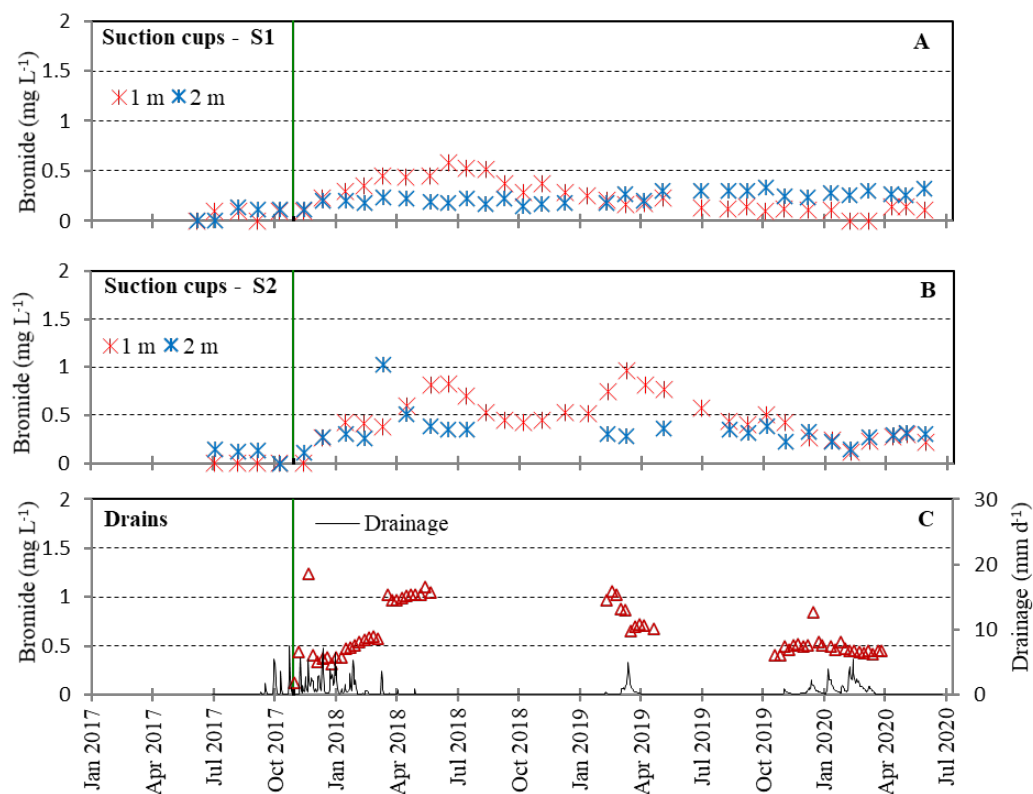
**Table 7.1.** Annual water balance for Lund (mm yr<sup>-1</sup>) applying precipitation from Tokkerup for the period July 2018 – 30 June 2020.

	Normal precipitation <sup>1)</sup>	Precipitation <sup>2)</sup>	Actual Evapotranspiration <sup>3)</sup>	Measured drainage	Simulated drainage	Groundwater Recharge <sup>4)</sup>
01.07.18–30.06.19	577	602	466	38	29	98
01.07.19–30.06.20	577	588	518	131	56	-61

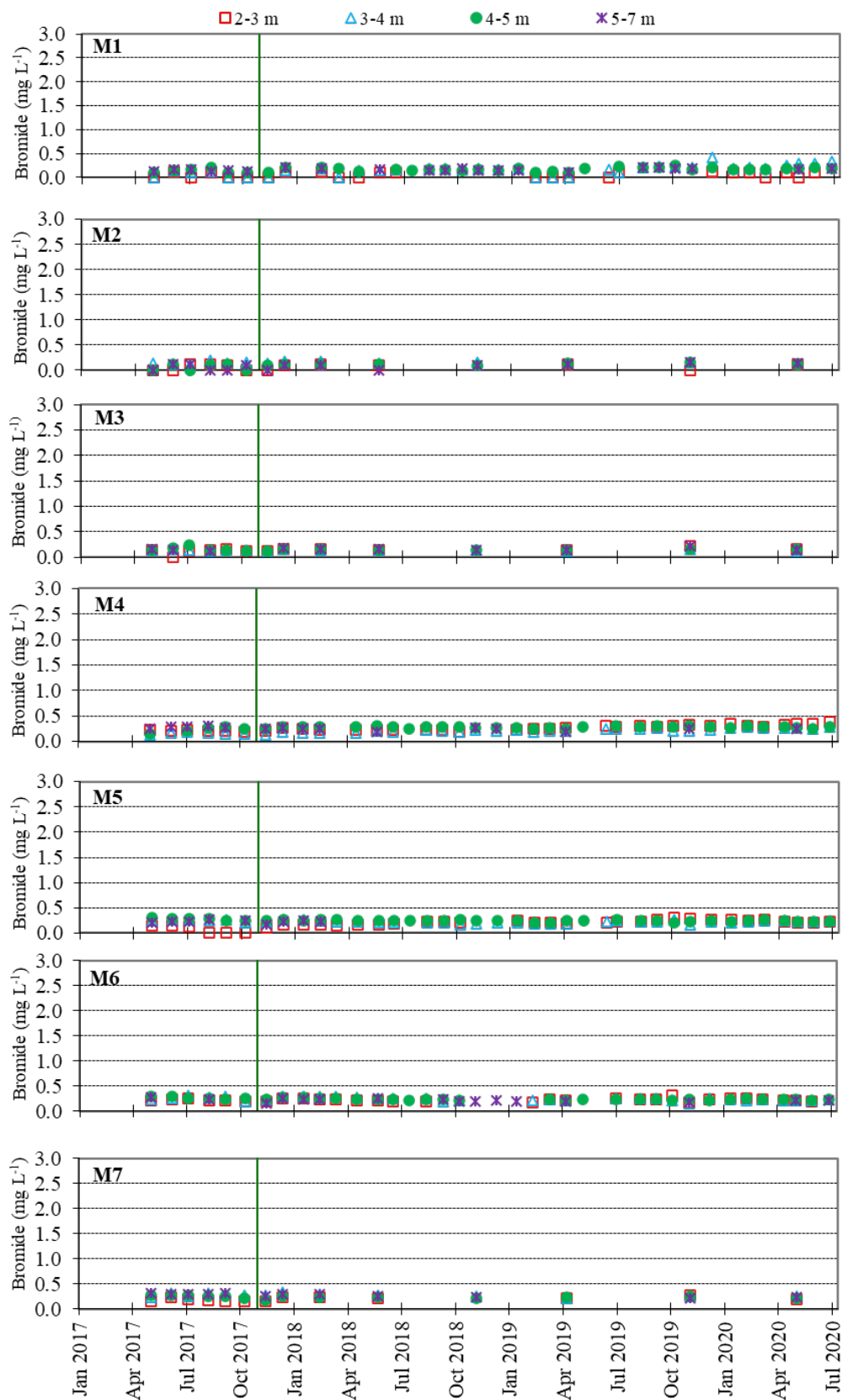
<sup>1)</sup> Normal values based on time series for 1961–1990. <sup>2)</sup> Precipitation is corrected to the soil surface according to the method of Allerup and Madsen (1979). <sup>3)</sup> Actual evapotranspiration is estimated by the MACRO-model applying climate data including potential evapotranspiration <sup>4)</sup> Groundwater recharge calculated as precipitation - actual evapotranspiration - measured drainage.

### 7.2.2 Bromide leaching

Measurements of bromide concentrations at Lund differ substantially compared to the other fields. Firstly, the overall concentration magnitudes in the variably saturated zone and drainage (Figure 7.3), or groundwater (Figure 7.4) are the lowest measured in all the monitored fields. Secondly, the background concentrations measured in groundwater before the bromide application do not seem to differ compared to concentrations measured after the application (Figure 7.4). The reason for these apparent deviations is not currently known and needs further examination. Perhaps the application concentration was erroneous, or the screens are not sufficiently in hydraulic contact with the groundwater system. Planning of further investigations of well screen connectivity with their surroundings and additional bromide application is ongoing and will be further explored in the coming months. Therefore, analyses of the bromide measurements at Lund are not currently conducted.



**Figure 7.3.** Bromide concentrations at Lund. A and B refer to suction cups located at S1 and S2 (see Figure 7.1). The bromide concentration is also shown for drainage water (C). The green vertical line indicates the dates of bromide application.

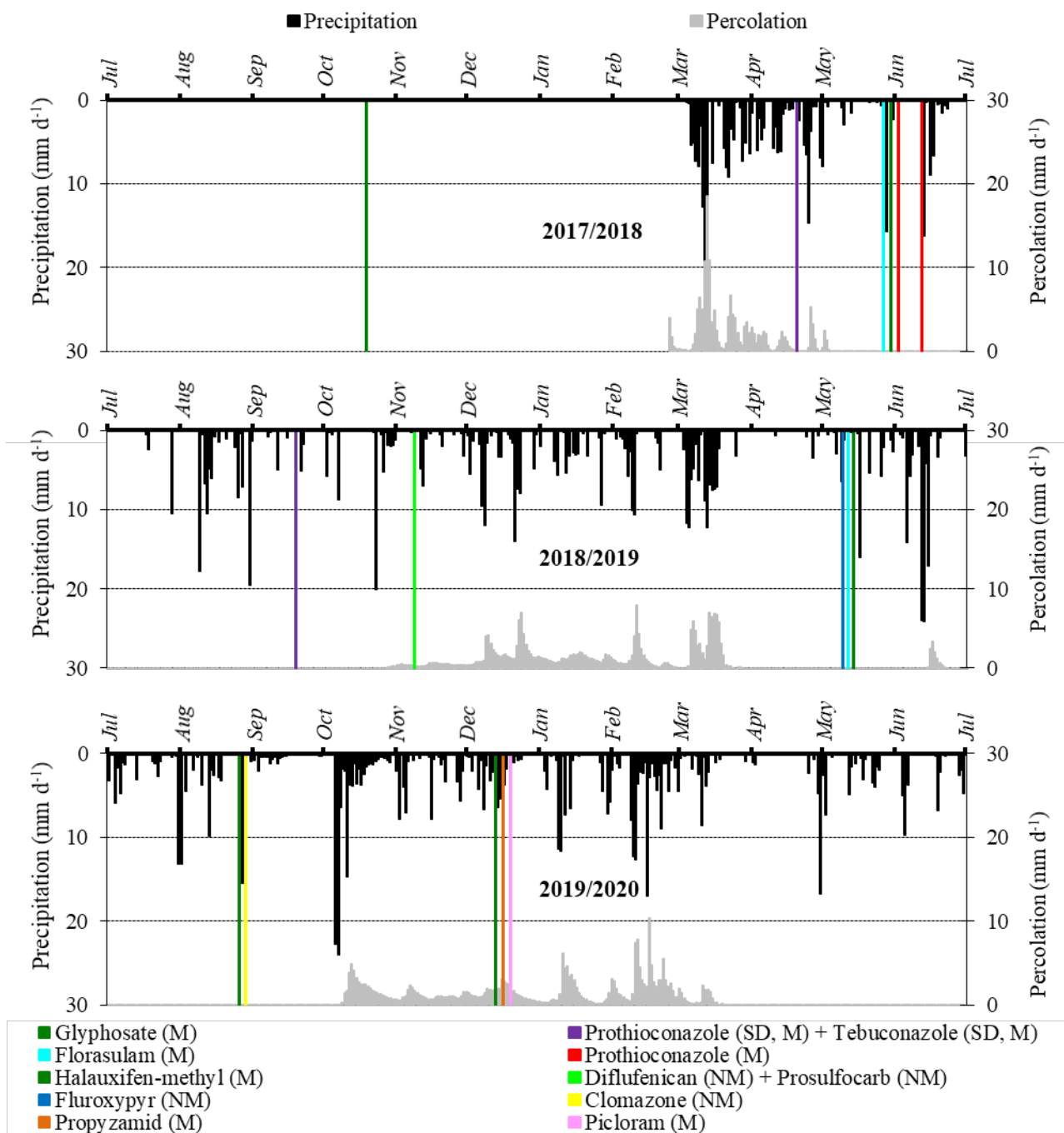


**Figure 7.4.** Bromide concentrations in the groundwater at Lund. The data derive from the vertical monitoring wells M1-M7. Screen depth is indicated in mbgs. The green vertical lines indicate the date of bromide application.

### **7.2.3 *Pesticide leaching***

Monitoring at Lund began in May 2017, but as mentioned in section 7.1.1 pesticide monitoring data for this field should still be interpreted with caution. Especially, groundwater data obtained before November 2019 from all monitoring wells, might be impacted by poor hydraulic contact due to clogging of the screens.

The applied pesticides, as well as their degradation products, are shown in Table 7.1 together with information on seed dressings as given by the commercial agribusiness supplier. Water was collected monthly from the upper two waterfilled screens in all the seven vertical monitoring wells. The application time of the pesticides included in the monitoring is shown together with the available precipitation in Figure 7.5. The precipitation is corrected to the soil surface according to Allerup and Madsen (1979) and measurements are only available from January 2018.



**Figure 7.5.** Application of pesticides at Lund in the period July 2017-June 2020. Pesticides are marked (M) if the pesticide and/or its degradation products are included in the monitoring programme, or (NM) if they are not monitored. Substances applied as seed dressing are marked SD. Measured precipitation is given on the primary axis and simulated percolation 1 mbgs on the secondary axis.

**Table 7.2.** Pesticides analysed at Lund. Precipitation (precip.) and percolation (percol.) are accumulated within the first year (Y 1<sup>st</sup>), and month (M 1<sup>st</sup>) after application. C<sub>mean</sub> is average leachate concentration at 1 mbgs. See Appendix 2 for the calculation method.

Crop – Year of harvest	Applied Product	Analysed Pesticide (P) / Degradation product (M)	Application date	End of monitoring	Y 1 <sup>st</sup> Precip. (mm)	Y 1 <sup>st</sup> Percol. (mm)	M 1 <sup>st</sup> Precip. (mm)	M 1 <sup>st</sup> Percol. (mm)	C <sub>mean</sub> (µg L <sup>-1</sup> )
<b>Spring barley 2017</b> SD: Fungazil A (Imazalil)	Fighter 480	Bentazon (P)	May 17	Mar 19	nd	nd	nd	Nd	nd
	Amistar	Azoxystrobin (P)	Jun 17	Mar 19	nd	nd	nd	nd	nd
	Glyphonova 450 Plus	CyPM (M) Glyphosate(P) AMPA(M)	Oct 17	Sept 19 Sept 19	nd nd	nd nd	nd nd	nd nd	nd nd
<b>Spring barley 2018</b> SD: Redigo Pro 170 FS (Prothioconazole + tebuconazole)	Zypar Florasulam (P)	TSA (M)	May 18	Jun 20*	537	92	39	-25	<0.01
	Proline 250 EC Prothioconazole (P)	1,2,4-triazole (M)	May 18	Jun 20*	564	95	36	-25	n
<b>Winter barley 2019</b> SD: Redigo Pro 170 FS (Prothioconazole + tebuconazole)	Zypar Florasulam (P)	TSA (M)	May 18	Jun 20*	525	89	22	-24	<0.01
	Halauxifen-methyl (P)	X-729 (M)		Jun 20*	525	89	22	-24	<0.01
<b>Winter rape 2020</b>	Kerb 400 SC	Propyzamid (P)	Dec 19	Jun 20*	-	-	53	49	-
		RH-24644 (M)		Jun 20*	-	-	53	49	-
		RH-24580 (M)		Jun 20*	-	-	53	49	-
	Belkar Picloram (P)	Picloram (P)	Dec 19	Jun 20*	-	-	53	49	-
		Halauxifen-methyl (P)		Jun 20*	-	-	53	49	-

\*Monitoring continues the following year.

<sup>x</sup> Due to a high background content of 1,2,4-triazole, the results of the analysis cannot be linked directly to the specific application, why C<sub>mean</sub> is not presented.

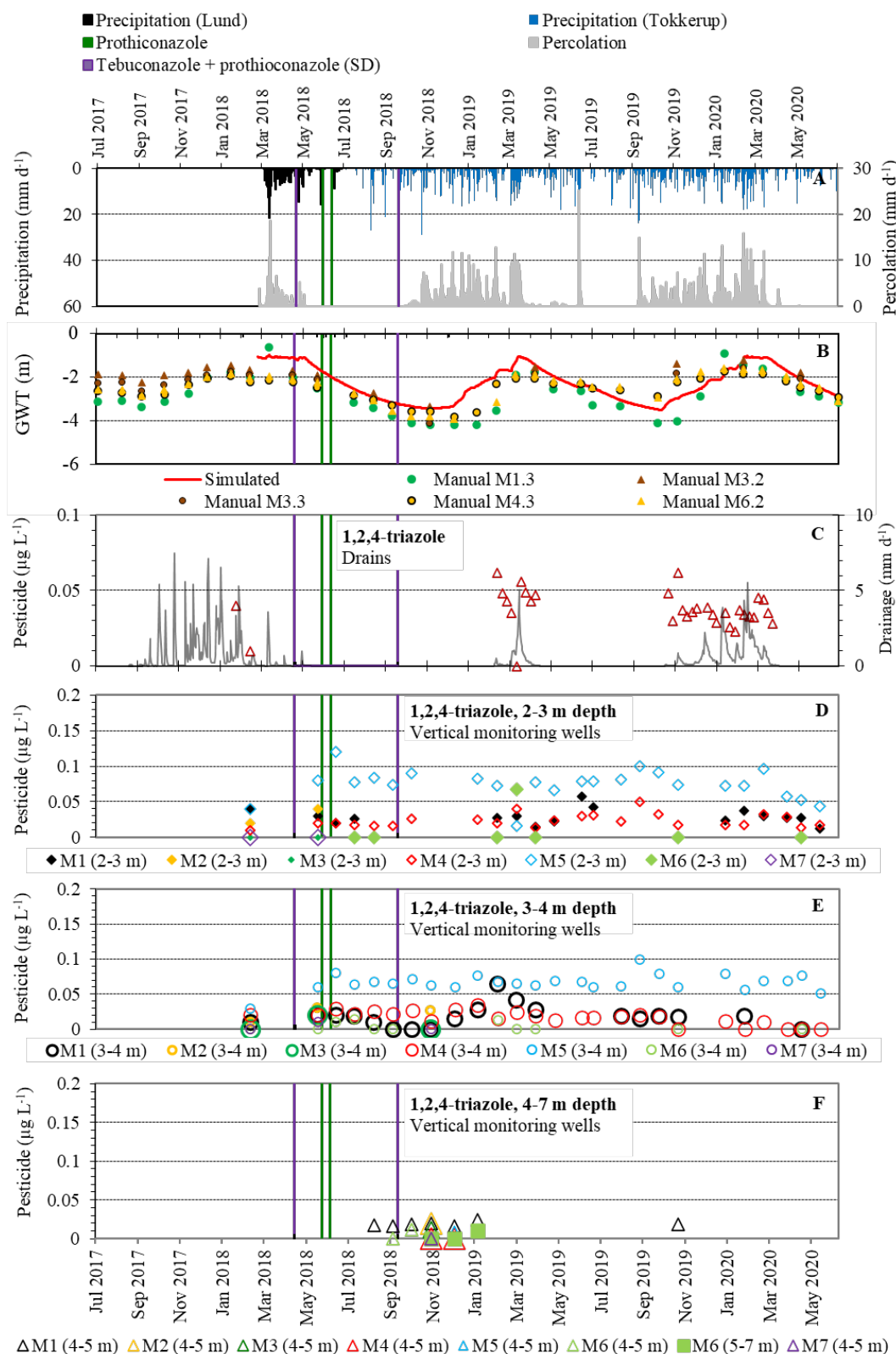
### Azole fungicides and 1,2,4-triazole monitoring

Before application of azole-containing products in the field, the background level of 1,2,4-triazole in drainage and groundwater was measured. This was done to evaluate whether 1,2,4-triazole background concentrations in the groundwater were too high to conduct meaningful future azole tests at this field. Water samples were collected in January 2018 (one drainage sample only) and February 2018 (one drainage sample and groundwater from the two uppermost screens of all the wells). The results showed that 1,2,4-triazole was present in the drainage with a maximum concentration of 0.04 µg L<sup>-1</sup> in January 2018 (Figure 7.6C). Background concentrations in the downstream wells M2, M4, and M5 showed a maximum concentration of 0.04 µg L<sup>-1</sup>, which is similar to the upstream well, M1, also with a maximum concentration of 0.04 µg L<sup>-1</sup> (Figure 7.6D). The last available drainage sample collected before April 2018 (sowing with azole coated seeds) showed a 1,2,4-triazole concentration of 0.01 µg L<sup>-1</sup> (no drainage available from March 2018 - February 2019). In conclusion, 1,2,4-triazole was omnipresent in water from the field and water upstream from the field before the first azole application in April 2018, however in concentrations < 0.1 µg L<sup>-1</sup>.

In the entire monitoring period from January 2018 to June 2020, only two drainage events from February-April 2019 and October 2019-March 2020 were measured after azole applications in the field. Here, 32 drainage samples were collected and 1,2,4-triazole was detected in all but one sample (97%), and the concentration was fluctuating around 0.04 µg L<sup>-1</sup>. No detections in concentrations > 0.1 µg L<sup>-1</sup> were observed (Figure 7.9C), and the highest detected concentration of 0.062 µg L<sup>-1</sup> was observed twice.

From groundwater, a total of 190 samples were collected, and 1,2,4-triazole was detected in 149 (78%) of these. One sample (0.5%) in a concentration > 0.1 µg L<sup>-1</sup> (0.12 µg L<sup>-1</sup>; Figure 7.9D). Except

for the single background sample collected in January 2018, the general 1,2,4-triazole content in the groundwater is at a constant level during the monitoring period (Figure 7.9D-F), and this includes the samples collected immediately before the two sprayings with prothioconazole (May 2018). In evaluating the results according to screen depth, there seems to be a pattern of lower concentration with increasing depth. Especially in groundwater samples from the two upper screens in downstream well M5 (located downstream of the expected groundwater flow field), concentrations are often  $> 0.06 \mu\text{g L}^{-1}$ , whereas the concentration in the deepest screen level is consistently  $< 0.04 \mu\text{g L}^{-1}$ . Detections from groundwater collected from the upstream well M1 are generally lower than the concentrations detected in the well M5. Contribution of 1,2,4-triazole from upstream fields to the groundwater immediately below the Lund field seems to be of minor importance for the level of detections and the concentration of the water samples collected from M5.



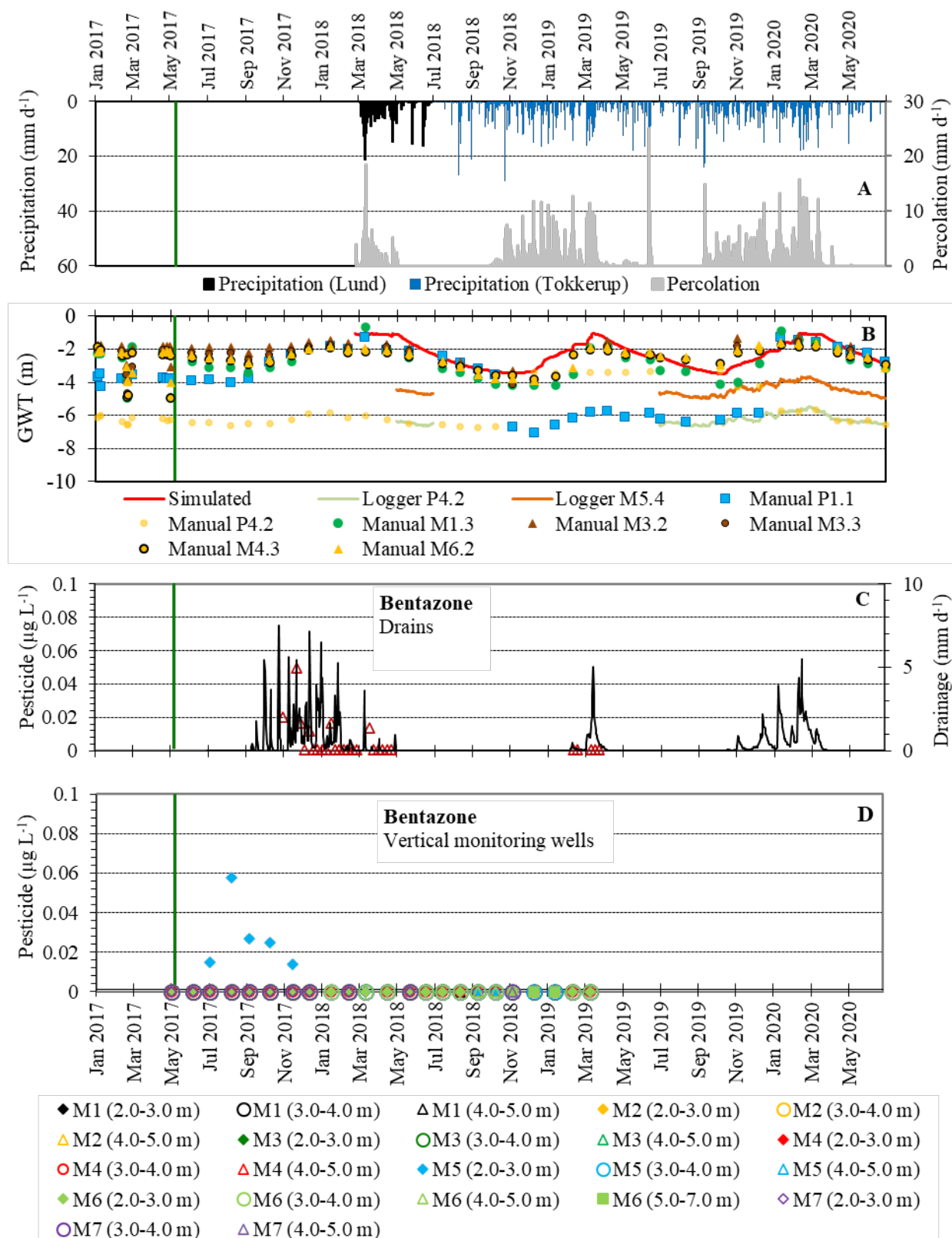
**Figure 7.6.** 1,2,4-triazole monitoring at Lund. Precipitation and simulated percolation 1 mbgs (A); measured and simulated groundwater level (B); concentration of 1,2,4-triazole in the variably saturated zone (C) and saturated zone (D-F). It is noted that M1 is regarded as an upstream monitoring well. The green vertical lines indicate the dates of prothioconazole application. The purple vertical lines indicate the application of seeds coated with tebuconazole and prothioconazole. Seed dressings used before 2017 were not registered.



Lund was used for conventional cropping before its inclusion in PLAP in 2017. Hence, the use of azole products in the previous crop rotations is confirmed, and from summer 2013 to spring 2016, epoxiconazole, tebuconazole, propiconazole, and prothioconazole were applied in the field (Haarder *et al.* 2021). The first monitored PLAP usage of azoles in Lund was sowing with azole coated seeds in April 2018. However, the previous azole sprayings and use of azole coated seeds might contribute to azoles in the plough layer, and could explain the detected 1,2,4-triazole leaching (Albers *et al.*, 2022). Possible azole accumulation in the plough layer is mentioned in the EFSA conclusion on tebuconazole (EFSA, 2014) and therefore may cause continuous degradation of azoles into 1,2,4-triazole leading to long-term leaching to the groundwater. It is therefore not possible to discern between the previous and present azole applications and leaching of 1,2,4-triazole. To do so detailed fate studies of azoles in soils are needed. Monitoring of 1,2,4-triazole is ongoing

### **Bentazone and degradation products, 6-hydroxy-bentazone, 8-hydroxy-bentazone, and N-methyl-bentazone**

The herbicide bentazone was applied on spring barley in May 2017 to test its leaching potential together with the leaching potential of its three degradation products, 6-hydroxy-bentazone, 8-hydroxy-bentazone, and N-methyl-bentazone. Bentazone was detected in six out of 27 drainage samples, but not in concentrations  $> 0.1 \mu\text{g L}^{-1}$  (Figure 7.7B), while 6-hydroxy-bentazone and 8-hydroxy-bentazone were not detected, and N-methyl-bentazone was detected in one out of 22 samples ( $0.022 \mu\text{g L}^{-1}$ ). In water from the vertical monitoring wells M1-M7 bentazone is found in five out of 240 groundwater samples and not in concentrations  $> 0.1 \mu\text{g L}^{-1}$ . All detections are in monitoring well, M5 (1.5-2 m depth). Here bentazone was detected two months after the application and onwards for around six months with a maximum concentration of  $0.058 \mu\text{g L}^{-1}$ . No bentazone is detected in groundwater samples after November 2017 (Figure 7.7C) and the last bentazone detection was in drainage in March 2018. The fact that bentazone is not detected in any of the samples from drainage or groundwater after the beginning of 2018 (Figure 7.7B and 7.7C) could indicate that bentazone is degraded into other degradation products not included in the monitoring, fully degraded, or leached beyond the screen depths. Monitoring of bentazone ended in March 2019. The degradation products are not found in any of the 146 groundwater samples. Monitoring of the three degradation products was stopped in April 2018.

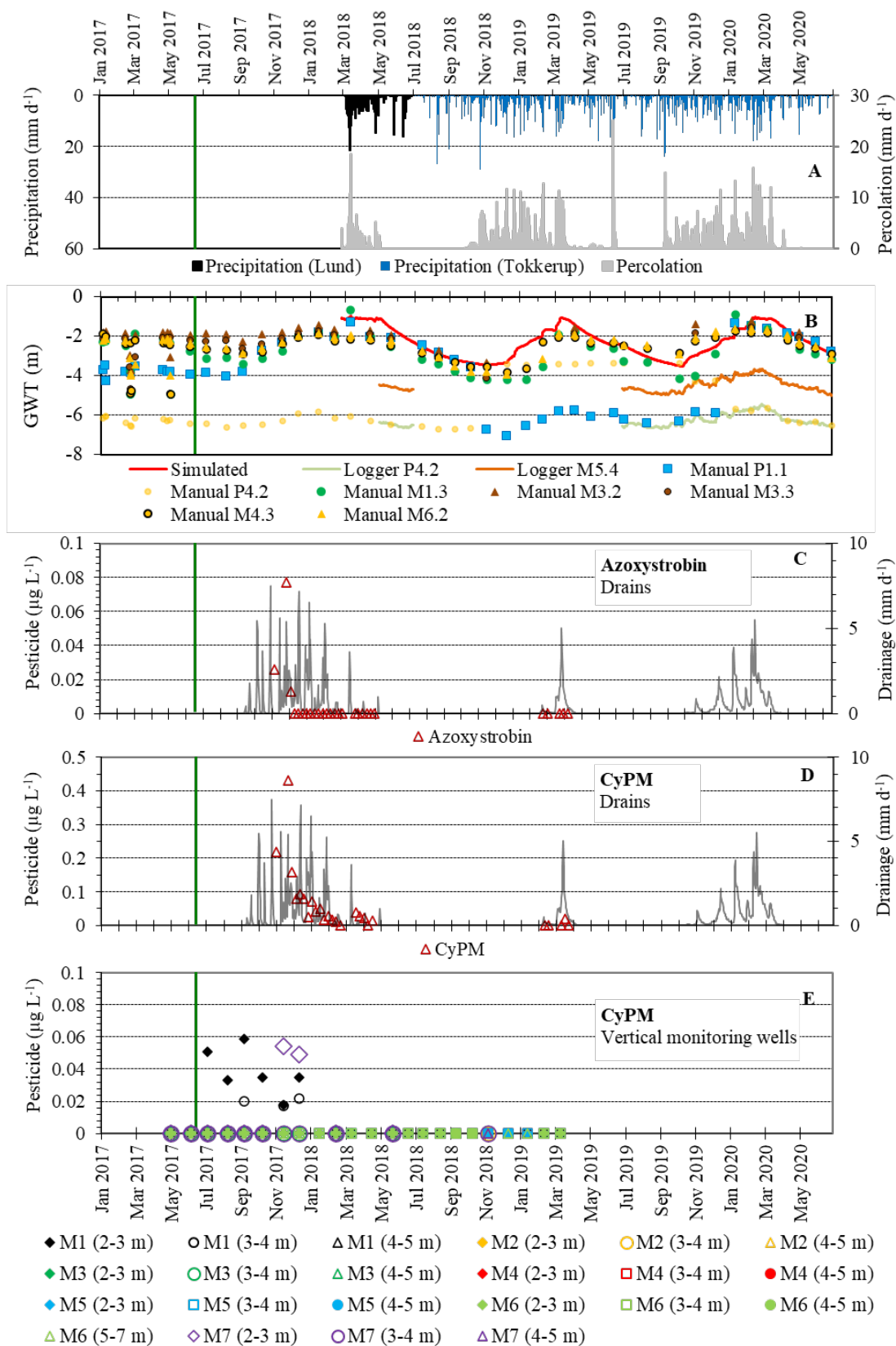


**Figure 7.7.** Bentazone monitoring at Lund. Precipitation (Lund and Tokkerup) and simulated percolation 1 mbgs (A); measured and simulated groundwater level (B); concentration of bentazone in the variably saturated zone (C) and saturated zone (D). It is noted that M1 is regarded as an upstream monitoring well. The green vertical line indicates the date of bentazone application. Note that monitoring of bentazone ended in March 2019.

### **Azoxystrobin and degradation product CyPM**

The fungicide azoxystrobin was applied in June 2017 on spring barley to evaluate the leaching potential of azoxystrobin and its degradation product CyPM (Figure 7.7). None of the two compounds were detected in groundwater before application. Since no water was flowing in the tile drain system immediately before application of the fungicide, a background sample and hence concentration in the drainage could not be obtained.

In drainage, azoxystrobin is detected in three out of 27 samples (11%), none  $> 0.1 \mu\text{g L}^{-1}$  (Figure 7.7C). CyPM is found in 19 out of 25 samples (76%). Of these samples, three (12%) show CyPM concentrations  $> 0.1 \mu\text{g L}^{-1}$  (Figure 7.8D). Common for detections of both azoxystrobin and CyPM is that the highest detections are seen during the drainage events around November 2017. In fact, the first three drainage samples following the azoxystrobin application contained the highest CyPM concentrations detected (max.  $0.43 \mu\text{g L}^{-1}$ ) during the entire monitoring period (Figure 7.8C).

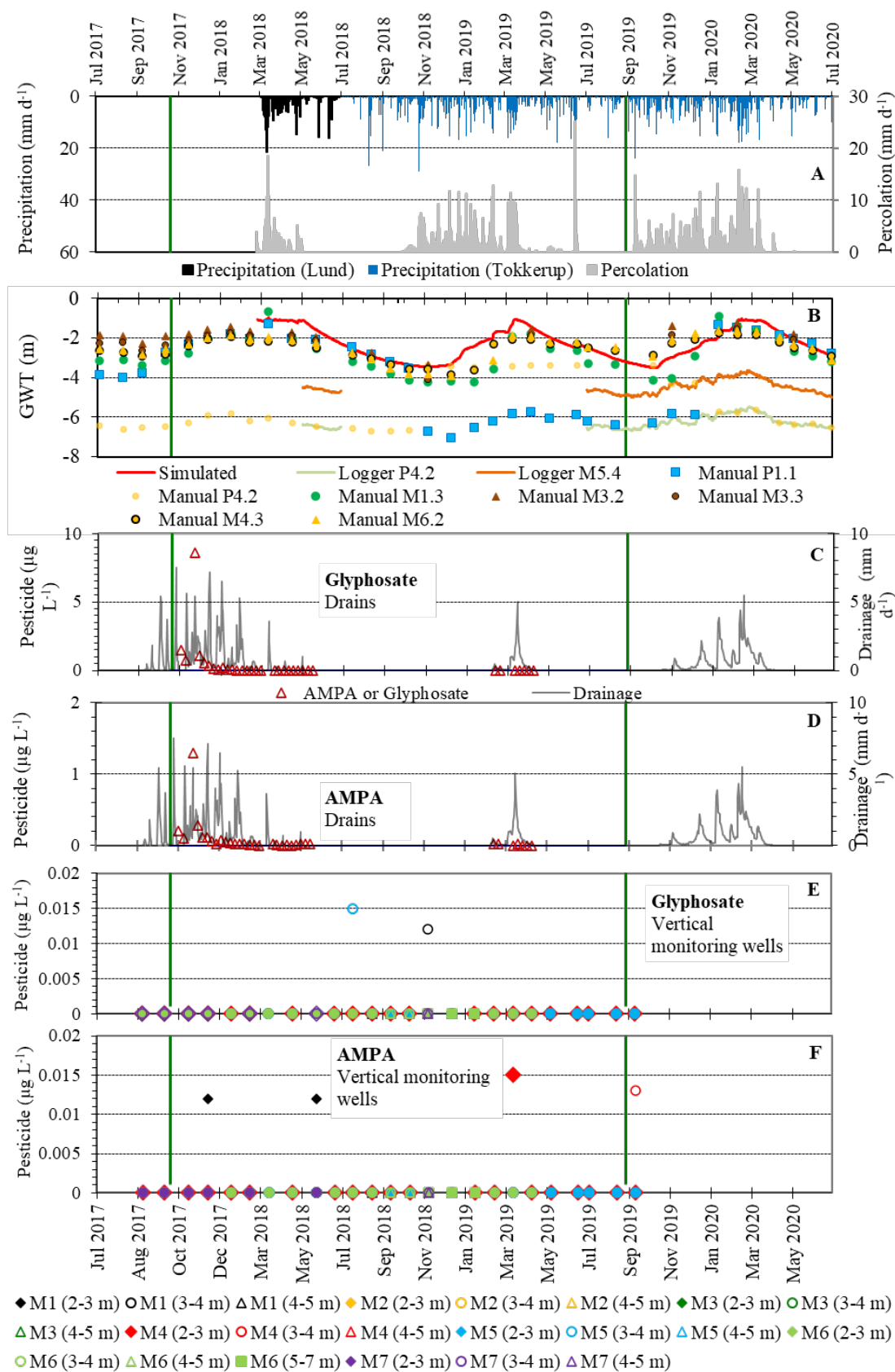


**Figure 7.8.** Azoxystrobin and degradation product, CyPM monitoring at Lund. Precipitation and simulated percolation 1 mbgs (A); measured and simulated groundwater level (B); concentration of azoxystrobin and CyPM in the variably saturated zone (C-D) and concentration of CyPM in the saturated zone (D). It is noted that M1 is regarded as an upstream monitoring well. The green vertical lines indicate the date of azoxystrobin application. Note that the scale is different on the y-axis for azoxystrobin and CyPM in drains (C, D).

Azoxystrobin is not detected in any of the 240 collected groundwater samples, while CyPM is detected in 11 of the samples (5%), but none of them in concentrations  $> 0.1 \mu\text{g L}^{-1}$ . The detections are obtained from samples collected from the upstream well M1 and the downstream well M7. In the upstream well, CyPM was detected with a maximum concentration of  $0.06 \mu\text{g L}^{-1}$  two months earlier than in groundwater from the downstream well M7 (Figure 7.8E). During the monitoring period, CyPM was detected in groundwater from M7 in November ( $0.054 \mu\text{g L}^{-1}$ ) and December 2017 ( $0.049 \mu\text{g L}^{-1}$ ). These detections in M7 coincide with the detected maximum concentration of both azoxystrobin and CyPM in drainage. (Figure 7.8C and 7.8D). A contribution of CyPM from upstream fields to the groundwater collected from M7 can, however, not be excluded. The monitoring of azoxystrobin and CyPM ended in March 2019.

### **Glyphosate and degradation product, AMPA**

Glyphosate, a herbicide, was applied in October 2017 to kill off the grass clover ley, and glyphosate and AMPA were included in the monitoring until September 2019. Glyphosate was additionally applied in winter rape ultimo August 2019, but not included in the monitoring. Therefore, only data from July 2019 to September 2019 are added since the evaluation in last year's report (Rosenbom *et al.* 2021). In this period, no drainage was available, but 15 groundwater samples were collected, with no detections of glyphosate and one detection of AMPA ( $0.013 \mu\text{g L}^{-1}$ ) in September 2019, two weeks after the 2019 application.



**Figure 7.9.** Glyphosate and AMPA monitoring at Lund. Precipitation and simulated percolation 1 mbgs (A); measured and simulated groundwater level (B); concentration of glyphosate and AMPA in the variably saturated zone (C-D) and in the saturated zone (E-F). It is noted that M1 is regarded as an upstream monitoring well. The green vertical lines indicate the dates of glyphosate application. Note different scales for glyphosate and AMPA in drainage.

Since no water was collected in the tile drain system just before application of glyphosate, a background sample and hence concentration in the drainage was not obtained. Glyphosate and AMPA were both detected in drainage. A total of 33 drainage samples were collected, 21 contained glyphosate, eight samples with concentrations  $> 0.1 \mu\text{g L}^{-1}$  (24%). The maximum glyphosate concentration is  $8.6 \mu\text{g L}^{-1}$  and was detected in November 2017 (Figure 7.8B). Glyphosate was not detected in any drainage samples after May 2018. Leaching of the degradation product, AMPA, to drainage showed a similar pattern as that of glyphosate (but a factor of 10 lower in concentration level) with three samples showing detections in the recent period (July 2019-June 2020) (Figure 7.8D). As of yet, 26 out of 33 drainage samples contained AMPA, where five samples (15%) had concentrations  $> 0.1 \mu\text{g L}^{-1}$ .

In the groundwater, glyphosate and AMPA were not detected before the application (Figure 7.9D and E). In the 218 groundwater samples analysed, glyphosate and AMPA, were detected in two (1%) and four (2%) samples, respectively, all in concentrations  $< 0.1 \mu\text{g L}^{-1}$ . Monitoring ended in September 2019.

#### **Florasulam and degradation product, TSA and halauxifen-methyl degradation product, X-729**

Florasulam and halauxifen-methyl were applied on spring barley in May 2018 and on winter barley in May 2019, and halauxifen-methyl (together with picloram, see section below) was applied again in December 2019 in winter rape. Just before the May 2018 application, background samples were collected for analysis of the florasulam degradation product TSA. There were no detections of TSA in the 30 drainage samples and 176 groundwater samples collected from May 2018 to June 2020. In addition to TSA, the halauxifen-methyl degradation product, X-729 was included in the monitoring programme after the May 2019 application. X-729 was not detected in the 22 drainage- and 80 groundwater samples. As the analytical method was not ready when the monitoring of X-729 was planned to start, collected samples were stored ( $-20^{\circ}\text{C}$ ) until ready. As the stability of X-729, when frozen for several months, is currently unknown, the presence of false-negative results may be possible. Results on X-729 from April 2019 until September 2019 should therefore be regarded as tentative (Chapter 8). Monitoring of TSA and X-729 continues, and the influence of freezing on the quality of X-729 analyses is currently investigated.

#### **Propyzamide and degradation products, RH-24644 and RH-24580, and picloram**

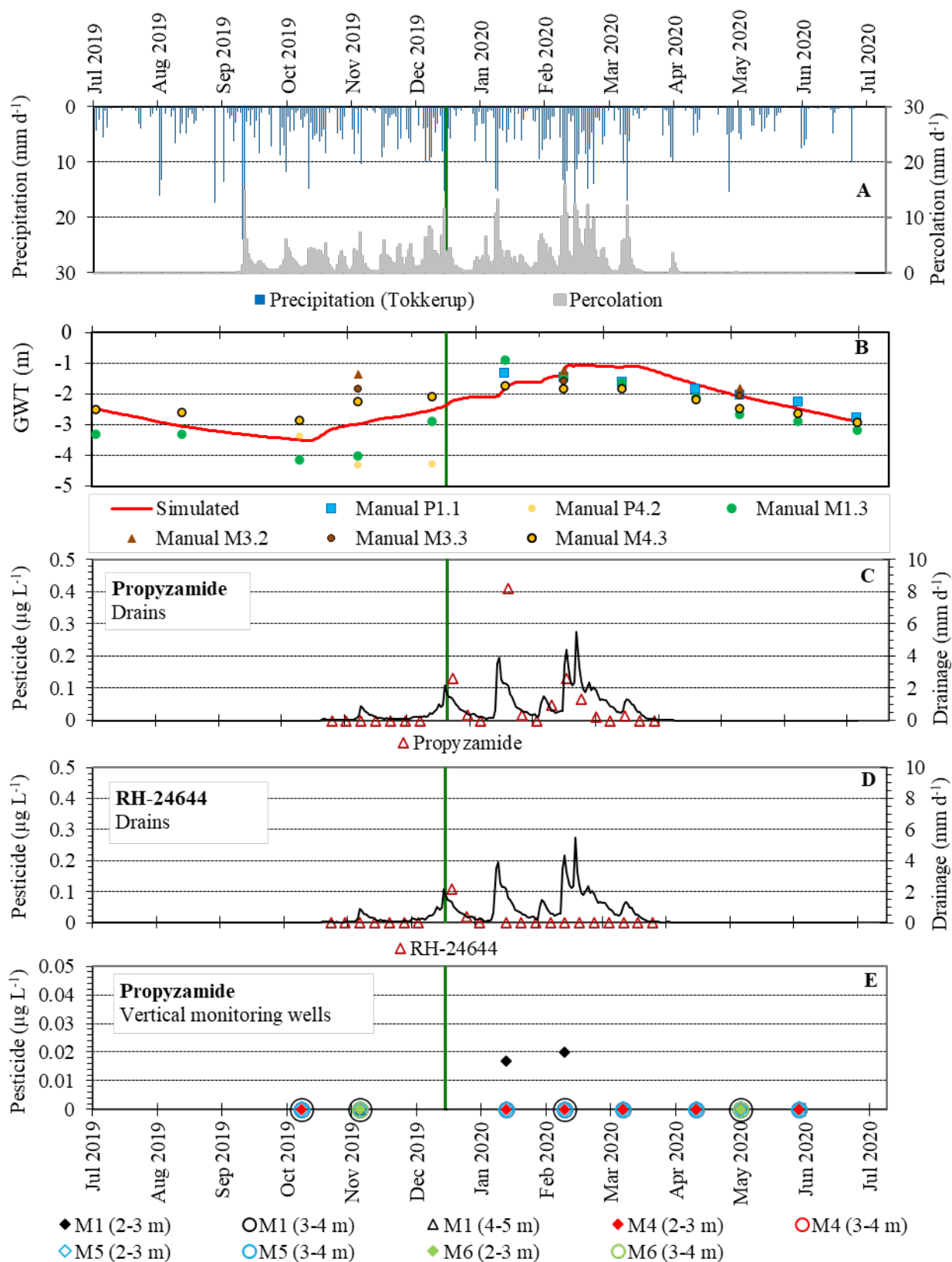
Propyzamide and picloram were applied on winter rape in December 2019 and included in the monitoring together with two propyzamide degradation products, RH-24644 and RH-24580. None of the compounds were detected in the background samples collected before the application - neither in the drainage nor in groundwater samples (Figure 7.10).

Propyzamid was detected in all three drainage events in December 2019, and January and February 2020 following the application. The first detection of propyzamide was immediately after application in December 2019. Propyzamide is found in nine of 21 drainage samples (43%), in three samples (14%) in a concentration  $> 0.1 \mu\text{g L}^{-1}$  (Figure 7.10C). Only the degradation product RH-24644 was detected in drainage and only in two samples out of 21 (10%) right after the application in December 2019 and January 2020. RH-24644 was detected in a concentration  $> 0.1 \mu\text{g L}^{-1}$  in one drainage (5%) sample in December 2019 (Figure 7.10D).

In 47 groundwater samples, propyzamide is detected in two samples (4%) (Figure 7.10E), both from the monitoring well M1, located upstream of the field. The degradation products RH-24644 and RH-24580 were not detected in any of the 47 groundwater samples.

Picloram was detected in one (5%) out of 21 drainage samples in January 2020 ( $0.011 \mu\text{g L}^{-1}$ ), and it was not detected in any of the 42 groundwater samples from December 2019 to July 2020. Monitoring of all four compounds continues.





**Figure 7.10.** Propyzamide and RH-24644 monitoring at Lund. Precipitation and simulated percolation 1 mbgs (A); measured and simulated groundwater level (B); concentration of propyzamide and RH-24644 in the variably saturated zone (C-D) and concentration of propyzamide in the saturated zone (E). It is noted that M1 is regarded as an upstream monitoring well. The green vertical line indicates the date of propyzamide application.



## 8 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 is supported by intensive quality assurance entailing continuous evaluation of the analyses employed. Two types of samples are used in the quality control 1) samples with known pesticide composition and concentration are used for *internal monitoring* of the laboratory method (internal QC), and 2) *externally spiked samples* that are used to incorporate additional procedures such as sample handling, transport, and storage (external QC). Pesticide analysis quality assurance (QA) data for the period July 2019 to June 2020 are presented below, while those for the preceding monitoring periods are presented in previous monitoring reports (available on [www.plap.dk](http://www.plap.dk)).

### 8.1 Materials and methods

All pesticide analyses were carried out at a commercial laboratory selected based on a competitive tender. 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.

#### 8.1.1 Internal QA

With each batch of samples, the laboratory analysed 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<sup>-1</sup>. 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):

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

#### 8.1.2 External QA

Three times during the period July 2019 to June 2020, two external control samples per test field were analysed at the laboratory (except at Faardrup, see below) along with the various water samples from the five fields. In this reporting period, the three external control sample times were in October/November 2019 (where the groundwater table was too low for sampling at Faardrup), February, and April/May 2020. Two standard solutions of different concentrations were prepared from stock mixtures in ampoules prepared by Dr. Ehrenstorfer/LGC, Germany (Table 8.1). New ampoules were used for each set of standard solutions. The standard solutions were prepared two days before a sampling day and stored cold (5°C) and dark until use. For the preparation of standard 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 at 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 in the measuring flasks was diluted with groundwater from a defined groundwater well in each field. After thorough mixing, the control sample was decanted to a sample bottle like 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 samples shipped for analysis in the laboratory were 0.050 µg L<sup>-1</sup> for the spiked low-level sample and 0.117 µg L<sup>-1</sup> for the high-level sample. Unfortunately, three of the compounds (AE1394083, E/Z BH 517-TSO, and X-729) selected for external QC were not stable in the ampoule solution. The compounds had a lower initial concentration and the concentration decreased further during storage, from the first sample time in October 2019 to the last time in May 2020. The three compounds are therefore not discussed in the *External QA* section. The compounds included in the External QA, their concentration in the initial ampoule, and the final QC samples sent for analysis are listed in Table 8.1.

Every month, blank samples consisting only of ultra-pure HPLC water were included as control for false-positive findings in the external QA procedure. 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 8.1.** Pesticides and *degradation products* included in the external QC control samples in the period 1.7.2019-30.6.2020. Ampoule concentrations in both the original ampoules and in the final high-level and low-level external control samples used. Compounds in ampoules were dissolved in ampoule no. 1 in methyl tert-butyl ether, ampoule no. 2 and 3 in acetonitrile.

Compound	Ampoule concentration (µg L <sup>-1</sup> )	Ampoule No.	Lot no.	High-level control (µg L <sup>-1</sup> )	Low-level control (µg L <sup>-1</sup> )
<i>1,2,4-triazole</i>	1000	1	1029860MB	0.117	0.050
<i>AE F099095</i>	1000	2	1-1029876AL	0.117	0.050
<i>AE1394083</i>	<1000	2	1-1029876AL	-	-
<i>CGA290291*</i>	1000	3	1-1029861AL	0.117	0.050
<i>Desamino-metamitron</i>	1000	3	1-1029861AL	0.117	0.050
<i>E/Z BH 517-TSO*</i>	<1000	2	1-1029876AL	-	-
Metconazole	1000	3	1-1029861AL	0.117	0.050
Propyzamide	1000	3	1-1029861AL	0.117	0.050
<i>TSA</i>	1000	2	1-1029876AL	0.117	0.050
<i>X-729*</i>	<1000	3	1-1029861AL	-	-

\* compounds were unstable in the ampoule solution.

## 8.2 Results and discussion

### 8.2.1 Comments on results from the monitoring period June 2018 to July 2020

Several compounds should have been introduced in the analytical programme in May 2018 and April 2019, but due to delay in internal procedures regarding the selection of compounds for the monitoring programmes these years, and thus delays in both the procurement of the analytical standards and consequently analytical method development this was not possible. Consequently, samples collected from May 2018 and onward, and from April 2019 and onward for analysis of compounds listed in Table 8.2 were stored at -20°C for several months until the analytical methods were ready for sample analysis. As the stability of the compounds of concern, when frozen for several months, is unknown,

results from these periods should be considered tentative. Currently, compound stability studies in frozen samples are planned for initiation shortly. For future need of sample storage, stability and recovery studies in spiked samples will be set up, if possible, in parallel with the collected and stored water samples or as soon as possible thereafter.

**Table 8.2.** Water samples collected in the periods from initiated sampling and until initiation of analysis were stored at -20°C. Results from these periods should be considered tentative given unknown stability of the specified analytes. Samples were stored due to delays in internal procedures regarding the selection of compounds for the monitoring programmes, and thus delays in both the procurement of the analytical standard and consequently analytical method development. Monitored compound (Pesticides and *degradation products*).

Monitored compound	Pesticide under evaluation	Water sampling initiated	Analysis of stored samples initiated	Maximum storage at -20°C (months)
<i>Carbendazim</i>	Thiophanat-methyl	1. May 2018	October 2018	4
<i>AE1394083</i>	Thiencarbazone-methyl	1. May 2018	January 2019	9
<i>MTM-126-ATM</i>	Metamitron	16. May 2018	April 2019	11
<i>IN-MM671</i>	Proquinazid	1. April 2019	September 2019	5
<i>IN-MM991</i>	Proquinazid	1. April 2019	September 2019	5
<i>CGA 287422</i>	Propaquizifop	1. April 2019	December 2019	8
<i>CGA 294972</i>	Propaquizifop	1. April 2019	December 2019	8
<i>CGA 290291</i>	Propaquizifop	1. April 2019	December 2019	8
<i>PPA</i>	Propaquizifop	1. April 2019	December 2019	8
<i>X-729</i>	Halauxifen-methyl	1. April 2019	September 2019	5
Metconazole	Metconazole	1. April 2019	September 2019	5

### 8.2.2 Internal QA

Ideally, the analytical procedure provides precise and accurate results. However, in reality, results from the analysis are subject to a certain standard deviation. Such standard deviation may be the combined result of several contributing factors and overall, the accuracy of an analytical result reflects two types of error: Random errors related to precision and systematic errors relating to bias. In a programme like PLAP, it is relevant to consider possible changes in analytical reliability over time. As random and systematic errors may change over time, it is relevant to distinguish between standard deviations resulting from *within-day* variation as opposed to those associated with *between-day* variation in the analytical results. To this end, control samples are included in the analytical process as described above. Thus, from utilizing 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: *between-day* variation and *within-day* variation (Funk *et al.*, 1995; Miller *et al.*, 2000). This kind of analysis can provide an extra 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 are 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 compound specific. In the current reporting period, internal quality data were available for 28 compounds and QC plots for all included compounds are presented in Appendix 6. The results of the internal QA statistical analysis for each pesticide are presented in Table 8.2. For reference, estimated  $S_b$  values are listed for all compounds, including those where the between-day variance is not significantly greater than the within-day variance. ANOVA details and variance estimates are also included, even for compounds, 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,  $S_b$  0.008 and  $S_t$  was 0.013  $\mu\text{g L}^{-1}$ , levels that are considered suitable when relating to the residue limit for pesticides (0.1  $\mu\text{g L}^{-1}$ ).

As a rule of thumb, the between-day standard deviation should be no more than double the within-day standard deviation. Table 8.2 shows that  $S_b/S_w$  ratios greater than two were observed for four compounds this year (AE-F160459, glyphosate, IN-MM671 and X-757). For these compounds, the results indicate that day-to-day variation makes a significant contribution, but none of the between day contributions are, however, significant on the 0.05 significance level.

In last year's PLAP-report covering QA for the period 2018-2019, three pesticides (metconazole, propyzamide, metamitron) and six degradation products (AE-F147447, AE1394083, carbendazim, desamino-metamitron, MTM-126-AMT and X-729) were introduced in the analytical QA-programme.

This present report includes monitoring of one new pesticide (picloram) and nine degradation products (CGA287422, CGA290291, CGA294972, IN-MM671, IN-MM991, PPA, RH-24580 and RH-24644) in the QA-programme.

In general, data for some of the compounds rely on very few duplicate samples, either because the compound is newly introduced or because monitoring of the compound is ended early in the reporting QA period. All methods of analysis are continuously optimized and improved.

**1,2,4-triazole** (common degradation product from triazole fungicides), **glyphosate** and **AMPA** (glyphosate degradation product): All three compounds have been included in the analytical programme for several years and continuously monitored. The analytical methods for all three compounds are in good control, with very low deviations ( $S_t$  0.003-0.006  $\mu\text{g L}^{-1}$ ) in addition to low  $S_b/S_w$ -ratios of 1.0 (1,2,4-triazole) and 0.3 (AMPA). The ratio for glyphosate is slightly higher (2.6), but the ratio is only based on four data points with very low standard deviations.

**AE1394083** (thiencarbazone-methyl degradation product): AE1394083 was introduced in the monitoring programme in May 2018. The statistics rely on data from 22 duplicate samples and analysis has a  $S_b/S_w$ -ratio of 0.5 and both  $S_w$  and  $S_b$  are low and acceptable, and the analytical method is in good control.

**AE-F099095**, **AE-F147447** and **AE-F160459** (mesosulfuron-methyl degradation products): AE-F099095 and AE-F160549 were introduced in the monitoring programme in 2017 and AE-F147447 was introduced in 2018. The degradation products AE-F099095 and AE-F147447 have  $S_b/S_w$  ratios

< 2.0, whereas AE-F160459 has a  $S_b/S_w$  ratio of 2.6. The slightly elevated  $S_b/S_w$  ratio of AE-F160459 is due to a between-day standard deviation ( $S_b$  0.015  $\mu\text{g L}^{-1}$ ) being relatively high compared to the within-day deviation ( $S_w$  0.006  $\mu\text{g L}^{-1}$ ). The standard deviations of AE-F160459 are slightly higher than the other two degradation products, but the analysis has improved during the reporting period, and the analysis of all three compounds is in good control.

**BH 517-T2SO2** and **E/Z BH 517-TSO** (cycloxydim degradation products): both degradation products were introduced in the programme in May 2017. The statistics rely on data from 31 duplicate samples and the analyses of both BH 517-T2SO2 and E/Z BH 517-TSO have  $S_b/S_w$  ratios < 2.0 and very low within-day and between-day deviations:  $S_w$  0.005 and 0.005 and  $S_b$  0.005 and 0.010  $\mu\text{g L}^{-1}$ , respectively. The methods of analysis are in good control.

**Carbendazim** (thiophanate-methyl degradation product): the degradation product was introduced in the programme in October 2018 and the statistical data relies on 35 duplicate samples. Last year, carbendazim had a ratio above two (6.5), but this year the  $S_b/S_w$  ratio is lowered (1.9), due to a low between-day deviation ( $S_b$ : 0.010  $\mu\text{g L}^{-1}$ ) compared to a relatively high  $S_w$  (0.054  $\mu\text{g L}^{-1}$ ). However, carbendazim has an acceptable total standard deviation  $S_t$  of 0.055  $\mu\text{g L}^{-1}$  and the analysis has improved during the reporting period and is in good control.

**CGA287422**, **CGA290291**, **CGA294972** and **PPA** (propaquizafop degradation products): the degradation products were introduced in the programme in April 2019. The three degradation products CGA287422, CGA294972 and PPA all have a chiral centre. As the analytical method used for analysis of the compounds does not separate the *R*- and *S*-forms, the differentiation of the *R/S*-forms in the samples cannot be done. The product (Agil 100 EC) applied in the field contains propaquizafop only in its *R*-form. The statistical data analysis of CGA287422, CGA290291 and CGA294972 relies on 22 duplicate samples, and 24 for PPA. The analyses of all four degradation products have  $S_b/S_w$  ratios < 2.0 and very low within-day and between-day deviations with  $S_w$  0.004-0.005,  $S_b$  0.003-0.006 and  $S_t$  is ranging from 0.005-0.008  $\mu\text{g L}^{-1}$ . The methods of analysis are in good control.

**IN-KF311** (flupyrsulfuron-methyl degradation product): the degradation product was introduced in the programme in October 2017. In October 2019, the concentration in the internal control samples was changed from 0.1  $\mu\text{g L}^{-1}$  to 0.05  $\mu\text{g L}^{-1}$ . Only data for the latter concentration was used for this year's statistical analysis. The statistical analysis of IN-KF311 relies on 22 duplicate samples. The analytical procedure of IN-KF311 improved compared to previous years. The  $S_b/S_w$  ratio is now 1.7, and both the between-day ( $S_b$  0.011  $\mu\text{g L}^{-1}$ ) and with-in day ( $S_w$  0.006  $\mu\text{g L}^{-1}$ ) decreased. The method of analysis is in good control.

**IN-MM671** and **IN-MM991** (proquinazid degradation products): both degradation products were introduced in the programme in April 2019. The data analyses rely on 29 duplicate samples. IN-MM671 has a  $S_b/S_w$  ratio > 2.0 (3.4), but the analytical method is actually in very good control with low standard deviations ( $S_w$ , 0.003,  $S_b$  0.009 and  $S_t$  0.010  $\mu\text{g L}^{-1}$ ) on the analysis of control samples with a concentration of 0.05  $\mu\text{g L}^{-1}$ . IN-MM991 has a  $S_b/S_w$  ratio < 2.0 and low standard deviations and the method of analysis is in good control.

**Metamitron** and its degradation products **MTM-126-AMT** and **desamino-metamitron**: in May 2018, metamitron and desamino-metamitron were reintroduced in the programme and MTM-126-AMT was introduced for the first time in May 2018. The data analyses are based on 22 duplicate

samples. All three compounds have a  $S_b/S_w$  ratio  $< 2.0$  and the analytical methods are in very good control with very low standard deviations ranging from:  $S_w$  0.002-0.005,  $S_b$  0.003-0.006 and  $S_t$  0.004-0.008  $\mu\text{g L}^{-1}$ .

**Metconazole:** The compound was introduced in the monitoring programme in April 2019. The data analysis is based on 26 duplicate samples. Metconazole has a  $S_b/S_w$  ratio  $< 2.0$  and very low within-day, between-day and total deviations:  $S_w$  0.003,  $S_b$  0.004 and  $S_t$  0.005  $\mu\text{g L}^{-1}$ . The method of analysis is in good control.

**Picloram:** The compound was introduced in the programme in November 2019. The data analysis of picloram is based on 22 duplicate samples. Picloram has a  $S_b/S_w$  ratio  $< 2.0$  and very low within-day and between-day and total deviations:  $S_w$  0.003,  $S_b$  0.003 and  $S_t$  0.004  $\mu\text{g L}^{-1}$ . The method of analysis is in good control.

**Propyzamide** and its degradation products **RH-24580** and **RH-24644**: propyzamide was reintroduced in the monitoring programme in October 2018 and the two degradation products in October 2019. The data analysis of propyzamide is based on 40 duplicate samples and 21 duplicate samples for RH-24580 and RH-24644. All three compounds have  $S_b/S_w$  ratios  $< 2.0$ . Propyzamide and RH-24644 have very low within-day and between-day deviations:  $S_w$  0.004 and 0.004,  $S_b$  0.005 and 0.006,  $S_t$  0.006, and 0.007  $\mu\text{g L}^{-1}$ , respectively. The methods of analysis are in good control. The within-day deviation for RH-24580 is slightly higher (0.059  $\mu\text{g L}^{-1}$ ), which is due to the difference within the duplicates, but results are still within the acceptance criteria for the method. The between-day deviation is low ( $S_b$  0.009  $\mu\text{g L}^{-1}$ ) and the method of analysis is in good control.

**TSA** (florasulam degradation product): the degradation product was introduced in the monitoring programme in April 2017. The statistical analysis is based on 29 duplicate samples. The analytical method was optimized since last year. TSA has a  $S_b/S_w$  ratio  $< 2.0$  and very low within-day, between-day and total deviations:  $S_w$  0.003,  $S_b$  0.005 and  $S_t$  0.005  $\mu\text{g L}^{-1}$ . The method of analysis is in good control.

**X-757** and **X-729** (halauxifen-methyl degradation products): the degradation products X-757 and X-729 were introduced in the monitoring programme in April 2017 and 2019, respectively. As the statistical analysis presented in this report is based on data from June 2019 to July 2020 and monitoring of X-757 ended in June 2019, the data analysis for X-757 presented here is only based on five duplicate samples and thus not sufficient to do a thorough statistical analysis. Data should therefore be considered tentatively. Last year, the analytical procedure for X-757 was improved. The between-day deviation of X-757 decreased from  $S_b$  0.045 to  $S_b$  0.017  $\mu\text{g L}^{-1}$  and from Figure A6.8 it seems the method has stabilised. In the year July 2018- July 2019, the  $S_b/S_w$  ratio was 1.4, which was an improvement from the year before where the ratio was  $> 2$ . In this years' reporting period, high  $S_b/S_w$  ratio (9.4) reflects the very low number of samples in the dataset. The relatively high in-between day variation is caused by deviations in one duplicate sample pair. However, the method of analysis met the criterion of normality in last years' reporting period and is in good control. The data analysis of X-729 is based on 32 duplicate samples. X-729 has a  $S_b/S_w$  ratio  $< 2.0$  and low within-day, between-day and total deviations:  $S_w$  0.007,  $S_b$  0.005, and  $S_t$  0.009  $\mu\text{g L}^{-1}$ , why the method of analysis is in good control.



**Table 8.3.** Internal QA of analysis of pesticides and *degradation products* carried out in the period 1.7.2019-30.6.2020. For each compound, the following are presented: 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), the number of duplicate samples (n) and compound concentration in internal QC sample (Conc.). The P-value  $\alpha=0.05$  was used for testing.

Compound	Normal distribut.	Significant $S_b$ between-day contribut.	$S_w$ ( $\mu\text{g L}^{-1}$ )	$S_b$ ( $\mu\text{g L}^{-1}$ )	$S_t$ ( $\mu\text{g L}^{-1}$ )	Ratio $S_b/S_w$	n	Conc. ( $\mu\text{g L}^{-1}$ )
<i>1,2,4-triazole</i>	Yes	-	0.002	0.002	0.003	1.0	49	0.03
<i>AE-F099095</i>	0.000	-	0.004	0.004	0.006	1.0	36	0.05
<i>AE-F147447</i>	0.016	-	0.005	0.007	0.008	1.4	24	0.05
<i>AE-F160459</i>	0.009	-	0.006	0.015	0.016	<b>2.6</b>	34	0.05
<i>AE1394083</i>	0.000	Yes	0.007	0.003	0.008	0.5	22	0.05
<i>AMPA</i>	Yes	Yes	0.005	0.001	0.005	0.3	4	0.03
<i>BH 517-T2SO2</i>	0.017	-	0.005	0.005	0.008	1.0	31	0.05
<i>CGA287422</i>	Yes	-	0.004	0.004	0.005	1.0	21	0.05
<i>CGA290291</i>	Yes	-	0.005	0.006	0.008	1.0	21	0.05
<i>CGA294972</i>	Yes	-	0.005	0.006	0.007	1.2	21	0.05
Carbendazim	0.000	Yes	0.054	0.010	0.055	0.2	35	0.05
<i>Desamino-metamitron</i>	0.019	-	0.002	0.003	0.004	1.9	22	0.05
<i>EZ-BH 517-TSO</i>	0.018	-	0.005	0.010	0.011	1.9	31	0.05
Glyphosate	Yes	-	0.002	0.006	0.006	2.6	4	0.03
<i>IN-KF311</i>	0.000	-	0.006	0.011	0.012	1.7	22	0.05
<i>IN-MM671</i>	0.000	-	0.003	0.009	0.010	<b>3.4</b>	29	0.05
<i>IN-MM991</i>	Yes	-	0.006	0.005	0.008	0.8	29	0.05
<i>MTM-126-AMT</i>	0.000	-	0.005	0.006	0.008	1.2	22	0.05
Metamitron	0.000	-	0.004	0.003	0.005	0.7	22	0.05
Metconazole	Yes	-	0.003	0.004	0.005	1.2	26	0.05
<i>PPA</i>	Yes	Yes	0.005	0.003	0.006	0.6	24	0.05
Picloram	0.000	-	0.003	0.003	0.004	0.9	22	0.05
Propyzamide	0.000	-	0.004	0.005	0.006	1.4	40	0.05
<i>RH-24580</i>	0.000	Yes	0.059	0.009	0.060	0.2	21	0.05
<i>RH-24644</i>	Yes	-	0.004	0.006	0.007	1.6	21	0.05
<i>TSA</i>	0.033	-	0.003	0.005	0.005	1.7	29	0.03
<i>X-729</i>	Yes	-	0.007	0.005	0.009	0.8	32	0.05
<i>X-757</i>	0.028	-	0.005	0.045	0.045	<b>9.4</b>	5	0.1

$S_t$  of the various analyses of pesticides and degradation products is within the range of 0.002-0.055  $\mu\text{g L}^{-1}$  with the highest values observed for carbendazim, RH-24580 and X-757. In general, the data suggest that the analytical method used for quantification of the compounds are acceptable and has improved or is in line with last year's reported programme. There is however still room for improvement and optimisation of, especially, the between-day variation ( $S_b$ ) for some of the compounds.

### 8.2.3 External QA

As described above the external QA program was based on samples spiked in the field. As part of the quality control, a set of blank samples consisting of HPLC water were prepared in the field and analysed to evaluate the possibility of false-positive findings. From these results, it can be concluded that contamination of samples during collection, storage and analysis is not likely to occur. A total of 21 blank samples were analysed and no compounds were detected in any of these analysed blank samples. Therefore, samples analysed in the monitoring program and detected to contain pesticides and/or degradation products are regarded as true positive findings.

**Table 8.3.** Recovery of externally spiked samples was carried out in the period 1.7.2019-30.6.2020. Average recovery (%) of the nominal concentration at low/high concentration level is indicated for each field. For each compound, Det.,  $n_{low}$ , and  $n_{high}$  refer to the number of samples with detections of 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 control samples). Bold font is used for recoveries outside the range of 70-120%.

Compound/Field*	Jynde vad %		Silstrup %		Estrup %		Faardrup %		Lund %		Avg. %	Det. $n_{low}/$ $n_{high}$	$n_{total}$ analysed
	Low	High	Low	High	Low	High	Low	High	Low	High			
1,2,4-triazole	<b>142</b>	102	<b>126</b>	100	<b>138</b>	114	<b>159</b>	111	<b>122</b>	97	120	14/14	28
AE-F099095	81	80	86	86	86	90					85	6/6	12
CGA290291			97	90							93	2/2	4
Desamino-metamitron							104	84			94	1/1	2
Metconazole					97	90					94	3/3	6
Propyzamide			95	88					121	99	100	6/6	12
TSA			94	74	-**	74			<b>138</b>	88	102	4/5	10

\*The Tylstrup field was set on standby at the end of 2018, hence no Q-data is available.

\*\* TSA concentration in QC Low sample at Estrup was  $< 0.01 \mu\text{g L}^{-1}$ .

Table 8.3 provides an overview of the recovery of all externally spiked samples. Since the results for each field in Table 8.3 are based on very few observations for each concentration level (high/low) and that each concentration level is not spiked in duplicate in the fields, the data should be interpreted with precaution and not too rigorously. Unfortunately, as the year 2019 was dry at Faardrup, water was scarce. Consequently, externally spiked samples could only be prepared twice (February and April 2020) as no groundwater was available at the first control sample event in October 2019.

A total of 28 samples were spiked in this reporting period. In general, the recovery of the spiked compounds is acceptable (i.e. in the range of 70% to 120%). This year, only 1,2,4-triazole and TSA have recoveries  $> 120\%$ . Water used for making the spiked samples is taken on location from upstream wells. For this reason, minor background content may be present in some of the water used for spiking. For the low-level QC samples, in particular, this background content of the specific compound can cause an elevated recovery percentage. For this reason, the QC data must be considered tentatively and used only to keep track of possible changes in the quality of the program from period to period.

In 2015, a new procedure was implemented in the QA programme. Subsequently, every year upon arrival of the new ampoules and when the last QC sample event is done, the concentration of the compounds in the ampoules is confirmed by the commercial laboratory. This procedure was implemented due to the previous experience with the flawed production of AMPA and glyphosate ampoules. This year, this procedure revealed that the concentrations of AE1394083, E/Z BH 517-TSO, and X-729 were out of range of the acceptable initial concentration in the ampoules and the concentrations decreased further over time.

In general, all recoveries of the low external QC (concentration in  $QC_{low}$  is  $0.05 \mu\text{g L}^{-1}$ ) are within the acceptable range of 70-120%, except for 1,2,4-triazole (in all fields) and TSA (in Lund).

The degradation product 1,2,4-triazole (from azoles) has an elevated recovery of up to 159% ( $QC_{low}$  at Faardrup) and recoveries in all  $QC_{low}$  samples were around 120% or above. The high recoveries reflect the background concentration (ranging from  $0.015$  to  $0.052 \mu\text{g L}^{-1}$ ) of 1,2,4-triazole in the water from all monitoring wells used for preparation of the spiked samples. The recoveries of 1,2,4-triazole rely on 28 spiked samples and in combination with the internal QC samples, the QA program confirms that the analytical method is in good control and fulfils all criteria (Table 8.2 and Appendix 6, Figure A6.1).

The recovery of TSA (degradation product of florasulam) in the externally spiked QC<sub>Low</sub> sample at Lund is higher than acceptable (138%). This elevated recovery is not due to a background content of TSA in the groundwater and cannot be explained. All other QC samples (except one QC<sub>Low</sub> sample from Estrup with TSA concentration < 0.01 µg L<sup>-1</sup>) were within the acceptable range, and the internal QC data shows that the analytical method for TSA is acceptable and in good control.

All compounds included in the external spiking procedure (Table 8.1) are detected in all spiked QC samples by the commercial laboratory. The external and internal QA data plots relating to pesticides and degradation products reported here are presented in Appendix 6.

### 8.3 Summary and concluding remarks

The QA system showed that:

- Analysis results of compounds in waters samples collected in the periods defined in table 8.2 should be considered tentatively as the samples were frozen before analysis (-20°C), due to delays in both the procurement of the analytical standards and consequently analytical method development. The influence of freezing on the quality of analyses is currently investigated.
- The low total standard deviation ( $S_t$ ) (ranging from 0.003 to 0.060 µg L<sup>-1</sup>) on the internal QC data indicates that the reproducibility of the analyses is in general very good.
- The recovery of compounds in externally spiked samples (External QA) is generally precise (within 70 to 120% recovery), except for 1,2,4-triazole (recoveries in all QC<sub>Low</sub> samples > 120%) and TSA (only one QC<sub>Low</sub> sample with a high recovery of 138%).
- The recovery of 1,2,4-triazole in the External QA samples was higher than the defined criteria (recovery of 70 to 120%) in all QC<sub>Low</sub> samples, but the discrepancy relates to the background content of 1,2,4-triazole in the groundwater used for preparation of the spiked external QA samples. Both the QA programme and the analytical methods were in good control.
- Three of the compounds (AE1394083, E/Z BH 517-TSO, and X-729) selected for External QA were not stable in the mixed ampoule solution used for spiking of the external QC samples and therefore excluded from the External QA programme.
- Based on the results from analysis of blank samples, consisting of HPLC water (shipped together with the true monitoring samples), it was concluded that contamination of samples during collection, storage, and analysis was not likely to occur. No false-positive samples were detected.



## 9 Leaching results from the entire monitoring period

In this report, the evaluation of compounds comprising the full monitoring period from 1999 to July 2020 is omitted due to structural changes in the report. Likewise, the table with colour-codings (Table 9.1 and 9.3 in previous PLAP reports) is currently being updated. The upcoming report will again include a historical perspective together with a colour-coded table. A complete summary of previous monitoring data from the entire monitoring period covering 1999 to July 2019 is available in the previous report, Rosenbom *et al.* 2021 (available online at [www.plap.dk](http://www.plap.dk)). For the full perspective of the monitoring period including July 2019 to July 2020, the authors advise reading chapters 2 to 7 in this report as a continuation of chapter 9 in the previous report. All previous reports and associated peer-reviewed articles can be found at [www.plap.dk](http://www.plap.dk).

Until June 2020, 151 pesticides and/or degradation products (52 pesticides and 99 degradation products) have been analysed in PLAP comprising six agricultural fields (ranging between 1.2 and 2.4 ha in size) cultivated with different crops. 22 new compounds have been added for evaluation in the period July 2018-June 2020.

A summary of all monitoring data from the variably saturated zone (drainage and suction cups at 1 mbgs) is presented in Table 9.1, and from groundwater in Table 9.2. A detailed description of monitoring results for each field is summarised in Appendix 5.

**Table 9.1.** Monitoring results from 1999 to 2020 from the variably saturated zone (drainage and suction cups at 1 m depth, suction cups at Tylstrup at 2 m depth). Total number of analysed samples (n), number of samples with detections (Det.), number of samples with detections in concentrations > 0.1 µg L<sup>-1</sup> and the maximum detected concentration (Max µg L<sup>-1</sup>). The pesticide and degradation products are listed under Analyte. All listed pesticides are applied in PLAP, but for some, only monitoring of the degradation product(s) was included in the programme.

Analyte	Tylstrup				Jyndevad				Silstrup				Estrup				Faardrup				Lund			
	n	Det.	>0.1 µg L <sup>-1</sup>	Max µg L <sup>-1</sup>	n	Det.	>0.1 µg L <sup>-1</sup>	Max µg L <sup>-1</sup>	n	Det.	>0.1 µg L <sup>-1</sup>	Max µg L <sup>-1</sup>	n	Det.	>0.1 µg L <sup>-1</sup>	Max µg L <sup>-1</sup>	n	Det.	>0.1 µg L <sup>-1</sup>	Max µg L <sup>-1</sup>	n	Det.	>0.1 µg L <sup>-1</sup>	Max µg L <sup>-1</sup>
<b>Acetamiprid</b>																								
IM-1-4 <sup>v</sup>					6	0	0	-																
IM-1-5 <sup>v</sup>					6	0	0	-																
<b>Aclonifen</b>	68	0	0	-	43	0	0	-																
<b>Amidosulfuron</b>					23	3	1	0.11	1	0	0	-	100	0	0	-								
desmethyl-amidosulfuron					23	0	0	-	1	0	0	-												
<b>Aminopyralid</b>	91	0	0	-									96	0	0	-								
<b>Azoxystrobin</b>	95	0	0	-	65	0	0	-	188	23	1	0.11	415	141	15	1.4	106	0	0	-	27	3	0	0.077
CyPM	95	0	0	-	65	0	0	-	211	152	24	0.56	415	376	150	2.1	106	4	0	0.059	25	19	3	0.43
<b>Bentazone</b>	202	4	0	0.022	230	109	17	4.5	120	45	5	6.4	440	226	16	20	202	28	6	43	27	6	0	0.05
2-amino-N-isopropyl-benzamide	72	0	0	-	47	2	0	0.034	65	0	0	-	243	1	0	0.06	68	1	0	0.057				
6-hydroxy-bentazone	65	0	0	-	43	0	0	-													22	0	0	-
8-hydroxy-bentazone	65	0	0	-	43	0	0	-													22	0	0	-
N-methyl-bentazone	65	0	0	-	43	0	0	-													22	1	0	0.022
<b>Bifenox</b>	22	0	0	-	56	2	0	0.036	68	5	2	0.38	95	4	1	0.15	62	6	0	0.085				
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	-	62	6	1	0.16				
<b>Boscalid</b>	56	0	0	-																				
<b>Bromoxynil</b>	72	0	0	-	61	0	0	-	48	0	0	-	142	3	2	0.6	174	0	0	-				
<b>Chlormequat</b>					28	0	0	-	21	1	0	0.01	46	1	0	0.017								
<b>Clomazone</b>	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	0.3				
<b>Clopyralid</b>	107	2	1	0.72					79	4	3	4.094	1	0	0	-	32	1	0	0.076				
<b>Cyazofamid</b>	68	0	0	-	32	0	0	-																
DMSA <sup>v</sup>					6	0	0	-																
N,N-DMS <sup>v</sup>					6	0	0	-																
CCIM <sup>v</sup>					6	0	0	-																
CTCA <sup>v</sup>					6	0	0	-																
<b>Cycloxydim</b>																								
BH 517-T2SO2					39	0	0	-	43	0	0	-												
EZ-BH 517-TSO					39	11	3	0.53	43	9	1	0.11												
<b>Desmedipham</b>									159	0	0	-					128	0	0	-				
EHPC									100	0	0	-					99	0	0	-				
<b>Diffenican</b>					38	0	0	-	66	11	1	0.12	57	27	12	0.49								
AE-B107137					52	0	0	-	61	5	1	0.13	58	18	0	0.088								
AE-0542291					38	0	0	-	66	0	0	-	57	0	0	-								
<b>Dimethoate</b>	65	0	0	-	52	0	0	-	109	1	1	1.417	111	0	0	-	77	0	0	-				
<b>Epoxiconazole</b>	74	0	0	-	90	0	0	-	36	0	0	-	49	14	2	0.39	81	0	0	-				
<b>Ethofumesate</b>									201	20	3	0.227	126	35	8	3.362	192	15	6	12				
<b>Fenpropimorph</b>	89	0	0	-	79	1	0	0.038	109	0	0	-	106	1	0	0.01	174	0	0	-				
Fenpropimorph acid	75	0	0	-	79	0	0	-	109	1	0	0.019	103	0	0	-	174	0	0	-				
<b>Flamprop-M-isopropyl</b>	65	0	0	-					109	12	1	0.109	155	20	0	0.069	71	1	0	0.037				
Flamprop	65	0	0	-					108	7	0	0.096	155	13	0	0.031	77	1	0	0.089				

Analyte	Tylstrup				Jyndeved				Silstrup				Estrup				Faardrup				Lund			
	n	Det.	>0.1 µg L <sup>-1</sup>	Max µg L <sup>-1</sup>	n	Det.	>0.1 µg L <sup>-1</sup>	Max µg L <sup>-1</sup>	n	Det.	>0.1 µg L <sup>-1</sup>	Max µg L <sup>-1</sup>	n	Det.	>0.1 µg L <sup>-1</sup>	Max µg L <sup>-1</sup>	n	Det.	>0.1 µg L <sup>-1</sup>	Max µg L <sup>-1</sup>	n	Det.	>0.1 µg L <sup>-1</sup>	Max µg L <sup>-1</sup>
<b>Florasulam</b>					54	0	0	-					92	0	0	-								
Florasulam-desmethyl					28	0	0	-					81	0	0	-								
TSA									58	0	0	-					35	0	0	-	30	0	0	-
5-OH-florasulam <sup>✓</sup>									2	0	0	-												
DFP-ASTCA <sup>✓</sup>									2	0	0	-												
DFP-TSA <sup>✓</sup>									2	0	0	-												
<b>Fluazifop-P-butyl</b>																	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	-				
<b>Fludioxonil</b>																								
CGA 192155	65	0	0	-	34	0	0	-																
CGA 339833	65	0	0	-	34	0	0	-																
<b>Flupyrsulfuron-methyl</b>					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	-				
IN-KF311					31	0	0	-	69	0	0	-												
IN-JE127 <sup>III</sup>					31	0	0	-	41	0	0	-												
<b>Fluroxypyr</b>	70	0	0	-	55	0	0	-	50	0	0	-	90	3	2	1.4	256	1	1	0.19				
Fluroxypyr-methoxypyridine																	29	0	0	-				
Fluroxypyr-pyridinol																	29	0	0	-				
<b>Foramsulfuron</b>									75	10	2	0.24	92	20	3	0.32								
AE-F092944					2	0	0	-	75	0	0	-	92	1	0	0.012								
AE-F130619									75	10	0	0.067	92	6	0	0.055								
<b>Glyphosate</b>					72	0	0	-	257	108	22	4.7	601	343	109	31	236	5	0	0.093	33	21	8	8.6
AMPA					72	1	0	0.014	258	203	18	0.35	601	499	120	1.6	236	15	1	0.11	33	26	5	1.3
<b>Haluxifen-methyl</b>																								
X-757									53	0	0	-					34	0	0	-				
X-729													30	0	0	-	1	0	0	-	22	0	0	-
<b>Iodosulfuron-methyl-natrium</b>																								
Iodosulfuron-methyl									60	0	0	-												
Metsulfuron-methyl									60	0	0	-	154	1	0	0.054								
<b>Ioxynil</b>	72	0	0	-	61	0	0	-	48	0	0	-	142	20	5	0.25	173	1	0	0.011				
<b>Linuron</b>	67	0	0	-																				
<b>Mancozeb</b>																								
EBIS	27	0	0	-	10	0	0	-																
ETU	44	7	0	0.038																				
<b>MCPA</b>					56	0	0	-	51	0	0	-	103	12	2	3.894	143	2	1	0.28				
2-methyl-4-chlorophenol					56	0	0	-	51	0	0	-	103	1	0	0.046	143	1	1	0.24				
<b>Mesosulfuron-methyl</b>					78	0	0	-					75	13	0	0.059								
Mesosulfuron					45	0	0	-					74	0	0	-								
AE-F147447					46	0	0	-	51	0	0	-	20	0	0	-								
AE-F099095	54	0	0	-	43	0	0	-	51	0	0	-	48	0	0	-								
AE-F160459	54	0	0	-	43	0	0	-	51	0	0	-	48	0	0	-								
<b>Mesotrione</b>					67	0	0	-	76	13	7	1.1	93	40	10	3.3								
AMBA					67	0	0	-	76	0	0	-	93	4	0	0.039								
MNBA					67	0	0	-	76	8	0	0.09	93	11	1	0.46								

Analyte	Tylstrup				Jynde vad				Silstrup				Estrup				Faardrup				Lund			
	n	Det.	>0.1 µg L <sup>-1</sup>	Max µg L <sup>-1</sup>	n	Det.	>0.1 µg L <sup>-1</sup>	Max µg L <sup>-1</sup>	n	Det.	>0.1 µg L <sup>-1</sup>	Max µg L <sup>-1</sup>	n	Det.	>0.1 µg L <sup>-1</sup>	Max µg L <sup>-1</sup>	n	Det.	>0.1 µg L <sup>-1</sup>	Max µg L <sup>-1</sup>	n	Det.	>0.1 µg L <sup>-1</sup>	Max µg L <sup>-1</sup>
<b>Metalaxyl-M</b> CGA 108906 CGA 62826	156	4	0	0.03	95	11	0	0.037																
	153	128	35	4.8	105	68	34	3.7																
	154	35	5	0.12	105	73	20	1.2																
<b>Metamitron</b> Desamino-metamitron MTM-126-AMT									200	49	11	0.551	123	42	15	26.369	228	12	2	1.7				
									201	64	7	0.67	125	49	11	5.549	228	16	4	2.5				
																	33	0	0	-				
<b>Metconazole</b>													30	0	0	-								
<b>Metrafenone</b>													120	20	0	0.072	59	0	0	-				
<b>Metribuzin</b> Desamino-diketo-metribuzin Desamino-metribuzin Diketo-metribuzin	91	2	0	0.024	6	0	0	-																
	249	81	51	2.1	6	0	0	-																
	87	0	0	-	4	0	0	-																
	334	253	61	0.69	6	3	0	0.088																
<b>Pendimethalin</b>	144	0	0	-	71	0	0	-	105	14	0	0.064	243	72	29	32	57	2	0	0.041				
<b>Phenmedipham</b> 3-aminophenol MHPC									160	0	0	-					128	0	0	-				
									109	0	0	-												
									160	0	0	-					128	2	1	0.19				
<b>Picloram</b>									1	0	0	-					1	0	0	-	19	1	0	0.011
<b>Picolinafen</b> CL153815					36	1	0	0.015					81	17	0	0.07								
					36	0	0	-					81	31	11	0.5								
<b>Pirimicarb</b> Pirimicarb-desmethyl Pirimicarb-desmethyl-formamido	82	0	0	-	69	0	0	-	233	14	0	0.054	205	40	0	0.077	228	7	0	0.056				
	81	0	0	-	69	1	0	0.011	233	1	0	0.052	198	0	0	-	129	6	0	0.053				
	52	0	0	-	69	0	0	-	161	0	0	-	230	26	13	0.379	129	3	0	0.039				
<b>Propaquizafop</b> CGA287422 CGA294972 CGA290291 PPA									32	0	0	-												
									32	0	0	-												
									32	0	0	-												
									32	0	0	-												
<b>Propiconazole</b>	89	0	0	-	89	0	0	-	109	6	0	0.033	241	26	3	0.862	251	0	0	-				
<b>Propyzamide</b> RH-24580 RH-24644 RH-24655	82	0	0	-					114	38	12	5.1	5	0	0	-	125	4	2	0.51	21	9	3	0.41
	82	0	0	-					66	2	0	0.016					125	0	0	-	21	0	0	-
	82	0	0	-					66	15	0	0.051					125	4	0	0.022	21	2	1	0.11
	58	0	0	-					66	0	0	-					124	1	0	0.017				
<b>Proquinazid</b> IN-MM671 IN-MM991					30	0	0	-	1	0	0	-					39	0	0	-				
					30	0	0	-	1	0	0	-					39	0	0	-				
<b>Prosulfocarb</b>	74	1	0	0.03					74	5	1	0.18					78	0	0	-				
<b>Pyridate</b> PHCP					39	0	0	-																
					59	0	0	-	66	4	4	2.69												
<b>Pyroxsulam</b> Amitrol <sup>IV</sup> PSA <sup>V</sup> 6-Cl-7-OH-XDE-742 <sup>V</sup> 5-OH-XDE-742 <sup>V</sup> 7-OH-XDE-742 <sup>V</sup> Pyridine sulfonamide <sup>V</sup>									3	0	0	-												
									2	0	0	-												
									2	0	0	-												
									2	0	0	-												
									2	0	0	-												
									2	0	0	-												
<b>Rimsulfuron</b> PPU PPU-desamino	65	0	0	-	52	0	0	-																
	268	194	3	0.15	233	194	64	0.29	1	0	0	-												
	268	63	0	0.042	233	123	6	0.18	1	0	0	-												



Analyte	Tylstrup				Jyndevad				Silstrup				Estrup				Faardrup				Lund			
	n	Det.	>0.1 µg L <sup>-1</sup>	Max µg L <sup>-1</sup>	n	Det.	>0.1 µg L <sup>-1</sup>	Max µg L <sup>-1</sup>	n	Det.	>0.1 µg L <sup>-1</sup>	Max µg L <sup>-1</sup>	n	Det.	>0.1 µg L <sup>-1</sup>	Max µg L <sup>-1</sup>	n	Det.	>0.1 µg L <sup>-1</sup>	Max µg L <sup>-1</sup>	n	Det.	>0.1 µg L <sup>-1</sup>	Max µg L <sup>-1</sup>
<b>Tebuconazole</b> 1,2,4-triazole <sup>i</sup>	77	0	0	-	58	0	0	-	19	2	0	0.084	81	41	17	2	54	4	0	0.045	32	31	0	0.062
	98	20	2	0.16	123	75	9	0.27	82	81	6	0.17	186	185	175	0.45	106	103	4	0.2				
<b>Terbuthylazine</b> 2-hydroxy-desethyl-terbuthylazine	72	0	0	-	79	0	0	-	91	60	9	1.55	161	112	34	11	110	41	11	10				
Desethyl-terbuthylazine	72	5	0	0.016	150	20	0	0.056	71	28	1	0.11	131	87	24	6.3	68	8	1	1				
Desisopropylatrazine	72	2	0	0.012					116	108	44	1.08	164	146	35	8.2	110	89	7	8.3				
Hydroxy-terbuthylazine	72	17	0	0.042					71	43	0	0.041	161	71	1	0.44	110	25	1	0.36				
	72	1	0	0.04					71	26	0	0.039	131	88	16	0.99	110	21	1	0.58				
<b>Thiacloprid</b> M34 Thiacloprid sulfonic acid Thiacloprid-amide													47	0	0	-								
													55	0	0	-								
													56	0	0	-								
													47	1	0	0.012								
<b>Thiamethoxam</b> CGA 322704	64	0	0	-													68	0	0	-				
	64	0	0	-													68	0	0	-				
<b>Thiencarbazone-methyl</b> AE1394083																	35	0	0	-				
<b>Thiophanate-methyl</b> Carbendazim					42	0	0	-					54	3	0	0.015								
<b>Triasulfuron</b> Triazinamin <sup>ii</sup>	82	0	0	-																				
	76	0	0	-					88	0	0	-	210	0	0	-								
<b>Tribenuron-methyl</b> Triazinamin-methyl	138	0	0	-	77	0	0	-	109	0	0	-	55	2	0	0.042	77	0	0	-				
<b>Triflurosulfuron-methyl</b> IN-D8526 IN-E7710 IN-M7222									32	0	0	-					63	0	0	-				
									32	5	0	0.014					63	0	0	-				
									32	0	0	-					63	0	0	-				
									32	0	0	-					63	0	0	-				

<sup>i</sup> Can include 1,2,4-triazole degraded from the pesticides: epoxiconazole, propiconazole, prothioconazole and metconazole.

<sup>ii</sup> Can include triazinamin/IN-A4098 degraded from iodosulfuron-methyl, metsulfuron-methyl, tribenuron-methyl, triflurosulfuron-methyl.

<sup>iii</sup> IN-JE127 (degradation product from flupyrsulfuron-methyl) is unstable in aquatic solution – Results should be disregarded.

<sup>iv</sup> Amitrol was included in the monitoring of pyroxsulam as it was suspected to be a groundwater pollutant in the Danish groundwater monitoring programme (GRUMO) in relation to the yearly screenings in 2019. Pyroxsulam was therefore tested as a theoretical source of origin to amitrol. The findings of amitrol in the groundwater screening were later shown to be an analytical artefact and the monitoring of amitrol in PLAP was thus suspended.

<sup>v</sup> The compound was included in PLAP in spring 2020. Data evaluation is not included in this report but will be discussed in next year's report covering 2019-2021.

**Table 9.2.** Monitoring results from 1999 to 2020 from the groundwater (1.5-9 mbgs). Total number of analysed samples (n), number of samples with detections (Det.), number of samples with detections in concentrations > 0.1 µg L<sup>-1</sup> and the maximum detected concentration (Max µg L<sup>-1</sup>). The pesticide and degradation products are listed under Analyte. All listed pesticides are applied in PLAP, but for some, only monitoring of the degradation product(s) was included in the programme.

Analyte	Tylstrup				Jydelevad				Silstrup				Estrup				Faardrup				Lund			
	n	Det.	>0.1 µg L <sup>-1</sup>	Max µg L <sup>-1</sup>	n	Det.	>0.1 µg L <sup>-1</sup>	Max µg L <sup>-1</sup>	n	Det.	>0.1 µg L <sup>-1</sup>	Max µg L <sup>-1</sup>	n	Det.	>0.1 µg L <sup>-1</sup>	Max µg L <sup>-1</sup>	n	Det.	>0.1 µg L <sup>-1</sup>	Max µg L <sup>-1</sup>	n	Det.	>0.1 µg L <sup>-1</sup>	Max µg L <sup>-1</sup>
<b>Acetamiprid</b>																								
IM-1-4 <sup>v</sup>					26	0	0	-																
IM-1-5 <sup>v</sup>					26	0	0	-																
<b>Aclonifen</b>	127	0	0	-	171	0	0	-																
<b>Amidosulfuron</b>					88	0	0	-					143	0	0	-								
desmethyl-amidosulfuron					88	0	0	-																
<b>Aminopyralid</b>	213	3	0	0.058									152	0	0	-								
<b>Azoxystrobin</b>	216	0	0	-	233	0	0	-	644	8	0	0.025	766	3	0	0.04	286	0	0	-	240	0	0	-
CyPM	216	0	0	-	233	0	0	-	764	100	12	0.52	766	41	5	0.46	286	0	0	-	240	11	0	0.059
<b>Bentazone</b>	509	0	0	-	905	3	0	0.026	406	29	3	0.44	744	44	0	0.049	527	21	4	0.6	240	5	0	0.058
2-amino-N-isopropyl-benzamide	191	0	0	-	178	0	0	-	205	0	0	-	351	1	0	0.026	193	0	0	-				
6-hydroxy-bentazone	179	0	0	-	229	0	0	-													146	0	0	-
8-hydroxy-bentazone	179	0	0	-	229	0	0	-													146	0	0	-
N-methyl-bentazone	179	0	0	-	229	0	0	-													146	0	0	-
<b>Bifenox</b>	49	0	0	-	222	2	0	0.05	183	5	0	0.1	193	0	0	-	104	0	0	-				
Bifenox acid	49	0	0	-	170	0	0	-	182	27	20	3.1	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	-				
<b>Boscalid</b>	111	0	0	-																				
<b>Bromoxynil</b>	192	0	0	-	218	0	0	-	159	0	0	-	166	0	0	-	306	0	0	-				
<b>Chlormequat</b>					14	0	0	-	102	0	0	-	74	0	0	-								
<b>Clomazone</b>																								
FMC 65317	208	0	0	-	106	0	0	-	49	0	0	-	98	0	0	-	235	0	0	-				
<b>Clopyralid</b>	138	0	0	-					286	1	0	0.026					96	0	0	-				
<b>Cyazofamid</b>	127	0	0	-	135	0	0	-																
DMSA <sup>v</sup>					26	0	0	-																
N,N-DMS <sup>v</sup>					26	3	0	0.048																
CCIM <sup>v</sup>					26	0	0	-																
CTCA <sup>v</sup>					26	0	0	-																
<b>Cycloxydim</b>																								
BH 517-T2SO2					200	0	0	-	122	0	0	-												
EZ-BH 517-TSO					200	2	0	0.03	122	29	0	0.052												
<b>Desmedipham</b>									348	1	0	0.033					232	0	0	-				
EHPC									207	0	0	-					176	0	0	-				
<b>Diflufenican</b>					152	0	0	-	201	1	1	0.47	71	0	0	-								
AE-B107137					152	0	0	-	201	1	0	0.021	89	2	0	0.032								
AE-0542291					152	0	0	-	201	0	0	-	71	0	0	-								
<b>Dimethoate</b>	176	0	0	-	190	0	0	-	222	1	0	0.085	200	0	0	-	207	0	0	-				
<b>Epoxiconazole</b>	199	0	0	-	324	1	0	0.011	179	0	0	-	88	0	0	-	209	0	0	-				
<b>Ethofumesate</b>									529	5	0	0.038	204	0	0	-	362	31	6	1.4				
<b>Fenpropimorph</b>	313	0	0	-	258	1	0	0.029	222	0	0	-	189	0	0	-	306	1	0	0.015				
Fenpropimorph acid	276	0	0	-	264	0	0	-	222	0	0	-	158	0	0	-	306	0	0	-				
<b>Flamprop-M-isopropyl</b>	176	0	0	-					222	1	0	0.024	263	0	0	-	199	0	0	-				
Flamprop	176	0	0	-					222	0	0	-	263	0	0	-	207	0	0	-				

Analyte	Tylstrup				Jyndeved				Silstrup				Estrup				Faardrup				Lund			
	n	Det.	>0.1 µg L <sup>-1</sup>	Max µg L <sup>-1</sup>	n	Det.	>0.1 µg L <sup>-1</sup>	Max µg L <sup>-1</sup>	n	Det.	>0.1 µg L <sup>-1</sup>	Max µg L <sup>-1</sup>	n	Det.	>0.1 µg L <sup>-1</sup>	Max µg L <sup>-1</sup>	n	Det.	>0.1 µg L <sup>-1</sup>	Max µg L <sup>-1</sup>	n	Det.	>0.1 µg L <sup>-1</sup>	Max µg L <sup>-1</sup>
<b>Florasulam</b>					191	0	0	-					160	0	0	-								
Florasulam-desmethyl													130	0	0	-								
TSA									182	0	0	-	12	0	0	-	141	0	0	-	176	0	0	-
5-OH-florasulam <sup>v</sup>									18	0	0	-	12	0	0	-								
DFP-ASTCA <sup>v</sup>									18	0	0	-	12	0	0	-								
DFP-TSA <sup>v</sup>									18	0	0	-	12	0	0	-								
<b>Fluazifop-P-butyl</b>																	232	0	0	-				
Fluazifop-P	178	0	0	-	190	0	0	-	442	1	0	0.072					299	6	1	0.17				
TFMP	3	0	0	-	3	0	0	-	435	87	16	0.29					238	0	0	-				
<b>Fludioxonil</b>																								
CGA 192155	184	0	0	-	232	1	0	0.048																
CGA 339833	184	0	0	-	221	1	1	0.37																
<b>Flupyrsulfuron-methyl</b>					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	-				
IN-KF311					150	0	0	-	144	0	0	-	4	0	0	-								
IN-JE127 <sup>III</sup>					150	0	0	-	86	0	0	-	4	0	0	-								
<b>Fluroxypyr</b>	194	0	0	-	193	0	0	-	216	0	0	-	155	1	0	0.058	515	1	0	0.072				
Fluroxypyr-methoxypyridine																	146	0	0	-				
Fluroxypyr-pyridinol																	146	0	0	-				
<b>Foramsulfuron</b>									215	5	0	0.04	153	0	0	-								
AE-F092944					7	0	0	-	220	0	0	-	153	0	0	-								
AE-F130619									215	9	0	0.032	153	0	0	-								
<b>Glyphosate</b>					223	0	0	-	646	40	0	0.052	1017	53	6	0.67	451	5	0	0.025	219	2	0	0.015
AMPA					223	2	0	0.022	646	40	0	0.08	1018	8	0	0.07	451	2	0	0.029	218	4	0	0.015
<b>Haluxifen-methyl</b>																								
X-757									150	0	0	-					136	0	0	-				
X-729													62	0	0	-	4	0	0	-	80	0	0	-
<b>Iodosulfuron-methyl-natrium</b>																								
Iodosulfuron-methyl									250	0	0	-												
Metsulfuron-methyl									250	0	0	-	263	0	0	-								
<b>Ioxynil</b>	198	0	0	-	218	0	0	-	159	0	0	-	166	0	0	-	306	1	0	0.01				
<b>Linuron</b>	271	0	0	-																				
<b>Mancozeb</b>																								
EBIS	78	0	0	-	99	0	0	-																
ETU	200	2	0	0.024																				
<b>MCPA</b>					210	0	0	-	190	0	0	-	146	1	0	0.019	365	0	0	-				
2-methyl-4-chlorophenol					210	0	0	-	191	0	0	-	146	0	0	-	365	0	0	-				
<b>Mesosulfuron-methyl</b>					285	0	0	-					126	0	0	-								
Mesosulfuron					12	0	0	-					107	0	0	-								
AE-F147447	146	0	0	-	189	2	0	0.038	124	0	0	-	35	0	0	-								
AE-F099095	146	0	0	-	189	0	0	-	131	0	0	-	87	0	0	-	1	0	0	-				
AE-F160459					189	0	0	-	131	0	0	-	87	0	0	-	1	0	0	-				
<b>Mesotrione</b>					237	0	0	-	223	0	0	-	157	5	1	0.13								
AMBA					237	0	0	-	223	0	0	-	157	0	0	-								
MNBA					237	0	0	-	223	0	0	-	155	1	0	0.017								

Analyte	Tylstrup				Jyndeved				Silstrup				Estrup				Faardrup				Lund			
	n	Det.	>0.1	Max	n	Det.	>0.1	Max	n	Det.	>0.1	Max	n	Det.	>0.1	Max	n	Det.	>0.1	Max	n	Det.	>0.1	Max
			µg L <sup>-1</sup>	µg L <sup>-1</sup>			µg L <sup>-1</sup>	µg L <sup>-1</sup>			µg L <sup>-1</sup>	µg L <sup>-1</sup>			µg L <sup>-1</sup>	µg L <sup>-1</sup>			µg L <sup>-1</sup>	µg L <sup>-1</sup>			µg L <sup>-1</sup>	µg L <sup>-1</sup>
<b>Metalaxyl-M</b>	352	21	0	0.084	392	88	23	1.3																
CGA 108906	352	288	47	1.5	392	278	84	2.7																
CGA 62826	352	17	0	0.04	392	174	9	0.68																
<b>Metamitron</b>									529	29	2	0.168	204	0	0	-	474	24	4	0.63				
Desamino-metamitron									529	30	4	0.19	203	0	0	-	474	48	12	1.3				
MTM-126-AMT																	108	0	0	-				
<b>Metconazole</b>													64	0	0	-								
<b>Metrafenone</b>													189	1	0	0.04	168	0	0	-				
<b>Metribuzin</b>	388	1	0	0.014	26	0	0	-																
Desamino-diketo-metribuzin	525	236	5	0.204	26	20	13	1.831																
Desamino-metribuzin	366	0	0	-	26	0	0	-																
Diketo-metribuzin	526	453	315	0.554	26	26	19	1.372																
<b>Pendimethalin</b>	436	0	0	-	257	0	0	-	344	0	0	-	381	1	0	0.052	180	0	0	-				
<b>Phenmedipham</b>									348	0	0	-					232	2	0	0.025				
3-aminophenol									245	0	0	-												
MHPC									348	0	0	-					232	1	0	0.053				
<b>Picloram</b>																	4	0	0	-	42	0	0	-
<b>Picolinafen</b>					35	0	0	-					158	0	0	-								
CL153815					35	0	0	-					158	0	0	-								
<b>Pirimicarb</b>	301	0	0	-	251	0	0	-	646	3	0	0.011	293	1	0	0.015	437	2	0	0.035				
Pirimicarb-desmethyl	301	0	0	-	251	0	0	-	646	0	0	-	289	0	0	-	232	3	0	0.042				
Pirimicarb-desmethyl-formamido	173	0	0	-	251	0	0	-	468	0	0	-	337	0	0	-	232	2	0	0.076				
<b>Propaquizafop</b>									84	0	0	-												
CGA287422									84	0	0	-												
CGA294972									84	0	0	-												
CGA290291									84	0	0	-												
PPA									84	0	0	-												
<b>Propiconazole</b>	313	0	0	-	297	0	0	-	222	0	0	-	397	2	0	0.022	511	1	0	0.035				
<b>Propyzamide</b>	221	0	0	-					346	27	6	0.22	7	0	0	-	365	1	0	0.033	47	2	0	0.02
RH-24580	221	0	0	-					227	0	0	-					364	0	0	-	47	0	0	-
RH-24644	221	0	0	-					227	2	0	0.032					364	0	0	-	47	0	0	-
RH-24655	157	0	0	-					227	0	0	-					360	0	0	-				
<b>Proquinazid</b>					119	0	0	-									77	0	0	-				
IN-MM671					119	0	0	-									77	0	0	-				
IN-MM991																								
<b>Prosulfocarb</b>	168	4	0	0.032					226	1	0	0.027					187	0	0	-				
<b>Pyridate</b>					116	0	0	-																
PHCP					184	0	0	-	189	14	4	0.309												
<b>Pyroxsulam</b>									23	0	0	-	12	0	0	-								
Amitrol <sup>IV</sup>									18	0	0	-	12	0	0	-								
PSA <sup>V</sup>									18	0	0	-	12	0	0	-								
6-Cl-7-OH-XDE-742 <sup>V</sup>									18	0	0	-	12	0	0	-								
5-OH-XDE-742 <sup>V</sup>									18	0	0	-	12	0	0	-								
7-OH-XDE-742 <sup>V</sup>									18	0	0	-	12	0	0	-								
Pyridine sulfonamide <sup>V</sup>									18	0	0	-	12	0	0	-								
<b>Rimsulfuron</b>	178	0	0	-	189	0	0	-																
PPU	656	58	0	0.045	863	374	12	0.23																
PPU-desamino	656	9	0	0.03	863	98	0	0.089																

Analyte	Tylstrup				Jyndevad				Silstrup				Estrup				Faardrup				Lund			
	n	Det.	>0.1	Max	n	Det.	>0.1	Max	n	Det.	>0.1	Max	n	Det.	>0.1	Max	n	Det.	>0.1	Max	n	Det.	>0.1	Max
	$\mu\text{g L}^{-1}$				$\mu\text{g L}^{-1}$				$\mu\text{g L}^{-1}$				$\mu\text{g L}^{-1}$				$\mu\text{g L}^{-1}$				$\mu\text{g L}^{-1}$			
<b>Tebuconazole</b>	196	1	0	0.011	214	1	0	0.014	38	0	0	-	162	5	2	0.12	174	1	0	0.01	190	149	1	0.12
1,2,4-triazole <sup>I</sup>	265	111	0	0.06	607	380	6	0.18	222	107	4	0.2	303	270	73	0.26	406	35	0	0.04				
<b>Terbutylazine</b>	179	0	0	-	260	0	0	-	316	36	1	0.124	286	1	0	0.022	283	51	21	1.9				
2-hydroxy-desethyl-terbutylazine	191	1	0	0.026	517	27	0	0.023	236	1	0	0.016	230	0	0	-	193	7	0	0.092				
Desethyl-terbutylazine	191	0	0	-					375	161	2	0.143	298	7	0	0.053	283	66	30	0.94				
Desisopropylatrazine	191	1	0	0.014					236	4	0	0.047	286	27	0	0.034	283	60	0	0.04				
Hydroxy-terbutylazine	191	0	0	-					236	0	0	-	230	0	0	-	283	34	0	0.069				
<b>Thiacloprid</b>													100	0	0	-								
M34													100	0	0	-								
Thiacloprid sulfonic acid													100	0	0	-								
Thiacloprid-amide													100	0	0	-								
<b>Thiamethoxam</b>	175	0	0	-													184	0	0	-				
CGA 322704	175	0	0	-													184	0	0	-				
<b>Thiencarbazone-methyl</b>																								
AE1394083																	111	0	0	-				
<b>Thiophanat-methyl</b>																								
Carbendazim					169	0	0	-					96	0	0	-								
<b>Triasulfuron</b>	301	0	0	-																				
Triazinamin <sup>II</sup>	291	0	0	-					341	0	0	-	346	1	0	0.042								
<b>Tribenuron-methyl</b>																								
Triazinamin-methyl	446	0	0	-	252	0	0	-	222	0	0	-	107	0	0	-	205	0	0	-				
<b>Triflusulfuron-methyl</b>																								
IN-D8526									158	0	0	-					130	0	0	-				
IN-E7710									158	0	0	-					130	0	0	-				
IN-M7222									158	1	0	0.052					130	0	0	-				

<sup>I</sup> Can include 1,2,4-triazole degraded from the pesticides: epoxiconazole, propiconazole, prothioconazole and metconazole.

<sup>II</sup> Can include triazinamin/IN-A4098 degraded from iodosulfuron-methyl, metsulfuron-methyl, tribenuron-methyl, triflusulfuron-methyl.

<sup>III</sup> IN-JE127 (degradation product from flupyr-sulfuron-methyl) is unstable in aquatic solution – Results should be disregarded.

<sup>IV</sup> Amitrol was included in the monitoring of pyroxsulam as it was suspected to be a groundwater pollutant in the Danish groundwater monitoring programme (GRUMO) in relation to the yearly screenings in 2019. Pyroxsulam was therefore tested as a theoretical source of origin to amitrol. The findings of amitrol in the groundwater screening were later shown to be an analytical artefact and the monitoring of amitrol in PLAP was thus suspended.

<sup>V</sup> The compound was included in PLAP spring 2020. Data evaluation is not included in this report but will be discussed in next year's report covering 2019-2021.



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# Appendixes

## **Appendix 1**

Pesticides and degradation products included in PLAP

## **Appendix 2**

Sampling programme

Drainage sampling

## **Appendix 3**

Agricultural management

## **Appendix 4**

Precipitation at the PLAP fields

## **Appendix 5**

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

## **Appendix 6**

Internal- and external control sample plots for July 2018 to June 2020

## **Appendix 7**

Pesticides analysed at five PLAP fields in the period up to 2014/2015/2016

## **Appendix 8**

Horizontal wells

## **Appendix 9**

Groundwater age from recharge modelling and tritium-helium analysis



# Appendix 1

*Pesticides and degradation products included in PLAP*

**Table A1.1.** EFSA nomenclature (pesticide and analyte), systematic chemical nomenclature, CAS no. for the pesticides and degradation products included in PLAP. P (parent). M (degradation product). Analyte: compound included in the monitoring. N: Total number of samples analysed in PLAP including QC samples. Monitoring is ongoing if latest analysis date is in June 2020.

Pesticide	P/M	Analyte	CAS no.	Systematic name	Latest analysis	N
Acetamiprid	P	Acetamiprid	135410-20-7	N-[(6-chloropyridin-3-yl)methyl]-N'-cyano-N-methylethanimidamide	Not included in the monitoring programme	1
Acetamiprid	M	IM-1-4*	120739-62-0	1-(6-Chloro-3-pyridyl)-N-methylmethanamine; N-methyl(6-chloro-3-pyridyl)methylamine	07.06.2020	37
Acetamiprid	M	IM-1-5*	-	N-(6-chloropyridin-3-ylmethyl)-N-methylacetamide	07.06.2020	37
Acclonifen	P	Acclonifen	74070-46-5	2-chloro-6-nitro-3-phenoxyaniline	18.06.2013	471
Amidosulfuron	P	Amidosulfuron	120923-37-7	N-[[[(4,6-dimethoxy-2-pyrimidinyl)amino]carbonyl]-amino]sulfonyl]-N-methylmethanesulfonamide	01.03.2006	562
Amidosulfuron	M	Desmethyl-amidosulfuron (AEF101630)	-	3-(4-hydroxy-6-methoxypyrimidin-2-yl)-1-(N-methyl-N-methylsulfonyl-aminosulfonyl)-urea	01.03.2006	129
Aminopyralid	P	Aminopyralid	150114-71-9	4-amino-3,6-dichloropyridine-2-carboxylic acid	08.04.2015	619
Azoxystrobin	P	Azoxystrobin	131860-33-8	Methyl (E)-2-(1)-3-methoxyacrylate	16.06.2020	3714
Azoxystrobin	M	CyPM	1185255-09-7	E-2-(2-[6-cyanophenoxy]-pyrimidin-4-yloxy)-phenyl) – 3-methoxyacrylic acid	24.06.2020	3873
Bentazone	P	Bentazone	25057-89-0	3-(1-methylethyl)-1H-2,1,3-benzothiadiazin-4(3H)-one 2,2 dioxide	27.03.2019	5476
Bentazone	M	2-amino-N-isopropylbenzamide	30391-89-0	2-amino-N-isopropylbenzamide	28.06.2007	2139
Bentazone	M	N-methyl-bentazone	61592-45-8	3-isopropyl-1-methyl-1H-2,1,3-benzothiadiazin-4(3H)-one 2,2-dioxide	25.04.2018	735
Bentazone	M	6-hydroxy-bentazone	60374-42-7	6-Hydroxy-3-isopropyl-1H-2,1,3-benzothiadiazin-4(3H)-one 2,2-dioxide	25.04.2018	735
Bentazone	M	8-hydroxy-bentazone	60374-43-8	8-Hydroxy-3-(1-methylethyl)-1H-2,1,3-benzothiadiazin-4(3H)-one 2,2-dioxide	25.04.2018	733
Bifenox	P	Bifenox	42576-02-3	methyl 5-(2,4-dichlorophenoxy)-2-nitrobenzoate	27.12.2012	1190
Bifenox	M	Bifenox acid	53774-07-5	5-(2,4-dichlorophenoxy)-2-nitrobenzoic acid	27.12.2012	1109
Bifenox	M	Nitrofen	1836-75-5	2,4-dichlorophenyl 4'-nitrophenyl ether	27.12.2012	1190
Boscalid	P	Boscalid	188425-85-6	2-chloro-N-(4'-chlorobiphenyl-2-yl)nicotinamide	11.12.2012	190
Bromoxynil	P	Bromoxynil	1689-84-5	3,5-dibromo-4-hydroxybenzonitrile	13.03.2015	1989
Chlormequat	P	Chlormequat	999-81-5	2-chloroethyltrimethylammonium chloride	10.07.2008	335
Clomazone	P	Clomazone	81777-89-1	2-[(2-chlorophenyl)methyl]-4,4-dimethyl-3-isoxazolidione	08.04.2015	1124
Clomazone	M	FMC 65317	-	(N-[2-chlorophenyl)methyl]-3-hydroxy-2,2-dimethylpropanamide, (Propanamide-clomazone)	08.04.2015	1090
Clopyralid	P	Clopyralid	1702-17-6	3,6-Dichloropyridine-2-carboxylic acid	12.03.2009	843
Cyazofamid	P	Cyazofamid	120116-88-3	4-chloro-2-cyano-N,N-dimethyl-5-p-tolylimidazole-1-sulfonamide	12.06.2012	419
Cyazofamid	M	CCIM*	120118-14-1	Cyazofamid-dessulfonamide, 4-chloro-5-(4-methylphenyl)-1H-imidazole-2-carbonitrile	07.06.2020	37
Cyazofamid	M	CTCA*	1287189-46-1	4-chloro-5-(4-methylphenyl)-1H-imidazole-2-carboxylic acid	07.06.2020	37
Cyazofamid	M	DMSA*	6623-40-1	dimethylsulfamic acid; N,N-dimethylsulfamic acid	07.06.2020	37
Cyazofamid	M	N,N-DMS*	3984-14-3		07.06.2020	37
Cycloxydim	M	E/Z BH 517-TSO	-	2-[1-(ethylimino)butyl]-3-hydroxy-5-(tetrahydro-2H-thiopyran-3-yl)-2-cyclohexen-1-one S-oxide	24.06.2020	445
Cycloxydim	M	BH 517-T2SO2	-	2-propyl-6-(3-thienyl)-4,5,6,7-tetrahydrobenzoxazol-4-one S-dioxide	24.06.2020	445
Desmedipham	P	Desmedipham	13684-56-5	Ethyl 3-(phenylcarbamoyloxy)phenylcarbamate	24.06.2003	973
Desmedipham	M	EHPC	7159-96-8	Carbamic acid, (3-hydroxyphenyl)-ethyl ester	24.06.2003	652
Diflufenican	P	Diflufenican	83164-33-4	2',4'-difluoro-2-(α,α,α-trifluoro-m-tolyloxy)nicotinilide	08.04.2015	662
Diflufenican	M	AE-B107137	36701-89-0	2-[3-(trifluoromethyl)phenoxy]pyridine-3-carboxylic acid	08.04.2015	690
Diflufenican	M	AE-05422291	-	2-[3-(trifluoromethyl)phenoxy]pyridine-3-carboxamide	08.04.2015	662
Dimethoate	P	Dimethoate	60-51-5	O,O-dimethyl S-methylcarbamoylmethylphosphorodithioate	13.06.2005	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	02.12.2009	1527
Ethofumesat	P	Ethofumesate	26225-79-6	(±)-2-ethoxy-2,3-dihydro-3,3-dimethylbenzofuran-5-yl-methanesulfonate	30.06.2011	1826
Fenpropimorph	P	Fenpropimorph	67564-91-4	Cis-4-[3-[4-(1,1-dimethylethyl)-phenyl]-2-methylpropyl]-2,6-imethylmorpholine	17.06.2003	2487
Fenpropimorph	M	Fenpropimorph acid	-	Cis-4-[3-[4-(2-carboxypropyl)-phenyl]-2-methylpropyl]-2,6-dimethylmorpholine	17.06.2003	2335
Flamprop-M-isopropyl	P	Flamprop-M-isopropyl	63782-90-1	Isopropyl N-benzoyl-N-(3-chloro-4-fluorophenyl)-D-alaninate	13.06.2005	1987
Flamprop-M-isopropyl	M	Flamprop	58667-63-3	N-benzoyl-N-(3-chloro-4-fluorophenyl)-D-alanine	13.06.2005	1996
Florasulam	P	Florasulam	145701-23-1	2',6',8-Trifluoro-5-methoxy-s-triazolo [1,5-c]pyrimidine-2-sulfonamide	03.05.2020	581
Florasulam	M	ASTCA	313963-93-8	3-sulfamoyl-1H-1,2,4-triazole-5-carboxylic acid	Unstable in aqueous solution – no data	-

Pesticide	P/M	Analyte	CAS no.	Systematic name	Latest analysis	N
Florasulam	M	Florasulam-desmethyl	-	N-(2,6-difluorophenyl)-8-fluoro-5-hydroxy[1,2,4]triazolo[1,5-c]pyrimidine-2-sulfonamide	19.06.2008	275
Florasulam	M	TSA	89517-96-4	1H-1,2,4-triazole-3-sulfonamide	24.06.2020	719
Florasulam	M	5-OH-floramsulam*	292085-54-2	N-(2,6-difluorophenyl)-8-fluoro-5-oxo-5,6-dihydro[1,2,4]triazolo[1,5-c]pyrimidine-2-sulfonamide	24.06.2020	39
Florasulam	M	DFP-ASTCA*	313963-92-7	3-[(2,6-difluorophenyl)sulfamoyl]-1H-1,2,4-triazole-5-carboxylic acid	24.06.2020	39
Florasulam	M	DFP-TSA*	-	N-(2,6-difluorophenyl)-1H-1,2,4-triazole-3-sulfonamide	24.06.2020	39
Fluazifop-P-buthyl	P	Fluazifop-P-butyl	79241-46-6	butyl (R)-2-{4-[5-(trifluoromethyl)-2-pyridyloxy]phenoxy} propionate	24.06.2003	402
Fluazifop-P-buthyl	M	Fluazifop-P	83066-88-0	(R)-2-(4-((5-(trifluoromethyl)-2-pyridinyl)oxy)phenoxy)propanoic acid	28.03.2012	1769
Fluazifop-P-buthyl	M	TFMP	33252-63-0	5-trifluoromethyl-pyridin-2-ol	08.04.2015	1010
Fludioxonil	M	CGA 192155	126120-85-2	2,2-difluoro-benzo[1,3]dioxol-4-carboxylic acid	05.04.2016	569
Fludioxonil	M	CGA 339833	-	3-carbamoyl-2-cyano-3-(2,2-difluoro-benzo[1,3]dioxol-4-yl)-oxirane-2-carboxylic acid	05.04.2016	558
Flupyr-sulfuron-methyl	P	Flupyr-sulfuron-methyl	144740-54-5	Methyl 2-[(4,6-dimethoxypyrimidin-2-ylcarbamoyl)sulfamoyl]-6-(trifluoromethyl)nicotinate monosodium salt	11.10.2016	513
Flupyr-sulfuron-methyl	M	IN-JE127	144740-59-0	methyl 2-sulfamoyl-6-(trifluoromethyl)nicotinate	27.03.2019	341
Flupyr-sulfuron-methyl	M	IN-JV460	-	1-(4,6-dimethoxypyrimidin-2-yl)-2,4-diketo-7-trifluoro-methyl-1,2,3,4-tetrahydropyridol(2,3-d)pyrimidine	11.10.2016	512
Flupyr-sulfuron-methyl	M	IN-KC576	-	1-(4-hydroxy-6-methoxypyrimidin-2-yl)-7-(trifluoromethyl)pyrido[2,3-d]pyrimidine-2,4(1H,3H)-dione	11.10.2016	512
Flupyr-sulfuron-methyl	M	IN-KF311	-	1-(4,6-dihydroxypyrimidin-2-yl)-7-(trifluoromethyl)pyrido[2,3-d]pyrimidine-2,4(1H,3H)-dione	25.03.2020	439
Flupyr-sulfuron-methyl	M	IN-KY374	-	N-(4,6-dimethoxypyrimidin-2-yl)-N-(3-methoxycarbonyl-6-trifluoromethylpyridine-2-yl)-amine	11.10.2016	512
Fluroxypyr	P	Fluroxypyr	69377-81-7	(4-amino-3,5-dichloro-6-fluoro-2-pyridinyl)oxyacetic acid	12.06.2008	2047
Fluroxypyr	M	Fluroxypyr-methoxypyridine	35622-80-1	4-amino-3,5-dichloro-6-fluoro-2-pyridinyl-2-methoxypyridine	08.05.2018	192
Fluroxypyr	M	Fluroxypyr-pyridinol	94133-62-7	4-amino-3,5-dichloro-6-fluoro-2-pyridinol	08.05.2018	192
Foramsulfuron	P	Foramsulfuron	173159-57-4	2-amino-4,6-dimethoxypyrimidine	08.05.2018	594
Foramsulfuron	M	AE-F092944	36315-01-2	4-amino-2-[3-(4,6-dimethoxypyrimidin-2-yl)ureidosulfonyl]-N, N-dimethylbenzamide	07.05.2019	620
Foramsulfuron	M	AE-F130619	-	4-amino-2-[3-(4,6-dimethoxypyrimidin-2-yl)ureidosulfonyl]-N, N-dimethylbenzamide	08.05.2018	594
Glyphosate	P	Glyphosate	1071-83-6	N-(phosphonomethyl)glycine	11.09.2019	4468
Glyphosate	M	AMPA	1066-51-19	Amino-methylphosphonic acid	11.09.2019	4467
Halaxifen-methyl	P	Halaxifen-methyl	943831-98-9	methyl 4-amino-3-chloro-6-(4-chloro-2-fluoro-3-methoxyphenyl)pyridine-2-carboxylate	Not included in the monitoring programme	-
Halaxifen-methyl	M	X-757	-	4-amino-3-chloro-6-(4-chloro-2-fluoro-3-hydroxyphenyl)pyridine-2-carboxylic acid	25.09.2019	412
Halaxifen-methyl	M	X-729	943832-60-8	4-amino-3-chloro-6-(4-chloro-2-fluoro-3-methoxyphenyl)pyridine-2-carboxylic acid (haluxifen)	24.06.2020	237
Iodosulfuron-methyl	M	Triazinamin/IN-A4098 <sup>A</sup>	1668-54-8	2-amino-4-methoxy-6-methyl-1,3,5-triazine	04.04.2018	655
Iodosulfuron-methyl	P	Iodosulfuron-methyl	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	22.12.2010	355
Iodosulfuron-methyl	M	metsulfuron-methyl	74223-64-6	Methyl 2-(4-methoxy-6-methyl-1,3,5-triazin-2-ylcarbamoylsulfamoyl)benzoate	22.12.2010	1346
Ioxynil	P	Ioxynil	1689-83-4	4-hydroxy-3,5-diiodobenzonitrile	31.03.2015	1994
Lambda-cyhalothrin	P	Lambda-cyhalothrin	91465-08-6	[(R)-cyano-(3-phenoxyphenyl)methyl] (1S,3S)-3-[(Z)-2-chloro-3,3,3-trifluoroprop-1-enyl]-2,2-dimethylcyclopropane-1-carboxylate	Not included in the monitoring programme	-
Linuron	P	Linuron	330-55-2	3-(3,4-dichlorophenyl)-1-methoxy-1-methylurea	13.09.2001	388
Mancozeb	M	EBIS	33813-20-6	ethylene bisisothiocyanate sulfide	19.03.2015	238
Mancozeb	M	ETU	96-45-7	Ethylene thiourea	03.04.2001	278
MCPA	P	MCPA	94-74-6	(4-chloro-2-methylphenoxy)acetic acid	29.06.2006	1465
MCPA	M	2-methyl-4-chlorophenol	1570-64-5	2-methyl-4-chlorophenol	29.06.2006	1458
Mesosulfuron-methyl	P	Mesosulfuron-methyl	208465-21-8	Methyl 2-[3-(4,6-dimethoxypyrimidin-2-yl)ureidosulfonyl]-4-methanesulfonamidomethylbenzoate	02.12.2009	649
Mesosulfuron-methyl	M	AE-F147447	-	N-[(1,1-Dioxido-3-oxo-2,3-dihydro-1,2-benzothiazol-6-yl)methyl]methanesulfonamide	25.03.2020	367
Mesosulfuron-methyl	M	AE-F099095	-	4,6-dimethoxypyrimidine-2-yl-urea	31.03.2020	880

Pesticide	P/M	Analyte	CAS no.	Systematic name	Latest analysis	N
Mesosulfuron-methyl	M	AE-F160459	-	Methyl-2-[[[(4-methoxy-6-oxo-1,6-dihydropyrimidin-2-yl)carbamoyl]sulfamoyl]-4-[(methylsulfonyl)amino]methyl] benzoate	31.03.2020	880
Mesosulfuron-methyl	M	Mesosulfuron	400852-66-6	2-[[[(4,6-dimethoxy-2-pyrimidinyl)amino]carbonyl]amino]sulfonyl]-4-[(methylsulfonyl)amino]methyl]benzoic acid	02.12.2009	270
Mesotrione	P	Mesotrione	104206-82-8	2-(4-mesyl-2-nitrobenzoyl)cyclohexane-1,3-dione	08.05.2018	949
Mesotrione	M	MNBA	110964-79-9	methylsulfonyl-2-nitrobenzoic acid	08.05.2018	947
Mesotrione	M	AMBA	393085-45-5	2-amino-4-methylsulfonylbenzoic acid	08.05.2018	949
Metalaxyl-M	P	Metalaxyl-M	70630-17-0	methyl N-(methoxyacetyl)-N-(2,6-xylyl)-D-alaninate	19.03.2015	1117
Metalaxyl-M	M	CGA 62826	75596-99-5	2-[(2,6-dimethylphenyl)(methoxyacetyl)amino]propanoic acid	19.03.2015	1127
Metalaxyl-M	M	CGA 108906	104390-56-9	2-[(1-carboxyethyl)(methoxyacetyl)amino]-3-methylbenzoic acid	19.03.2015	1124
Metamitron	P	Metamitron	41394-05-2	4-amino-4,5-dihydro-3-methyl-6-phenyl-1,2,4-triazin-5-one	31.03.2020	2040
Metamitron	M	Desamino-metamitron	-	4,5-dihydro-3-methyl-6-phenyl-1,2,4-triazine-5-one	31.03.2020	2037
Metamitron	M	MTM-126-AMT	70569-26-5	4-amino-3-methyl-1,2,4-triazin-5-one	31.03.2020	210
Metconazole	P	Metconazole	125116-23-6	5-[(4-chlorophenyl)methyl]-2,2-dimethyl-1-(1,2,4-triazol-1-ylmethyl)cyclopentan-1-ol	24.06.2020	109
Metrafenone	P	Metrafenone	220899-03-6	3'-bromo-2,3,4,6'-tetramethoxy-2',6'-dimethylbenzophenone	08.04.2015	608
Metribuzin	P	Metribuzin	21087-64-9	4-amino-6-tert-butyl-4,5-dihydro-3-methylthio-1,2,4-triazine-5-one	28.05.2002	576
Metribuzin	M	Desamino-metribuzin	35045-02-4	6-(1,1-dimethylethyl)-3-(methylthio)-1,2,4-triazin-5-(4H)-one	28.05.2002	541
Metribuzin	M	Diketo-metribuzin	56507-37-0	4-amino-6-tert-butyl-4,5-dihydro-1,2,4-triazine-3,5-dione	09.03.2011	977
Metribuzin	M	Desamino-diketo-metribuzin	52236-30-3	6-tert-butyl-4,5-dihydro-3-methylthio-1,2,4-triazine-3,5-dione	09.04.2008	891
Metsulfuron-methyl	M/P	Iodosulfuron-methyl/metsulfuron-methyl	74223-64-6	methyl 2-[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)-carbamoylsulfamoyl]benzoate	22.12.2010	1346
Metsulfuron-methyl	M	Triazinamin/IN-A4098 <sup>A</sup>	1668-54-8	2-amino-4-methoxy-6-methyl-1,3,5-triazine	25.03.2003	478
Pendimethalin	P	Pendimethalin	40487-42-1	N-(1-ethyl)-2,6-dinitro-3,4-xynile	10.12.2009	2881
Phenmedipham	P	Phenmedipham	13684-63-4	3-[(methoxycarbonyl)amino]phenyl (3-methylphenyl)carbamate	24.06.2003	974
Phenmedipham	M	3-aminophenol	137641-05-5	1-amino-3-hydroxybenzene	26.02.2002	391
Phenmedipham	M	MHPC	13683-89-1	Methyl-N-(3-hydroxyphenyl)-carbamate	24.06.2003	968
Picloram	P	Picloram	1918-02-1	4-Amino-3,5,6-trichloropyridine-2-carboxylic acid	03.06.2020	85
Picolinafen	P	Picolinafen	137641-05-5	4'-fluoro-6-(a,a,a-trifluoro-m-tolyloxy)pyridine-2-carboxanilide	30.03.2010	352
Picolinafen	M	CL153815	137640-84-7	6-(3-trifluoromethylphenoxy)-2-pyridine carboxylic acid	30.03.2010	352
Pirimicarb	P	Pirimicarb	23103-98-2	2-(dimethylamino)-5,6-dimethyl-4-pyrimidinyl dimethylcarbamate	26.06.2007	3432
Pirimicarb	M	Pirimicarb-desmethyl-formamido	27218-04-8	2-methylformamido-5,6-dimethylpyrimidine-4-yl dimethylcarbamate	26.06.2007	2678
Pirimicarb	M	Pirimicarb-desmethyl	30614-22-3	2-(dimethylamino)-5,6-dimethyl-4-pyrimidinylmethylcarbamate	26.06.2007	3078
Propaquizifop	P	Propaquizifop	111479-05-1	2-(propan-2-ylideneamino)oxyethyl (2R)-2-[4-(6-chloroquinoxalin-2-yl)oxyphenoxy]propanoate	Not included in the monitoring programme	1
Propaquizifop	M	CGA287422	-	2-[4-(6-chloroquinoxalin-2-yl)oxyphenoxy]-propanoic acid (quizalofop; quizalofop acid; propaquizafop acid)	24.06.2020	129
Propaquizifop	M	CGA290291	27925-27-5	6-chloro-3H-quinoxalin-2-one; 6-chloroquinoxalin-2-ol; hydroxy-quinoxaline	24.06.2020	129
Propaquizifop	M	CGA294972	-	2-[4-(6-chloro-3-hydroxy-quinoxalin-2-yloxy)-phenoxy]-propionic acid;hydroxy quizalofop; 3-OH-quizalofop acid	24.06.2020	129
Propaquizifop	M	PPA	94050-90-5	(R)-2-(4-hydroxy-phenoxy)-propionic acid	24.06.2020	129
Propiconazole	P	Propiconazole	60207-90-1	1-[[2-(2,4-dichlorophenyl)-4-propyl-1,3-dioxolan-2-yl]methyl]-1H-1,2,4-triazole	22.03.2005	3415
Propyzamide	P	Propyzamide	23950-58-5	3,5-dichloro-N-(1,1-dimethylprop-2-ynyl)benzamide	24.06.2020	1521
Propyzamide	M	RH-24644	-	2-(3,5-dichlorophenyl)-4,4-dimethyl-5-methylene-oxazoline	03.06.2020	1314
Propyzamide	M	RH-24655	-	3,5-dichloro-N-(1,1-dimethylpropenyl)benzamide	08.04.2015	1134
Propyzamide	M	RH-24580	-	N-(1,1-dimethylacetonyl)-3,5-dichlorobenzamide	03.06.2020	1314
Proquinazid	P	Proquinazid	189278-12-4	6-iodo-2-propoxy-3-propylquinazolin-4(3H)-one	Not included in the monitoring programme	-
Proquinazid	M	IN-MM671	-	2-propoxy-3-propylquinazolin-4(3H)-one	24.06.2020	313
Proquinazid	M	IN-MM991	-	3-propylquinazolin-2,4(1H,3H)-dione	24.06.2020	313
Prosulfocarb	P	Prosulfocarb	52888-80-9	N-[[3-(4-methoxy-6-methyl-1,3,5-triazin-2-yl)-3-[2-(3,3,3-trifluoro-propyl)phenylsulfonyl]urea	19.03.2015	921



Pesticide	P/M	Analyte	CAS no.	Systematic name	Latest analysis	N
Prothioconazole	P	Prothioconazole	178928-70-6	2-[2-(1-chlorocyclopropyl)-3-(2-chlorophenyl)-2-hydroxypropyl]-1,2-dihydro-3H-1,2,4-triazole-3-thione	Not included in the monitoring programme	4
Pyridate	P	Pyridate	55512-33-9	O-6-chloro-3-phenylpyridazin-4-yl S-octyl thiocarbonate	03.09.2002	183
Pyridate	M	PHCP	40020-01-7	3-phenyl-4-hydroxy-6-chloropyridazine	02.06.2004	571
Pyroxsulam	P	Pyroxsulam	422556-08-9	N-(5,7-dimethoxy-[1,2,4]triazolo[1,5-a]pyrimidin-2-yl)-2-methoxy-4-(trifluoromethyl)pyridine-3-sulfonamide	Not included in the monitoring programme	-
Pyroxsulam	M	5-OH-XDE-742*		5-OH-pyroxsulam; N-(5-hydroxy-7-methoxy[1,2,4]triazolo[1,5-a]pyrimidin-2-yl)-2-methoxy-4-(trifluoromethyl)-3-pyridinesulfonamide	24.06.2020	39
Pyroxsulam	M	6-Cl-7-OH-XDE-742*		6-Cl-7-OH-pyroxsulam; N-(6-chloro-7-hydroxy-5-methoxy[1,2,4] triazolo[1,5-a]pyrimidin-2-yl)-2-methoxy-4-(trifluoromethyl)pyridine -3-sulfonamide	24.06.2020	39
Pyroxsulam	M	7-OH-XDE-742*		7-OH-pyroxsulam; N-(7-hydroxy-5-methoxy[1,2,4]triazolo[1,5-a]pyrimidin-2-yl)-2-methoxy-4-(trifluoromethyl)pyridine-3-sulfonamide	24.06.2020	39
Pyroxsulam	M	Amitrol**	61-82-5	1H-1,2,4-triazol-5-amine	24.06.2020	45
Pyroxsulam	M	PSA*		2-methoxy-4-(trifluoromethyl)-3-pyridinesulfonic acid	24.06.2020	39
Pyroxsulam	M	Pyridine sulfonamide*		2-methoxy-4-(trifluoromethyl)pyridine-3-sulfonamide	24.06.2020	39
Rimsulfuron	P	Rimsulfuron	122931-48-0	N-[(4,6-dimethoxy-2-pyrimidinyl)amino]carbonyl]-3-(ethylsulfonyl)-2-pyridinesulfonamide	14.06.2006	561
Rimsulfuron	M	PPU-desamino	-	N-((3-(ethylsulfonyl)-2-pyridyl)-4,6-dimethoxy-2-pyrimidinamine (IN70942)	11.12.2012	2311
Rimsulfuron	M	PPU	138724-53-5	N-(4,6-dimethoxy-2-pyrimidinyl)-N-((3-ethylsulfonyl)-2-pyridinyl)urea (IN70941)	11.12.2012	2311
Tebuconazole	P	Tebuconazole	107534-96-3	a-[2-(4-chlorophenyl)ethyl]-a-(1,1-dimethylethyl)-1H-1,2,4-triazole-1-ethanol	27.12.2012	1220
Tebuconazole	M	1,2,4-triazole	288-88-0	1,2,4-triazole	24.06.2020	3014
Terbuthylazin	P	Terbuthylazine	5915-41-3	6-chloro-N-(1,1-dimethylethyl)-N-ethyl-1,3,5-triazine-2,4-diamine	25.03.2009	2116
Terbuthylazin	M	2-hydroxy-desethyl-terbuthylazine	-	6-hydroxy-N-(1,1-dimethylethyl)-1,3,5-triazine-2,4-diamine	19.06.2008	1371
Terbuthylazin	M	Desisopropylatrazine	1007-28-9	6-chloro-N-ethyl-1,3,5-triazine-2,4-diamine	25.03.2009	1618
Terbuthylazin	M	Desethyl-terbuthylazine	30125-63-4	6-chloro-N-(1,1-dimethylethyl)-1,3,5-triazine-2,4-diamine	10.06.2009	2619
Terbuthylazin	M	Hydroxy-terbuthylazine	66753-07-9	6-hydroxy-N-(1,1-dimethylethyl)-N'-ethyl-1,3,5-triazine-2,4-diamine	19.06.2008	1520
Thiacloprid	P	Thiacloprid	111988-49-9	(Z)-3-(6-chloro-3-pyridylmethyl)-1,3-thiazolidin-2-ylidenecyanamide	28.03.2012	168
Thiacloprid	M	Thiacloprid-amide	676228-91-4	(3-[(6-chloro-3-pyridinyl)methyl]-2-thiazolidinylidene) urea	28.03.2012	168
Thiacloprid	M	Thiacloprid sulfonic acid	-	Sodium,2-[[[(aminocarbonyl)amino]-carbonyl]][(6-chloro-3-pyridinyl)-methyl]amino]ethanesulfonate	28.03.2012	177
Thiacloprid	M	M34	-	2-{carbamoyle}[(6-chloropyridin-3-yl)-methyl]amino}-ethanesulfonic acid	28.03.2012	176
Thiamethoxam	P	Thiamethoxam	153719-23-4	3-(2-chloro-thiazol-5-ylmethyl)-5-methyl[1,3,5]oxadiazinan-4-ylidene-N-nitroamine	18.06.2008	559
Thiamethoxam	M	CGA 322704	210880-92-5	[C(E)]-N-[(2-chloro-5-thiazolyl)methyl]-N'-methyl-N'-nitroguanidine	18.06.2008	559
Thiencarbazone-methyl	P	Thiencarbazone-methyl	317815-83-1	Methyl-4-[(4,5-dihydro-3-methoxy-4-methyl-5-oxo-1H-1,2,4-triazol-1-yl)carbonylsulfamoyl]-5-methylthiophene-3-carboxylate	Not included in the monitoring programme	-
Thiencarbazone-methyl	M	AE1394083 (thiencarbazone)	936331-72-5	4-((4,5-Dihydro-3-methoxy-4-methyl-5-oxo-1H-1,2,4-triazol-1-yl)carbonylsulfamoyl)-5-methylthiophene-3-carboxylic acid (Thiencarbazone)	18.06.2019	92
Thifensulfuron-methyl	P	Thifensulfuron-methyl	79277-27-3	Methyl 3-(4-methoxy-6-methyl-1,3,5-triazin-2-ylcarbamoysulfamoyl)thiophene-2-carboxylate	Not included in the monitoring programme	-
Thifensulfuron-methyl	M	Triazinamin/IN-A4098 <sup>A</sup>	1668-54-8	2-amino-4-methoxy-6-methyl-1,3,5-triazine	04.04.2018	655
Thiophanat-methyl	M	Carbendazim	10605-21-7	methyl benzimidazol-2-ylcarbamate	24.06.2020	456
Triasulfuron	P	Triasulfuron	82097-50-5	1-[2-(2-chloroethoxy)phenylsulfonyl]-2-(4-methoxy-6-methyl-1,3,5-triazine-2-yl)-urea	04.03.2003	445
Triasulfuron	M	Triazinamin/IN-A4098 <sup>A</sup>	1668-54-8	2-amino-4-methoxy-6-methyl-1,3,5-triazine	04.03.2003	424
Tribenuron-methyl	P	Tribenuron-methyl	101200-48-0	Methyl-2-[4-methoxy-6-methyl-1,3,5-triazin-2-yl(methyl)-carbamoysulfamoyl]benzoate	09.06.2001	3
Tribenuron-methyl	M	Triazinamin-methyl	5248-39-5	4-methoxy-6-methyl-1,3,5-triazin-methylamine	29.08.2012	2379
Triflusulfuron-methyl	P	Triflusulfuron-methyl	126535-15-7	Methyl-2-[4-dimethylamino-6-(2,2,2-trifluoroethoxy)-1,3,5-triazin-2-ylcarbamoysulfamoyl]-m-toluate	30.06.2011	430
Triflusulfuron-methyl	M	IN-M7222	-	6-(2,2,2-trifluoroethoxy)-1,3,5-triazine-2,4-diamine	30.06.2011	430

Pesticide	P/M	Analyte	CAS no.	Systematic name	Latest analysis	N
Triflurosulfuron-methyl	M	IN-E7710	-	N-methyl-6-(2,2,2-trifluoroethoxy)-1,3,5-triazine-2,4-diamine	30.06.2011	430
Triflurosulfuron-methyl	M	IN-D8526	-	N,N-dimethyl-6-(2,2,2-trifluoroethoxy)-1,3,5-triazine-2,4-diamine	30.06.2011	430

<sup>A</sup> Triazinamin/IN-A4098 is a common degradation product from the 1,3,5-triazine sulfonylurea herbicides.

\* Parent compound was applied in spring 2020. Data evaluation is not included in this report but will be discussed in next year's report covering 2019-2021.

\*\*Amitrol was included in the monitoring of pyroxsulam as it was suspected to be a groundwater pollutant in the Danish groundwater monitoring programme (GRUMO) in relation to the yearly screenings in 2019. Pyroxsulam was therefore tested as a theoretical source of origin to amitrol. The findings of amitrol in the groundwater screening was later shown to be an analytical artefact and the monitoring of amitrol in PLAP was thus suspended.

## Appendix 2

### Sampling programme

From each of the PLAP fields, samples of groundwater, drainage water and soil water in the variably saturated zone are collected. A full description of the original monitoring design is found in Lindhardt *et al.* (2001), and later revisions and changes to the sampling procedure is described in previous reports (see [www.plap.dk](http://www.plap.dk)).

Table A2.1 provides an overview of the sampling programme for each of the active PLAP fields. Tylstrup was set on standby (January 1, 2019) and in connection with this, the sampling programme was revised. In general, less samples are collected from the fields compared to earlier reporting periods. The sampling programme is under constant revision as new knowledge about the hydrogeological conditions at the PLAP fields is continuously collected and processed.

**Table A2.1.** Pesticide monitoring programme in suction cups (S), horizontal monitoring wells (H) and vertical monitoring wells (M) July 2018-June 2020. Numbers in parentheses denote the number of samples collected from the well.

Field	Period	Monthly monitoring (Intensive)	Half-yearly monitoring (medium)	Half-yearly monitoring (Extensive)	Not monitored
Tylstrup	before 1/1-2019	M4(2), M5(2), S1a, S2a, H1(1) <sup>m</sup>	M1(3), M3(3), M4(2), M5(2), S1a, S2a, S1b, S2b	M1(3), M3(3), M4(5), M5(2), S1a, S2a, S1b, S2b, H1(1) <sup>m</sup>	M2, M6, M7
Jyndevad	before 1/1-2019	M1(2), M4(2), M7(3), S1a, S2a, H1(1) <sup>m</sup>	M1(2), M2(3), M4(2), M7(3), S1a, S2a, H1(1) <sup>m</sup>	M1(2), M2(3), M4(2), M5(2), M7(3), S1a, S2a, H1(1) <sup>m</sup>	M3, M6, S1b, S2b
	1/1-2019-30/6 2020	M1(2), M4(2), M7(2), S1a, S2a, H1(1) <sup>m</sup>	M1(2), M2(2), M4(2), M7(2), S1a, S2a, H1(1) <sup>m</sup>	M1(2), M2(2), M4(2), M5(2), M7(2), S1a, S2a, H1(1) <sup>m</sup>	M3, M6, S1b, S2b
Silstrup	1/7-2018-30/6-2020	M5(2), M9(1), H1.2, H3(1) <sup>m</sup>	-	M5(2), M9(2), M10(2), M12(2), H1.2, H3(1) <sup>m</sup>	M1-M4, M6-M8, M11, M13, H2
Estrup	before 1/1-2019	M4(2), M6(1), H1.2, H2(1) <sup>m</sup>	-	M1(2), M4(2), M5(2), M6(2), H1.2 H2(1) <sup>m</sup>	M2, M3, M7, S1, S2
	1/1-2019-30/6 2020	M4(2), H1.2, H2(1) <sup>m</sup>	-	M1(2), M4(2), M5(2), M6(2), H1.2 H2(1) <sup>m</sup>	M2, M3, M7, S1, S2
Faardrup	before 1/1-2019	M4(2), M5(2), M6(2), H2.3, H3 <sup>m</sup>	-	M2(2), M4(2), M5(2), M6(2), H2.3, H3 <sup>m</sup>	M1, M3, M7, H1, S1, S2
	1/1-2019-30/6 2020	M4(2), M5(1), H2.3, H3 <sup>m</sup>	-	M2(2), M4(2), M5(2), M6(2), H2.3, H3 <sup>m</sup>	M1, M3, M7, H1, S1, S2
Lund	before 1/1-2019	M1(2), M4(2), M5(2), M6(2)	-	M1(2), M2(2), M3(2), M4(2), M5(2), M6(2), M7(2)	S1, S2
	1/1-2019-30/6 2020	M1(1), M4(2), M5(2)	-	M1(2), M4(2), M5(2), M6(2)	M2, M3, S1, S2

S1a and S1b refer to suction cups installed 1 and 2 mbgs, respectively, at location S1, whereas S2a and S2b refer to suction cups installed 1 and 2 mbgs, respectively, at location S2.

<sup>m</sup> Mixed water samples from three screens.

### Drainage sampling

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 was 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<sub>i</sub> = Weekly accumulated drainage runoff (mm/week)

C<sub>i</sub> = Pesticide concentration collected by means of flow-proportional sampler (µg L<sup>-1</sup>). ND are included as 0 µg L<sup>-1</sup> calculating average concentrations.

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

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

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

where:

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

V<sub>i</sub> = Weekly accumulated drainage runoff (mm/week)

V<sub>f<sub>i</sub></sub> = Drainage runoff accumulated during a “flow event” (mm/storm event)

C<sub>f<sub>i</sub></sub> = Pesticide concentration in the “event samples” collected by means of the flow-proportional sampler (µg L<sup>-1</sup>)

C<sub>t<sub>i</sub></sub> = Pesticide concentration in the weekly samples collected by means of the time-proportional sampler (µg L<sup>-1</sup>)

Table 4.2, 5.2, 6.2 and 7.2 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 mbgs 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<sub>1</sub> = 0.5(t<sub>i-1</sub> + t<sub>i</sub>); t<sub>2</sub> = 0.5(t<sub>i</sub> + t<sub>i+1</sub>)

P<sub>t</sub> = daily percolation at 1 mbgs 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 mbgs

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 2020 growing seasons. The active ingredients of the various pesticides are indicated in parentheses.

Date	Management practice and growth stages – <b>Tylstrup</b>
22-03-2012	Ploughed - depth 24 cm
24-03-2012	Spring barley sown, cv. TamTam, seeding rate 185 kg ha <sup>-1</sup> , sowing depth 2.75 cm, row distance 12.5 cm. Using combine driller with a tubular packer roller. Final plant number 344 m <sup>-2</sup> . 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 <sup>-1</sup>
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 <sup>-2</sup> - 100% DM
21-05-2012	Fox 480 SC (bifenox) - weeds - 1.2 L ha <sup>-1</sup> (not analysed)
25-05-2012	Mustang Forte (aminopyralid/florasulam/2,4-D) - weeds - 0.75 L ha <sup>-1</sup>
25-05-2012	BBCH stage 29
31-05-2012	BBCH stage 32
31-05-2012	Irrigation 24 mm.
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 <sup>-2</sup> - 100% DM
28-06-2012	BBCH stage 59
28-06-2012	Bell (boscalid + epoxiconazole) - fungi - 1.5 L ha <sup>-1</sup> (epoxiconazole not analysed)
02-07-2012	BBCH stage 61
10-07-2012	BBCH stage 79
10-07-2012	Biomass 1138.3 g m <sup>-2</sup> - 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 <sup>-1</sup> (not analysed)
27-08-2012	BBCH stage 89
27-08-2012	Harvest of spring barley. Stubble height 15 cm, grain yield 62.0 hkg ha <sup>-1</sup> - 85% DM. Straw removed, yield 37.3 hkg ha <sup>-1</sup> - 100% DM
31-08-2012	Tracer (potassium bromide), 30 kg ha <sup>-1</sup>
20-09-2012	Ploughed - Depth 22 cm
23-09-2012	Winter rye sown, cv. Magnifico, seeding rate 64.0 kg ha <sup>-1</sup> , sowing depth 3.5 cm, row distance 13.0 cm. Final plant number 125 m <sup>-2</sup> . Sown with rotor harrow combine sowing machine
05-10-2012	BBCH stage 9 - emergence
10-10-2012	BBCH stage 11
12-10-2012	BBCH stage 12
12-10-2012	Boxer (prosulfocarb) - weeds - 4.0 L ha <sup>-1</sup>
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 <sup>-2</sup> - 100% DM
04-04-2013	Fertilisation - 56.7 N, 8.1 P, 27.0 K, kg ha <sup>-1</sup>
04-04-2013	BBCH stage 22
02-05-2013	BBCH stage 30-31
02-05-2013	Fertilisation - 71.4 N, 10.2 P, 34.0 K, kg ha <sup>-1</sup>
07-05-2013	BBCH stage 31
08-05-2013	Starane XL (fluroxypyr) - weeds - 1.2 L ha <sup>-1</sup>
24-05-2013	BBCH stage 50
24-05-2013	Biomass 422.8 g m <sup>-2</sup> - 100% DM



Date	Management practice and growth stages – Tylstrup
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 <sup>-2</sup> - 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. Stubble height 15 cm, grain yield 77.4 hkg ha <sup>-1</sup> - 85% DM. Straw removed, yield 33.8 hkg ha <sup>-1</sup> - 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 <sup>-1</sup>
03-04-2014	Fertilisation - 100 K, kg ha <sup>-1</sup>
15-04-2014	Maxim 100 FS (fludioxonil) - fungi - 250 ml ton <sup>-1</sup> potatoes ~ 625 mL ha <sup>-1</sup> 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 row distance 75 cm, plant distance 25 cm, depth 17 cm, final plant number 4 m <sup>-2</sup>
16-04-2014	BBCH stage 00
16-04-2014	Command CS (clomazone) - weeds - 0.25 L ha <sup>-1</sup> (not monitored)
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 <sup>-1</sup> (not monitored)
17-05-2014	BBCH stage 9 – emergence
22-05-2014	Titus WSB (rimsulfuron) + U46 M (MCPA) - weeds - 20 g ha <sup>-1</sup> + 100 mL ha <sup>-1</sup> (not monitored)
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.
18-06-2014	BBCH stage 47
18-06-2014	Biomass tubers 119.0 g Top 233.3 g m <sup>-2</sup> - 100% DM
20-06-2014	BBCH stage 53
20-06-2014	Irrigation 24 mm.
26-06-2014	BBCH stage 59
26-06-2014	Dithane NT (mancozeb) - fungi - 2.0 L ha <sup>-1</sup>
02-07-2014	Biomass tubers 388.9 g. Top 391.2 g m <sup>-2</sup> - 100% DM
02-07-2014	BBCH stage 60
03-07-2014	BBCH stage 60
04-07-2014	Irrigation 24 mm.
04-07-2014	Dithane NT (mancozeb) - fungi - 2.0 L ha <sup>-1</sup>
14-07-2014	BBCH stage 69
14-07-2014	Dithane NT (mancozeb) - fungi - 2.0 L ha <sup>-1</sup>
23-07-2014	BBCH stage 75
23-07-2014	Irrigation 24 mm.
24-07-2014	Dithane NT (mancozeb) - fungi - 2.0 L ha <sup>-1</sup>
24-07-2014	BBCH stage 75
30-07-2014	Irrigation 30 mm.
02-08-2014	Dithane NT (mancozeb) - fungi - 2.0 L ha <sup>-1</sup>
11-08-2014	BBCH stage 90
11-08-2014	Dithane NT (mancozeb) - fungi - 2.0 L ha <sup>-1</sup>

Date	Management practice and growth stages – Tylstrup
13-08-2014	Biomass tubers 1,270.3 g. Top 266.3 g m <sup>-2</sup> - 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 <sup>-1</sup>
25-08-2014	BBCH stage 92
25-08-2014	Dithane NT (mancozeb) - fungi - 2.0 L ha <sup>-1</sup>
12-09-2014	Harvest of potatoes. Tuber yield 107.1 hkg ha <sup>-1</sup> - 100% DM
15-09-2014	Liming - 4.0 t ha <sup>-1</sup>
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 <sup>-1</sup> , row distance 12.5 cm, final plant number 248 m <sup>-2</sup>
29-09-2014	BBCH stage 07-08
29-09-2014	Fertilisation - 24.5 N, kg ha <sup>-1</sup>
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 (flupyr-sulfuron) - weeds - 10 g ha <sup>-1</sup> (i.e. 4.6 g a.i. ha <sup>-1</sup> )
14-11-2014	BBCH stage 14-15
14-11-2014	Orius 200 EW (tebuconazole) - fungi – 1.25 L ha <sup>-1</sup> (i.e. 250 g a.i. ha <sup>-1</sup> )
17-12-2014	BBCH stage 22
17-12-2014	Biomass 16.1 g m <sup>-2</sup> - 100% DM
24-03-2015	BBCH stage 22
24-03-2015	Fertilisation - 49.6 N, 7.1 P, 23.6 K, kg ha <sup>-1</sup>
09-04-2015	BBCH stage 24
09-04-2015	Lexus 50 WG (flupyr-sulfuron) - weeds - 10 g ha <sup>-1</sup> (i.e. 4.6 g a.i. ha <sup>-1</sup> )
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 <sup>-1</sup>
14-05-2015	BBCH stage 32
14-05-2015	Starane XL (fluroxypyr + florasulam) - weeds - 1.2 L ha <sup>-1</sup> (i.e. 120 g a.i. ha <sup>-1</sup> + 3 g a.i. ha <sup>-1</sup> )
14-05-2015	Proline EC 250 (prothioconazole) - fungi - 0.8 L ha <sup>-1</sup> (i.e. 200 g a.i. ha <sup>-1</sup> )
26-05-2015	BBCH stage 33
12-06-2015	BBCH stage 49
12-06-2015	Proline EC 250 (prothioconazole) - fungi - 0.8 L ha <sup>-1</sup> (i.e. 200 g a.i. ha <sup>-1</sup> )
15-06-2015	BBCH stage 51
15-06-2015	Biomass 890.1 g m <sup>-2</sup> - 100% DM
13-07-2015	BBCH stage 71
21-07-2015	BBCH stage 75
21-07-2015	Irrigation 26 mm.
13-08-2015	BBCH stage 82
13-08-2015	Biomass 1673 g m <sup>-2</sup> – 100% DM
20-08-2015	BBCH stage 88
20-08-2015	Broad sown catch crop of oil seed rape cv. Akiro, 16 kg ha <sup>-1</sup> (on top of the soil)
20-08-2015	Glyphogan (glyphosate) - weeds - 2.7 l ha <sup>-1</sup> (sprayed simultaneously with the sowing of the catch crop) (i.e. 972 g a.i. ha <sup>-1</sup> ) (not monitored)
01-09-2015	BBCH stage 09 – emergence of catch crop
08-09-2015	BBCH stage 90
08-09-2015	Harvest of winter wheat. Stubble height 14 cm, grain yield 74.0 hkg ha <sup>-1</sup> 85% DM
10-09-2015	Straw removed, yield 46.4 hkg ha <sup>-1</sup> - 100% DM
22-03-2016	Ploughed - depth 23 cm
15-04-2016	Spring barley sown, cv. Evergreen, seeding rate 155 kg ha <sup>-1</sup> , sowing depth 2.8 cm, row distance 13 cm. Final plant number 272 m <sup>-2</sup> Sown with rotor harrow combine sowing machine
18-04-2016	Fertilization – 168 N, 24 P, 80 K, kg ha <sup>-1</sup>

Date	Management practice and growth stages – Tylstrup
21-04-2016	Under sowing of clover grass catch crop (AgrowGrass 350 MidiMaize) seeding rate 13 kg ha <sup>-1</sup> , sowing depth 1 cm, row distance 12 cm
01-05-2016	BBCH stage 09 - emergence
10-05-2016	BBCH stage 12
19-05-2016	BBCH stage 23
19-05-2016	Biomass 47.8 g m <sup>-2</sup> – 100% DM
19-05-2016	Fighter 480 (bentazone) – weeds - 1.5 L ha <sup>-1</sup> (i.e. 720 g a.i. ha <sup>-1</sup> )
19-05-2016	Catch crop – BBCH stage 11-12
02-06-2016	BBCH stage 36
09-06-2016	BBCH stage 50
09-06-2016	Irrigation 27 mm
10-06-2016	BBCH stage 50
10-06-2016	Biomass 414.8 g m <sup>-2</sup> – 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 <sup>-2</sup> - 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. Stubble height 15 cm, grain yield 61.9 hkg ha <sup>-1</sup> - 85% DM
29-08-2016	Straw remove, yield 27.0 hkg ha <sup>-1</sup> - 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 <sup>-1</sup> , sowing depth 4 cm, row distance 13 cm. Final plant number not determined.
04-04-2017	BBCH stage 6
06-04-2017	Fertilisation - 133 N, 19 P, 63 K, kg ha <sup>-1</sup>
11-04-2017	BBCH stage 09 - emergence
27-04-2017	BBCH stage 12
08-05-2017	BBCH stage 22
08-05-2017	Biomass 57.3 g m <sup>-2</sup> - 100% DM
09-05-2017	BBCH stage 22
09-05-2017	Hussar Plus OD (iodosulfuron-mesosulfuron) - weeds - 0.07 L ha <sup>-1</sup> (i.e. 3.5 g iodosulfuron and 0.525 g mesosulfuron, a.i. ha <sup>-1</sup> )
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 <sup>-1</sup> (i.e. 125 g propiconazole a.i. ha <sup>-1</sup> )
14-06-2017	BBCH stage 55
14-06-2017	Biomass 629.5 g m <sup>-2</sup> - 100% DM
14-06-2017	Bumper 25 EC (propiconazole) - fungi - 0.5 L ha <sup>-1</sup> (i.e. 125 g propiconazole a.i. ha <sup>-1</sup> )
03-07-2017	BBCH stage 77
17-07-2017	BBCH stage 80-83
17-07-2017	Biomass 629.3 g/m <sup>2</sup> - 100% DM
14-08-2017	Harvest of spring barley. Stubble height 15 cm, grain yield 67.1 hkg ha <sup>-1</sup> - 85% DM
14-08-2017	Straw removed - 28.6 hkg ha <sup>-1</sup> 100% DM
15-08-2017	Winter rape
15-08-2017	Stubble cultivated - depth 7 cm
16-08-2017	Stubble cultivated - depth 20 cm
17-08-2017	Winter rape sown - cv. DK Exclaim, depth 2.0 cm, row distance 13 cm seed amount 1.8 kg ha <sup>-1</sup> , final plant number 54 m <sup>-2</sup>
18-08-2017	Command CS (clomazone) - weeds - 0.25 L ha <sup>-1</sup> (i.e. 90 g clomazone a.i. ha <sup>-1</sup> )
24-08-2017	Fertilisation - 34 N, kg ha <sup>-1</sup>
30-08-2017	BBCH stage 09 - emergence
15-09-2017	Ploughed - depth 23 cm - due to poor emergence - crust had formed on surface due to heavy rain - impeding the emergence

Date	Management practice and growth stages – <b>Tylstrup</b>
16-09-2017	Winter barley sown, cv. Hejmdal, seeding rate 165 kg ha <sup>-1</sup> , sowing depth 4 cm, row distance 13 cm. Final plant number 320 m <sup>2</sup>
16-09-2017	Seed dressing Redigo Pro 170 FS (prothioconazole 12.38 g and 1.65 g tebuconazole a.i. ha <sup>-1</sup> )
23-09-2017	BBCH stage 09 - emergence
27-09-2017	BBCH stage 10
02-10-2017	BBCH stage 11
18-10-2017	BBCH stage 13
18-10-2017	Lexus 50 WG (flupyr-sulfuron) - weeds - 10 g ha <sup>-1</sup> (i.e. 4.63 g flupyr-sulfuron)
09-11-2017	BBCH stage 20
09-11-2017	Biomass 31.8 g m <sup>-2</sup> - 100% DM
09-04-2018	BBCH stage 24
09-04-2018	Fertilisation - 256.4 N, 36.6 P, 121 K, kg ha <sup>-1</sup>
01-05-2018	BBCH stage 32
18-05-2018	BBCH stage 50
18-05-2018	Biomass 520.4 g m <sup>-2</sup> - 100% DM
18-05-2018	Irrigation 40 mm.
24-05-2018	Irrigation 25 mm.
05-06-2018	Irrigation 18 mm.
06-06-2018	BBCH stage 75
06-06-2018	Biomass 1027.4 g m <sup>-2</sup> - 100% DM
09-06-2018	Irrigation 27 mm
19-06-2018	BBCH stage 82
11-07-2018	BBCH stage 91
11-07-2018	Harvest of winter barley, Stubble height 12 cm. Grain yield 46.24 hkg ha <sup>-1</sup> . Total N 1.61% and total-C 43.54% - 85 % DM.
12-07-2018	Straw removed - 28.6 hkg/ha 100% DM - 52.2 hkg ha <sup>-1</sup> , Total-N 0.61% and total-C 43.73% - 100% DM
28-09-2018	Liming - 3.0 t ha <sup>-1</sup>
12-03-2019	Ploughed - (depth not measured - likely depth 23 cm)
05-04-2019	Harrowed - depth unknown
12-04-2019	Spring oats sown
12-04-2019	BBCH stage 09 - emergence (estimated based on 7 years sowing of spring barley on the location)
30-04-2019	Fertilization - 95.5 N, 20.5 P, 102.3 K, kg ha <sup>-1</sup>
28-05-2019	BBCH stage 31
28-05-2019	U46M (MCPA) - weeds - 1 L/ha (i.e. 750 g a.i./ha) - not monitored
24-08-2019	Harvest of spring oats - grain yield 46.7 hkg ha <sup>-1</sup> - 85% DM
27-03-2020	Ploughed
28-03-2020	Fertilization - 143.2 N, 20.6 P, 68.2 K, kg ha <sup>-1</sup>
07-04-2020	Sowing a mixture of spring barley varieties (to reduce need for fungicidal spraying)
20-04-2020	BBCH stage 09 - emergence (estimated based on past cultivation of spring barley at the field)
07-05-2020	BBCH stage 20-21
29-05-2020	BBCH stage 33
29-05-2020	U46M (MCPA) - weeds - 1 L/ha (i.e. 750 g a.i. ha <sup>-1</sup> ) - not monitored

**Table A3.2.** Management practice at **Jynde vad** during the 2012 to 2020 growing seasons. The active ingredients of the various pesticides are indicated in parentheses.

Date	Management practice and growth stages – Jynde vad
30-03-2012	Ploughed. Depth 22 cm
02-04-2012	Rolled with concrete roller
30-04-2012	Fertilization 120 K, kg ha <sup>-1</sup>
30-04-2012	Fertilization 140 N, 17.7 P, 65.3 K, kg ha <sup>-1</sup>
03-05-2012	Sowing maize - cv. Atrium - seed distance 12 cm, row distance 75 cm, depth 6 cm. Seed rate 111,000 seeds ha <sup>-1</sup> , final plant number 12.8 m <sup>-2</sup>
03-05-2012	Fertilization 29.4 N, 14.7 P, kg ha <sup>-1</sup>
07-05-2012	Tracer (potassium bromide), 30.54 kg ha <sup>-1</sup>
17-05-2012	BBCH stage 09 – 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 <sup>-1</sup>
30-05-2012	BBCH stage 13
30-05-2012	Biomass 41.7 g m <sup>-2</sup> - 100% DM
05-06-2012	BBCH stage 15
05-06-2012	Callisto (mesotrione) - weeds - 1.5 L ha <sup>-1</sup>
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 <sup>-1</sup> + 0.06 L ha <sup>-1</sup> - weeds - (neither 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 <sup>-2</sup> - 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 <sup>-2</sup> - 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 <sup>-1</sup> - 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 cv. Alvestra, depth 5 cm, row distance 12 cm, seed rate 235 kg ha <sup>-1</sup> , using a combine drill, final plant number 92 m <sup>-2</sup>
26-04-2013	BBCH stage 09 – emergence
03-05-2013	BBCH stage 12
07-05-2013	Fighter 480 (bentazone) + Stomp (pendimethalin) 0.4 L ha <sup>-1</sup> + 0.6 L ha <sup>-1</sup> - 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	Bentazone 480 (bentazone) + Stomp (pendimethalin) 0.5 L ha <sup>-1</sup> + 0.6 L ha <sup>-1</sup> - weeds (pendimethalin not analysed)
17-05-2013	Fertilization 16.0 P, 83.2 K, kg ha <sup>-1</sup>
21-05-2013	BBCH stage 25

Date	Management practice and growth stages – Jynde vad
27-05-2013	BBCH stage 30
03-06-2013	BBCH stage 37
04-06-2013	Biomass 105.7 g m <sup>-2</sup> - 100% DM
06-06-2013	BBCH stage 38
06-06-2013	Irrigation - 30 mm ha <sup>-1</sup>
10-06-2013	BBCH stage 41
17-06-2013	BBCH stage 60
21-06-2013	Biomass 393.5 g m <sup>-2</sup> - 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 <sup>-1</sup>
15-07-2013	BBCH stage 69
15-07-2013	Biomass 722.5 g m <sup>-2</sup> - 100% DM
16-07-2013	Pirimor G (pirimicarb) - pests - 0.25 kg ha <sup>-1</sup> (not analysed)
22-07-2013	BBCH stage 78
29-07-2013	BBCH stage 81
05-08-2013	Biomass 737.2 g m <sup>-2</sup> - 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 <sup>-1</sup> - 86% DM. Straw yield 30.1 hkg ha <sup>-1</sup> - 100% DM, stubble height 10 cm. Straw shredded at harvest
14-08-2013	Harvest of the eastern half of the field - straw shredded at harvest
20-08-2013	Stubble 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 <sup>-1</sup>
10-04-2014	Fertilization 19.7 N, kg ha <sup>-1</sup>
15-04-2014	Planting potatoes. cv. Oleva, row distance 75 cm, plant distance 33 cm, depth 7 cm. Final plant number 4 m <sup>-2</sup>
15-04-2014	Maxim 100 FS (fludioxonil) - fungi - 625 mL ha <sup>-1</sup> sprayed at potatoes when planting
30-04-2014	BBCH stage 05-08 (crop not emerged yet)
30-04-2014	Command CS (clomazone) + Glyphogan (glyphosate) - weeds - 0.25 L ha <sup>-1</sup> + 1.5 L ha <sup>-1</sup> (neither included in monitoring)
06-05-2014	BBCH stage 08 (crop not emerged yet)
06-05-2014	Titus WSB (rimsulfuron) - weeds - 10 g ha <sup>-1</sup> (not included in monitoring)
14-05-2014	BBCH stage 09 – emergence
26-05-2014	BBCH stage 22
27-05-2014	Titus WSB (rimsulfuron) - weeds - 20 g ha <sup>-1</sup> (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 <sup>-1</sup>
14-06-2014	BBCH stage 47
14-06-2014	Irrigation - 20 mm ha <sup>-1</sup>
16-06-2014	BBCH stage 48
18-06-2014	BBCH stage 50
18-06-2014	Dithane NT (mancozeb) - fungi - 2.0 L ha <sup>-1</sup> + Mospilan SG (acetamiprid) - pests - 150 g ha <sup>-1</sup> (not included)
18-06-2014	Microcare - 1.0 L ha <sup>-1</sup> - manganese 0.368 kg ha <sup>-1</sup> + N 0.035 kg ha <sup>-1</sup>
19-06-2014	BBCH stage 50
19-06-2014	Irrigation - 25 mm ha <sup>-1</sup>
20-06-2014	Biomass tubers 195.3 g m <sup>-2</sup> - 100% DM. Top 299.5 g m <sup>-2</sup> row - 100% DM
23-06-2014	BBCH stage 50
27-06-2014	Dithane NT (mancozeb) - fungi - 2.0 L ha <sup>-1</sup> + Mospilan SG (acetamiprid) - pests - 150 g ha <sup>-1</sup> (not included)
27-06-2014	BBCH stage 65
30-06-2014	BBCH stage 66
01-07-2014	Biomass tubers 91.3 g m <sup>-2</sup> - 100% DM. Top 395.3 g m <sup>-2</sup> row - 100% DM
04-07-2014	BBCH stage 69
04-07-2014	Dithane NT (mancozeb) - fungi - 2.0 L ha <sup>-1</sup>

Date	Management practice and growth stages – Jynde vad
08-07-2014	BBCH stage 69
12-07-2014	Dithane NT (mancozeb) - fungi - 2.0 L ha <sup>-1</sup>
12-07-2014	BBCH stage 70
18-07-2014	BBCH stage 72
18-07-2014	Dithane NT (mancozeb) - fungi - 2.0 L ha <sup>-1</sup>
18-07-2014	Microcare - 1.0 L ha <sup>-1</sup> - manganese 0.368 kg ha <sup>-1</sup> + N 0.035 kg ha <sup>-1</sup>
21-07-2014	BBCH stage 79
21-07-2014	Irrigation - 25 mm ha <sup>-1</sup> .
24-07-2014	BBCH stage 81
24-07-2014	Dithane NT (mancozeb) - fungi - 2.0 L ha <sup>-1</sup>
29-07-2014	BBCH stage 82
29-07-2014	Irrigation - 25 mm ha <sup>-1</sup>
30-07-2014	Ranman (cyazofamid) - fungi - 0.2 L ha <sup>-1</sup>
30-07-2014	BBCH stage 85
04-08-2014	BBCH stage 86
04-08-2014	Irrigation - 25 mm ha <sup>-1</sup>
07-08-2014	BBCH stage 86
07-08-2014	Ranman (cyazofamid) - fungi - 0.2 L ha <sup>-1</sup>
11-08-2014	BBCH stage 93
12-08-2014	Biomass tubers 1881.1 g m <sup>-2</sup> - 100% DM. Top 211.5 g m <sup>-2</sup> row - 100% DM
14-08-2014	BBCH stage 93
14-08-2014	Dithane NT (mancozeb) - fungi - 2.0 L ha <sup>-1</sup>
01-09-2014	Rotor harrowed - 6 cm depth
16-09-2014	Harrowed diagonally - depth 6 cm.
18-09-2014	Winter wheat drilled directly in the potato stubble
26-09-2014	BBCH stage 09 – emergence
29-09-2014	BBCH stage 10
08-10-2014	BBCH stage 13
22-10-2014	BBCH stage 14
22-10-2014	Lexus 50 WG (flupyr-sulfuron) - weeds - 10 g ha <sup>-1</sup> (i.e. 4.6 g a.i. ha <sup>-1</sup> )
24-10-2014	BBCH stage 14
27-10-2014	BBCH stage 15
11-11-2014	BBCH stage 20
11-11-2014	Orius 200 EW (tebuconazole) - fungi – 1.25 L ha <sup>-1</sup> (i.e. 250 g a.i. ha <sup>-1</sup> )
17-11-2014	BBCH stage 20
27-11-2014	BBCH stage 21
09-03-2015	BBCH stage 22
17-03-2015	BBCH stage 22
18-03-2015	Fertilization 120.0 N, 15 P, 56 K, kg ha <sup>-1</sup>
20-03-2015	BBCH stage 22
20-03-2015	Lexus 50 WG (flupyr-sulfuron) - weeds - 10 g ha <sup>-1</sup> (i.e. 4.6 g a.i. ha <sup>-1</sup> )
07-04-2015	BBCH stage 23
15-04-2015	BBCH stage 30
15-04-2015	Biomass 64.5 g m <sup>-2</sup> - 100% DM
16-04-2015	Fertilization 4 P, 20 K, kg ha <sup>-1</sup>
17-04-2015	Fertilization 50.0 N, kg ha <sup>-1</sup>
20-04-2015	BBCH stage 31
28-04-2015	BBCH stage 32
04-05-2015	BBCH stage 33
08-05-2015	BBCH stage 34
	Opus + Comet (epoxiconazole + pyraclostrobin) - fungi - 1.0 L ha <sup>-1</sup> +1.0 L ha <sup>-1</sup> (i.e. 125g a.i. ha <sup>-1</sup> + 250g a.i. ha <sup>-1</sup> )
13-05-2015	BBCH stage 35
18-05-2015	BBCH stage 37
26-05-2015	BBCH stage 43
01-06-2015	BBCH stage 47
09-06-2015	BBCH stage 55
09-06-2015	Biomass 949.1 g m <sup>-2</sup> - 100% DM
11-06-2015	BBCH stage 57

Date	Management practice and growth stages – Jynde vad
11-06-2015	Irrigation - 27 mm ha <sup>-1</sup>
16-06-2015	BBCH stage 59
17-06-2015	Proline 250 EC (prothioconazole) - fungi - 0.8 L ha <sup>-1</sup> (i.e. 200 g a.i. ha <sup>-1</sup> )
23-06-2015	BBCH stage 60
29-06-2015	BBCH stage 65
30-06-2015	BBCH stage 65
30-06-2015	Irrigation - 30 mm ha <sup>-1</sup>
06-07-2015	BBCH stage 75
08-07-2015	BBCH stage 75
08-07-2015	Biomass 1358.8 g m <sup>-2</sup> - 100% DM
13-07-2015	BBCH stage 79
13-07-2015	Irrigation - 30 mm ha <sup>-1</sup>
14-07-2015	BBCH stage 79
21-07-2015	BBCH stage 81
03-08-2015	BBCH stage 83
10-08-2015	BBCH stage 87
20-08-2015	Harvest of winter wheat. Grain yield 79.7 hkg ha <sup>-1</sup> 85% DM, straw yield 71.5 hkg ha <sup>-1</sup> 100% DM, stubbleheight 15 cm. Straw shredded (left in field) at harvest.
20-08-2015	Rotor harrowed, 5-6 cm depth
07-03-2016	Ploughing - 22 cm depth
21-03-2016	Sowing spring barley cv. KWS Irena, depth 4.0 cm, row distance 12 cm, seed rate 170 kg ha <sup>-1</sup> , final plant number 345 m <sup>2</sup> - using a combine drill
21-03-2016	Rolled with concrete roller
21-03-2016	BBCH stage 0
30-03-2016	BBCH stage 09
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 <sup>-1</sup>
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 <sup>-1</sup>
10-05-2015	BBCH stage 20
10-05-2016	Emergence of catch crop – BBCH stage 09
12-05-2016	Biomass 27.7 g m <sup>-2</sup> - 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 <sup>-1</sup> (i.e. 125 g a.i. ha <sup>-1</sup> )
03-06-2016	Irrigation - 30 mm ha <sup>-1</sup>
03-06-2016	BBCH stage 50
03-06-2016	Biomass 721.7 g m <sup>-2</sup> - 100% DM
06-06-2016	BBCH stage 53
08-06-2016	BBCH stage 56
08-06-2016	Irrigation - 30 mm ha <sup>-1</sup>
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 <sup>-2</sup> - 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 <sup>-1</sup> 85% DM, stubble height 15 cm
30-08-2016	Removal of straw, straw yield 27.4 hkg ha <sup>-1</sup> 100% DM



Date	Management practice and growth stages – Jynde vad
03-02-2017	Ploughing - 22 cm depth
20-02-2017	Rolled with concrete roller
15-03-2017	Fertilization 28 P, 147 K, kg ha <sup>-1</sup>
23-03-2017	Sowing pea cv. Mascara, depth 6.0 cm, row distance 12 cm, seed rate 235 kg ha <sup>-1</sup> , using a combine drill, final plant number 74 m <sup>-2</sup>
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 <sup>-1</sup> (i.e. 455 gr a.i. ha <sup>-1</sup> ) (not included)
09-05-2017	Fighter 480 (bentazone) - weeds - 1.0 L ha <sup>-1</sup> (i.e. 480 gr a.i. ha <sup>-1</sup> )
19-05-2017	BBCH stage 52
19-05-2017	Biomass 335.1 g m <sup>-2</sup> - 100% DM
19-05-2017	Focus Ultra (cycloxydim) - weeds - 5.0 L ha <sup>-1</sup> (i.e. 500 g a.i. ha <sup>-1</sup> )
27-05-2017	BBCH stage 59
27-05-2017	Irrigation - 30 mm ha <sup>-1</sup>
30-05-2017	BBCH stage 60
08-06-2017	BBCH stage 64
08-06-2017	Biomass 64.8 g m <sup>-2</sup> - 100% DM
16-06-2017	BBCH stage 69
22-06-2017	BBCH stage 70
22-06-2017	Irrigation - 30 mm ha <sup>-1</sup>
27-06-2017	BBCH stage 71
27-06-2017	Biomass 704.3 g m <sup>-2</sup> - 100% DM
10-07-2017	BBCH stage 75
18-07-2017	BBCH stage 78
26-07-2017	BBCH stage 82
26-07-2017	Biomass 1003.3 g m <sup>-2</sup> - 100% DM
28-07-2017	BBCH stage 82
07-08-2017	BBCH stage 85
10-08-2017	BBCH stage 89
18-08-2017	Harvest of pea. Seed yield 64.4 hkg ha <sup>-1</sup> 86 % DM. Straw yield 38.9 hkg ha <sup>-1</sup> 100% DM, stubble height 10 cm. Straw shredded at harvest
18-08-2017	Rotor harrowed - incorporation of the straw and stubble, 6 cm depth
08-09-2017	Ploughing - 22 cm depth
10-09-2017	Rolled with concrete roller
21-09-2017	Sowing winter wheat cv. Sheriff (Redigo Pro 170FS as seed dressing) Depth 4.0 cm, seeding rate 168 kg ha <sup>-1</sup> , row distance 12.5 cm. Final plant number 320m <sup>-2</sup>
03-10-2017	BBCH stage 09 - emergence
16-10-2017	BBCH stage 12
16-10-2017	Lexus 50 WG (flupyr-sulfuron) - weeds - 10 g ha <sup>-1</sup> (i.e. 4,63 gr a.i. ha <sup>-1</sup> )
27-03-2018	BBCH stage 20
03-04-2018	BBCH stage 23
04-04-2018	Fertilization 54 N, kg ha <sup>-1</sup>
17-04-2018	BBCH stage 27
17-04-2018	Biomass 36.8 g m <sup>-2</sup> - 100% DM
20-04-2018	BBCH stage 28
20-04-2018	Hussar Plus OD - weeds - 0.14 L ha <sup>-1</sup> (i.e. 7 g a.i./ha iodosulfuron-methyl-Na and 1.05 g a.i. mesosulfuron-methyl)
27-04-2018	Pig slurry (sow) application - trail hose applied at surface - 45 t/ha - 110.4 Total-N, 73.9 NH <sub>4</sub> -N, 27.5 P, 55.4K, kg ha <sup>-1</sup> , DM of slurry 2.18 %
03-05-2018	BBCH stage 31
03-05-2018	Lexus 50 WG (flupyr-sulfuron) - weeds - 10 g/ha (i.e. 4.63 gr a.i. ha <sup>-1</sup> )
05-05-2018	BBCH stage 32
08-05-2018	BBCH stage 33
08-05-2018	U46M (MCPA) - weeds - 1 L ha <sup>-1</sup> (i.e. 750 g a.i. ha <sup>-1</sup> ) (not included)
13-05-2018	BBCH stage 41
13-05-2018	Irrigation - 30 mm ha <sup>-1</sup>

Date	Management practice and growth stages – Jynde vad
14-05-2018	BBCH stage 41
20-05-2018	BBCH stage 45
20-05-2018	Irrigation - 30 mm ha <sup>-1</sup>
24-05-2018	BBCH stage 50
24-05-2018	Biomass 65.0 g m <sup>-2</sup> - 100% DM
27-05-2018	BBCH stage 52
27-05-2018	Irrigation - 30 mm ha <sup>-1</sup>
02-06-2018	BBCH stage 65
02-06-2018	Irrigation - 30 mm ha <sup>-1</sup>
04-06-2018	BBCH stage 69
06-06-2018	BBCH stage 70
06-06-2018	Topsin WG (thiophanate-methyl) - fungi - 1.1 kg ha <sup>-1</sup> (i.e. 770 g a.i ha <sup>-1</sup> )
06-06-2018	Irrigation - 30 mm ha <sup>-1</sup>
10-06-2018	BBCH stage 70
10-06-2018	Irrigation - 30 mm ha <sup>-1</sup>
13-06-2018	BBCH stage 72
22-06-2018	BBCH stage 73
26-06-2018	BBCH stage 74
26-06-2018	Irrigation - 30 mm ha <sup>-1</sup>
04-07-2018	BBCH stage 75
04-07-2018	Irrigation 30 mm ha <sup>-1</sup>
09-07-2018	BBCH stage 75
09-07-2018	Biomass 3386.7 g m <sup>-2</sup> - 100% DM
17-07-2018	BBCH stage 80
25-07-2018	BBCH stage 89
26-07-2018	Harvest of winter wheat. Grain yield 82.4 hkg ha <sup>-1</sup> 85% DM, straw yield 44.8 hkg ha <sup>-1</sup> 100% DM, stubble height 14 cm. Straw removed at harvest.
22-08-2018	Glyfonova MAX HL (glyphosate) - weeds - 3.2 L ha <sup>-1</sup> (i.e. 1536 g a.i. ha <sup>-1</sup> )
18-10-2018	Ploughing - 20 cm depth
18-10-2018	Sowing winter rye cv. Bono. Depth 4.0 cm, seeding rate 105 kg ha <sup>-1</sup> , row distance 12.0 cm. Final plant number 220 m <sup>-2</sup>
18-10-2018	Celeste Formula M - 210 mL ha <sup>-1</sup> (5.25 g a.i. ha <sup>-1</sup> fludioxonil) - seed dressing
05-11-2018	BBCH stage 09 - emergence
21-03-2019	BBCH stage 22
21-03-2019	Fertilization 136 N, 26 P, 65 K kg ha <sup>-1</sup>
28-03-2019	BBCH stage 25
08-04-2019	BBCH stage 27
11-04-2019	BBCH stage 28
11-04-2019	Irrigation - 30 mm ha <sup>-1</sup>
12-04-2019	BBCH stage 29
12-04-2019	Biomass 77.0 g m <sup>-2</sup> - 100% DM
17-04-2019	BBCH stage 30
17-04-2019	Fertilization 63 N, 12 P, 30 K kg ha <sup>-1</sup>
19-04-2019	BBCH stage 30
22-04-2019	BBCH stage 30
22-04-2019	Irrigation - 30 mm ha <sup>-1</sup>
25-04-2019	BBCH stage 31
25-04-2019	Talius (proquinazid) - fungi - 0.25 L ha <sup>-1</sup> (i.e. 50 g a.i. ha <sup>-1</sup> )
05-05-2019	BBCH stage 38
05-05-2019	Irrigation - 30 mm ha <sup>-1</sup>
08-05-2019	BBCH stage 40
08-05-2019	Cerone (ethephone) - plant growth regulation - 1.0 L ha <sup>-1</sup> (i.e. 480 g a.i. ha <sup>-1</sup> ) - not monitored
08-05-2019	U46M (MCPA) - weeds - 1.0 L ha <sup>-1</sup> (i.e. 750 g a.i. ha <sup>-1</sup> ) - not monitored
09-05-2019	BBCH stage 41
09-05-2019	Talius (proquinazid) - fungi - 0.25 L ha <sup>-1</sup> (i.e. 50 g a.i. ha <sup>-1</sup> )
13-05-2019	BBCH stage 45
13-05-2019	Biomass 616.9 g m <sup>-2</sup> - 100% DM

Date	Management practice and growth stages – Jynde vad
20-05-2019	BBCH stage 48
24-05-2019	BBCH stage 50
24-05-2019	Irrigation - 30 mm ha <sup>-1</sup>
27-05-2019	BBCH stage 51
08-06-2019	BBCH stage 57
08-06-2019	Irrigation - 30 mm ha <sup>-1</sup>
10-06-2019	BBCH stage 59
24-06-2019	BBCH stage 65
26-06-2019	BBCH stage 66
26-06-2019	Irrigation - 30 mm ha <sup>-1</sup>
04-07-2019	BBCH stage 75
04-07-2019	Irrigation - 30 mm ha <sup>-1</sup>
09-07-2019	BBCH stage 77
09-07-2019	Biomass 1851.8 g m <sup>-2</sup> - 100% DM
22-07-2019	BBCH stage 85
02-08-2019	BBCH stage 89
11-08-2019	BBCH stage 91
11-08-2019	Harvest of winter rye. Grain yield 168.3 hkg ha <sup>-1</sup> 85% DM, straw yield 44.8 hkg ha <sup>-1</sup> 100% DM, stubble height 22 cm. Straw removed at harvest.
03-02-2020	Ploughing - 22 cm depth
25-04-2020	Planting of potatoes. cv. Kuras row distance 75 cm, plant distance 30 cm, depth 14 cm, final plant number
25-04-2020	Fertilization 135 kg K/ha
25-04-2020	Fertilization - 28 N kg ha <sup>-1</sup> placed when planting the potato tubers
25-04-2020	168 N, 6 P, 165 K kg ha <sup>-1</sup> with a pneumatic fertiliser spreader
20-05-2020	BBCH stage 08
20-05-2020	Glyphomax HL (glyphosate) - 2 L/ha (i.e. 960 g a.i. ha <sup>-1</sup> ) and Centium 36 CS (clomazone) 0.25 L ha <sup>-1</sup> (i.e. 90 g a.i. ha <sup>-1</sup> ) - weeds - neither monitored
24-05-2020	BBCH stage 09 - emergence
01-06-2020	BBCH stage 14
13-06-2020	BBCH stage 28
13-06-2020	Irrigation 20 mm ha <sup>-1</sup>
14-06-2020	BBCH stage 28
14-06-2020	Ranman Top (cyazofamid) - fungi – 0.5 L ha <sup>-1</sup> (80 g a.i. ha <sup>-1</sup> )
17-06-2020	Mechanical weeding - depth 5 cm (Einbøck Rollstar) - row hoe with rolling hoe stars
21-06-2020	BBCH stage 40
21-06-2020	Irrigation 20 mm ha <sup>-1</sup>
23-06-2020	BBCH stage 41
23-06-2020	Ranman Top (cyazofamid) - fungi - 0.5 L/ha (80 g a.i. ha <sup>-1</sup> )
23-06-2020	Mospilan SG (acetamiprid) - pests – 0.25 kg/ha (i.e. 50 g a.i. ha <sup>-1</sup> )
23-06-2020	Biomass root 55.7 g m <sup>-2</sup> and top 537.6 g m <sup>-2</sup> - 100 % DM
29-06-2020	BBCH stage 63

**Table A3.3.** Management practice at **Silstrup** during the 2012 to 2020 growing seasons. The active ingredients of the various pesticides are indicated in parentheses.

Date	Management practice and growth stages – <b>Silstrup</b>
15-03-2012	Fertilization 60 N, 32 S kg ha <sup>-1</sup>
13-04-2012	DFF (diflufenican) - weeds - 0.15 L ha <sup>-1</sup>
13-04-2012	BBCH stage 25
13-04-2012	Biomass 176.5 g m <sup>-2</sup> - 100% DM
19-04-2012	BBCH stage 25
19-04-2012	Fusilade Max (fluazifop-P-butyl) - weeds - 1.5 L ha <sup>-1</sup>
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 <sup>-1</sup>
22-05-2012	Biomass 441.9 g m <sup>-2</sup> - 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 <sup>-2</sup> - 100% DM
25-07-2012	Harvest of grass seed. Yield 14.16 hkg ha <sup>-1</sup> - 87% DM
25-07-2012	Straw removed - straw yield 48.3 hkg ha <sup>-1</sup> - 100% DM, stubble height 12 cm
25-07-2012	BBCH stage 89
10-09-2012	Tracer (potassium bromide) 30.0 kg ha <sup>-1</sup>
10-09-2012	Glyfonova 450 Plus (glyphosate) - weeds (killing the red fescue) - 4.8 L ha <sup>-1</sup>
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 <sup>-1</sup> , row distance 15.0 cm using a Horch Pronto 6 DC
17-10-2012	BBCH stage 5
24-10-2012	BBCH stage 09
24-10-2012	BBCH stage 09
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 <sup>-1</sup> + 0.2 L ha <sup>-1</sup>
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 <sup>-1</sup>
03-05-2013	Sowing spring barley cv. Quenc, replacing winter wheat injured by frost. Depth 3.8 cm, seeding rate 175 kg ha <sup>-1</sup> , row distance 15 cm, Horch Pronto 6 DC, final plant number 303 m <sup>-2</sup>
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 <sup>-1</sup>
14-05-2013	BBCH stage 08
16-05-2013	BBCH stage 09
22-05-2013	BBCH stage 12
29-05-2013	BBCH stage 22
29-05-2013	Biomass 23.3 g m <sup>-2</sup> - 100% DM
30-05-2013	BBCH stage 22
30-05-2013	Duotril 400 EC (ioxynil + bromoxynil) - weeds - 0.6 L ha <sup>-1</sup>
11-06-2013	BBCH stage 30
25-06-2013	BBCH stage 47
25-06-2013	Amistar (azoxystrobin) - fungi - 1.0 L ha <sup>-1</sup>
01-07-2013	Folicur 250 EC (tebuconazole) - fungi - 1.0 L ha <sup>-1</sup>
01-07-2013	BBCH stage 50
01-07-2013	Biomass 537.0 g m <sup>-2</sup> - 100% DM
09-07-2013	BBCH stage 58
19-07-2013	BBCH stage 70
06-08-2013	BBCH stage 80

Date	Management practice and growth stages – <b>Silstrup</b>
06-08-2013	Biomass 1332.1 g m <sup>-2</sup> - 100% DM
14-08-2013	BBCH stage 86
20-08-2013	Glyfonova 450 Plus (glyphosate) - weeds (killing the grass) - 2.4 L ha <sup>-1</sup>
20-08-2013	BBCH stage 87
30-08-2013	BBCH stage 89
06-09-2013	Harvest of spring barley. Grain yield 59.8 hkg ha <sup>-1</sup> - 85% DM, straw yield 46.0 hkg ha <sup>-1</sup> - 100% DM, stubble height 14 cm. Straw shredded at harvest
20-09-2013	Liming 3.2 t ha <sup>-1</sup>
23-09-2013	Ploughed - depth 24 cm – packed
25-09-2013	Sowing winter wheat cv. Hereford. Depth 4 cm, seeding rate 190 kg ha <sup>-1</sup> , final plant number 346 m <sup>-2</sup> , row distance 15.0 cm using a Horch Pronto 6 DC
01-10-2013	BBCH stage 06
07-10-2013	BBCH stage 09 – emergence
16-10-2013	BBCH stage 10
16-10-2013	Oxitril CM (bromoxynil + ioxynil) + DFF (diflufenican) - weeds – 0.08 L ha <sup>-1</sup> + 0.2 L ha <sup>-1</sup> (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 <sup>-1</sup>
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 <sup>-2</sup> - 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 <sup>-2</sup> - 100% DM
02-06-2014	BBCH stage 51
03-06-2014	BBCH stage 53
04-06-2014	Amistar (azoxystrobin) - fungi - 1.0 L ha <sup>-1</sup>
18-06-2014	BBCH stage 63
23-06-2014	BBCH stage 68
02-07-2014	Biomass 1776.5 g m <sup>-2</sup> - 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 <sup>-1</sup>
15-08-2014	BBCH stage 90
16-08-2014	Harvest of winter wheat. Grain yield 83.5 hkg ha <sup>-1</sup> - 85% DM, straw yield 113.8 hkg ha <sup>-1</sup> - 100% DM, stubble height 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 - acidified at application - trail hose applied at surface - 28.3 t ha <sup>-1</sup> – 126.2 Total-N, 75.6 NH <sub>4</sub> -N, 44.2 P, 46.7 K, kg ha <sup>-1</sup> , DM of slurry 5.33%
28-04-2015	Ploughed - 24 cm depth
30-04-2015	Fertilization 112.5 K kg ha <sup>-1</sup>
30-04-2015	Seedbed preparation, 5-8 cm depth
02-05-2015	Sowing maize cv. Ambition, depth 3.5 cm, row distance 75 cm, seed distance 14 cm seeding rate 10 m <sup>2</sup> . final plant number 7.4 m <sup>2</sup> (seeds were coated with thirame, fludioxonil and metalaxyl-M) (
02-05-2015	Fertilization 30 N, 12.9 P, kg ha <sup>-1</sup> (placed at sowing)
03-05-2015	BBCH stage 01
12-05-2015	BBCH stage 05
19-05-2015	BBCH stage 07
27-05-2015	BBCH stage 09 - emergence

Date	Management practice and growth stages – <b>Silstrup</b>
27-05-2015	Callisto (mesotrione) + Harmony SX (thifensulfuron-methyl) - weeds - (0.75 L ha <sup>-1</sup> + 5.625 g ha <sup>-1</sup> ) (i.e. 75 g a.i. ha <sup>-1</sup> + 2.813 g a.i. ha <sup>-1</sup> )
06-06-2015	BBCH stage 12
09-06-2015	BBCH stage 12
09-06-2015	Callisto (mesotrione) + MaisTer (foramsulfuron + iodosulfuron) - weeds - (0.75 L ha <sup>-1</sup> + 100 g ha <sup>-1</sup> ) (i.e. 75 g a.i. ha <sup>-1</sup> + 30 g a.i. ha <sup>-1</sup> + 1 g a.i. ha <sup>-1</sup> )
18-06-2015	BBCH stage 14
23-06-2015	BBCH stage 15
23-06-2015	MaisTer (foramsulfuron + iodosulfuron) - weeds - (50 g ha <sup>-1</sup> ) (i.e. 15 g a.i. ha <sup>-1</sup> + 0.5 g a.i. ha <sup>-1</sup> )
03-07-2015	BBCH stage 17-18
03-07-2015	Biomass 5.8 g m <sup>-2</sup> - 100% DM
14-07-2015	BBCH stage 19
22-07-2015	BBCH stage 31
12-08-2015	BBCH stage 51
13-08-2015	BBCH stage 51
13-08-2015	Biomass 303.8 g m <sup>-2</sup> - 100% DM
19-08-2015	BBCH stage 54
26-08-2015	BBCH stage 65
09-09-2015	BBCH stage 70
23-09-2015	BBCH stage 72
30-09-2015	BBCH stage 73
05-10-2015	BBCH stage 74
05-10-2015	Biomass 1086.2 g m <sup>-2</sup> - 100% DM
21-10-2015	BBCH stage 77
28-10-2015	BBCH stage 80
31-10-2015	Harvest of maize. Stubble height 25 cm. Total harvested yield 64.98 hkg ha <sup>-1</sup> - 100% DM.
05-11-2015	Maize stubble crushed with a cutter
28-04-2016	Stubble cultivated - depth 6 cm
09-05-2016	Pig slurry application – acidified at application – trail hose applied at surface – 34 t ha <sup>-1</sup> - 150.6 Total-N, 85.0 NH <sub>4</sub> -N, 70.7 P, 73.4 K, kg ha <sup>-1</sup> , 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 <sup>-1</sup>
12-05-2016	Rotary cultivated - depth 5.0 cm
13-05-2016	Fertilization 33.4 N, 17.5 P, kg ha <sup>-1</sup> (placed at sowing)
13-05-2016	Sowing maize cv. Activate, depth 3.5 cm, row distance 75 cm, seed distance 14.7 cm seeding rate 10 m <sup>2</sup> . Final plant number 8 m <sup>2</sup> (seeds were coated with Mesurol FS 500 - thirame, fludioxonil and metalaxyl-M) (not monitored)
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 (mesotrione) + Harmony SX (thifensulfuron-methyl) - weeds - (0.75 L ha <sup>-1</sup> + 5.625 g ha <sup>-1</sup> ) (i.e. 75 g a.i. ha <sup>-1</sup> + 2.813 g a.i. ha <sup>-1</sup> )
08-06-2016	BBCH stage 14
08-06-2016	Biomass 3.3 g m <sup>-2</sup> - 100% DM
22-06-2016	BBCH stage 16-17
22-06-2016	Callisto (mesotrione) + MaisTer (foramsulfuron + iodosulfuron) - weeds - (0.75 L ha <sup>-1</sup> + 150 g ha <sup>-1</sup> ) (i.e. 75 g a.i. ha <sup>-1</sup> + 45 g a.i. ha <sup>-1</sup> + 1.5 g a.i. ha <sup>-1</sup> )
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 <sup>-2</sup> - 100% DM
15-08-2016	BBCH stage 67
15-08-2016	Biomass 925.8 g m <sup>-2</sup> - 100% DM
15-09-2016	BBCH stage 75

Date	Management practice and growth stages – <b>Silstrup</b>
20-09-2016	Dry matter determination - 27.25%
29-09-2016	Dry matter determination - 29,74%
05-10-2016	Dry matter determination - 31.2%
11-10-2016	Harvest of maize. Stubble height 33 cm. Total harvested yield 120.86 hkg ha <sup>-1</sup> - 100% DM.
13-10-2016	Maize stubble crushed with a cutter
14-10-2016	Stubble 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 <sup>-1</sup>
29-04-2017	Spring barley sown, cv. KWS Irina, seeding rate 160 kg ha <sup>-1</sup> , sowing depth 3.4 cm, row distance 12.5 cm. Final plant number not determined.
29-04-2017	Seed dressing Redigo Pro 170 FS (12.0 g prothioconazole and 1.60 g tebuconazole g a.i. ha <sup>-1</sup> )
11-05-2017	BBCH stage 09
15-05-2017	BBCH stage 12
29-05-2017	BBCH stage 21-22
29-05-2017	Pig slurry application - acidified at application - trail hose applied at surface - 30 t ha <sup>-1</sup> - 110.4 Total-N, 69.3 NH <sub>4</sub> -N, 44.4 P, 51.9 K, kg ha <sup>-1</sup> , DM of slurry 4.88 %
29-05-2017	Biomass 50.7 g m <sup>-2</sup> - 100% DM
29-05-2017	BBCH stage 32
12-06-2017	BBCH stage 33
15-06-2017	Zypar (halauxifen-methyl + florasulam (not monitored)) - weeds - 1.0 L ha <sup>-1</sup> (6.25 g a.i. ha <sup>-1</sup> halauxifen-methyl + 5 g florasulam)
27-06-2017	BBCH stage 50
27-06-2017	Biomass 526.1 g m <sup>-2</sup> - 100% DM
27-06-2017	Bumper 25 EC (propiconazole) - fungi - 0.5 L ha <sup>-1</sup> (125 g a.i. ha <sup>-1</sup> propiconazole)
04-07-2017	BBCH stage 57
10-07-2017	BBCH stage 64
10-07-2017	Bumper 25 EC (propiconazole) - fungi - 0.5 l ha <sup>-1</sup> (125 g a.i. ha <sup>-1</sup> propiconazole)
19-07-2017	BBCH stage 70
26-07-2017	BBCH stage 75
01-08-2017	BBCH stage 80
29-08-2017	BBCH stage 89
02-09-2017	Harvest of spring barley. Stubble height 15 cm, grain yield 61.2 hkg ha <sup>-1</sup> - 85% DM,
02-09-2017	Straw removed, straw yield 13.19 hkg ha <sup>-1</sup> - 100% DM
26-09-2017	Ploughed - 25 cm depth
28-09-2017	Seedbed preparation - depth 10 cm
28-09-2017	Fertilization 12.6 N, 14.0 P, kg ha <sup>-1</sup> (placed at sowing)
28-09-2017	Winter barley sown, cv. Kosmos, seeding rate 190 kg ha <sup>-1</sup> , sowing depth 3.0 cm, row distance 13 cm, final plant number 216 m <sup>-2</sup>
28-09-2017	Seed dressing Redigo Pro 170 FS (prothioconazole 14.25 g and tebuconazole 1.9 g a.i. ha <sup>-1</sup> )
09-10-2017	BBCH stage 09 - emergence
18-10-2017	BBCH stage 11
18-10-2017	Lexus (flupyrsulfuron) - weeds - 10 g ha <sup>-1</sup> (i.e. 4.63 g a.i. ha <sup>-1</sup> )
27-10-2017	BBCH stage 12-13
10-04-2018	BBCH stage 20
10-04-2018	Fertilization 171.7 N, 24.5 P, 81.8 K, kg ha <sup>-1</sup>
18-04-2018	BBCH stage 22
18-04-2018	Biomass 461.8 g m <sup>-2</sup> - 100% DM
19-04-2018	BBCH stage 22
19-04-2018	Hussar Plus OD - weeds - 0.05 L ha <sup>-1</sup> (i.e. 2.5 g a.i. ha <sup>-1</sup> iodosulfuron-methyl-Na and 0.375 g a.i. ha <sup>-1</sup> mesosulfuron-methyl)
23-05-2018	Biomass 691.8 g m <sup>-2</sup> - 100% DM
23-05-2018	BBCH stage 53
23-05-2018	Proline 250 EC (prothioconazole) - fungi - 0.8 L ha <sup>-1</sup> (i.e. 200 g a.i. ha <sup>-1</sup> )
01-06-2018	BBCH stage 65
01-06-2018	Proline 250 EC (prothioconazole) - fungi - 0.8 L ha <sup>-1</sup> (i.e. 200 g a.i. ha <sup>-1</sup> )
06-06-2018	BBCH stage 77
06-06-2018	Biomass 1165.3 g m <sup>-2</sup> - 100% DM
21-06-2018	BBCH stage 83

Date	Management practice and growth stages – <b>Silstrup</b>
20-07-2018	BBCH stage 89
20-07-2018	Harvest of winter barley. Stubble height 10 cm, grain yield 71.9 hkg ha <sup>-1</sup> . Total N 1.65% and total C 43.48% - 85% DM
24-07-2018	Straw removed, straw yield 10.3 hkg ha <sup>-1</sup> . Total-N 0.37% and total-C 42.45% - 100% DM
17-08-2018	Sowing winter rape cv. DK Exclaim, sowing depth 2-3 cm, seeding rate 3.3 kg ha <sup>-1</sup> , row distance 45 cm, final plant number 33 m <sup>-2</sup>
17-08-2018	Seed dressing Thiram
23-08-2018	BBCH stage 09 – emergence
29-08-2018	BBCH stage 10
17-09-2018	BBCH stage 13 – 14
17-09-2018	Focus Ultra (cycloxydim) - weeds - 1.8 L ha <sup>-1</sup> - weeds - (i.e. 180 g a.i. ha <sup>-1</sup> )
26-09-2018	BBCH stage 15
10-10-2018	BBCH stage 15
17-10-2018	BBCH stage 16
24-10-2018	BBCH stage 16
24-10-2018	Biomass 71.8 g m <sup>-2</sup> - 100% DM
09-11-2018	BBCH stage 18
09-11-2018	Kerb 400 SC (propyzamide) - weeds - 1.25 L ha <sup>-1</sup> (i.e. 500 g a.i. ha <sup>-1</sup> )
01-03-2018	BBCH stage 30
01-03-2018	Fertilization 81.0 N, kg ha <sup>-1</sup>
02-04-2019	BBCH stage 52
02-04-2019	Pig slurry application - acidified at application 2 L 96% H <sub>2</sub> SO <sub>4</sub> (ton slurry) <sup>-1</sup> - trail hose applied at surface - 22.7 T ha <sup>-1</sup> - 92.8 Total-N, 57.2 NH <sub>4</sub> -N, 21.6 P, 37.0 K, kg ha <sup>-1</sup> , DM of slurry 4.19 %
04-04-2019	BBCH stage 53
04-04-2019	Biomass 271.4 g m <sup>-2</sup> - 100% DM
09-04-2019	BBCH stage 54
09-04-2019	Agil 100 EC (propaquizifop) - weeds - 1.2 L ha <sup>-1</sup> (i.e. 120 g a.i. ha <sup>-1</sup> )
16-04-2019	BBCH stage 55
24-04-2019	BBCH stage 60
29-04-2019	BBCH stage 63
08-05-2019	BBCH stage 66
15-05-2019	BBCH stage 68
28-05-2019	BBCH stage 76
04-06-2019	BBCH stage 79
02-07-2019	BBCH stage 80
17-07-2019	BBCH stage 83
24-07-2019	BBCH stage 85
14-08-2019	BBCH stage 90
14-08-2019	Harvest of winter rape. Seed yield 44.5 hkg ha <sup>-1</sup> - 91% DM. Stubble height 41 cm, straw shredded at harvest - amount not determined.
26-08-2019	Rape stubble crushed with a mower
19-09-2019	Ploughed - 25 cm depth
20-09-2019	Seedbed preparation - depth 7 cm
21-09-2019	Sowing winter wheat, cv. Benchmark, seeding rate 190 kg ha <sup>-1</sup> , sowing depth 5.0 cm, row distance 12.5 cm. Final plant number 240 m <sup>-2</sup>
21-09-2019	Celest Formula M, 380 mL ha <sup>-1</sup> (9.5 g a.i. ha <sup>-1</sup> fludioxonil) - seed dressing (not monitored)
07-10-2019	BBCH stage 09 - emergence
18-03-2020	BBCH stage 21
18-03-2020	Biomass 47.8 g m <sup>-2</sup> - 100% DM
25-03-2020	BBCH stage 21
25-03-2020	Fertilization 177.2 N, 25.3 P, 84.4 K, kg ha <sup>-1</sup>
07-04-2020	BBCH stage 30
07-04-2020	Broadway - weeds - 165 g ha <sup>-1</sup> (11.27 g a.i. ha <sup>-1</sup> pyroxsulam and 3.76 g a.i. ha <sup>-1</sup> florasulam)
15-04-2020	BBCH stage 30
27-04-2020	BBCH stage 32
07-05-2020	BBCH stage 32
19-05-2020	BBCH stage 37-39
26-05-2020	BBCH stage 41
28-05-2020	BBCH stage 42



Date	Management practice and growth stages – <b>Silstrup</b>
28-05-2020	Proline 250 EC (prothioconazole) - fungi - 0.8 L ha <sup>-1</sup> (200 g a.i. ha <sup>-1</sup> ) and Amistar (azoxystrobin) - fungi – 0.5 L ha <sup>-1</sup> (125 g a.i. ha <sup>-1</sup> )
03-06-2020	BBCH stage 50
08-06-2020	BBCH stage 53
08-06-2020	Biomass 1072.7 g m <sup>-2</sup> - 100% DM
16-06-2020	BBCH stage 68
16-06-2020	Proline 250 EC (prothioconazole) - fungi - 0.8 L ha <sup>-1</sup> (200 g a.i./ha) and Amistar (azoxystrobin) - fungi - 0.5 L ha <sup>-1</sup> (125 g a.i. ha <sup>-1</sup> )
24-06-2020	BBCH stage 69

**Table A3.4.** Management practice at **Estrup** during the 2012 to 2020 growing seasons. The active ingredients of the various pesticides are indicated in parentheses.

Date	Management practice and growth stages – <b>Estrup</b>
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 <sup>-1</sup>
29-03-2012	Rotor harrowed - depth 4 cm
30-03-2012	Spring barley sown, cv. Keops, seeding rate 159 kg ha <sup>-1</sup> , sowing depth 4.3 cm, row distance 12 cm. Final plant number 330 m <sup>-2</sup>
03-04-2012	Rolled with a Cambridge roller
22-04-2012	BBCH stage 09 – 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 <sup>-2</sup> - 100% DM
15-05-2012	Fox 480 SC (bifenox) - weeds - 1.2 L ha <sup>-1</sup>
18-05-2012	BBCH stage 23
18-05-2012	Mustang Forte (aminopyralid/florasulam/2,4-D) - weeds - 0.75 L ha <sup>-1</sup> (florasulam/2,4-D not monitored)
21-05-2012	BBCH stage 30
21-05-2012	Fertilization manganese nitrate (23.5%) - 2.0 L ha <sup>-1</sup>
29-05-2012	BBCH stage 37
29-05-2012	Fertilization manganese nitrate (23.5%) - 2.0 L ha <sup>-1</sup>
06-06-2012	BBCH stage 40
13-06-2012	BBCH stage 50
13-06-2012	Amistar (azoxystrobin) - fungi - 1.0 L ha <sup>-1</sup>
14-06-2012	BBCH stage 50
14-06-2012	Biomass 528.5 g m <sup>-2</sup> - 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 <sup>-2</sup> - 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. Stubble height 12 cm, grain yield 62.9 hkg ha <sup>-1</sup> - 85% DM.
13-08-2012	Straw shredded at harvest - 41.0 hkg ha <sup>-1</sup> - 100% DM
26-09-2012	Tracer (potassium bromide) - 30 kg ha <sup>-1</sup>
08-03-2013	Ploughed - depth 20 cm - packed with a Dalbo ring roller
05-04-2013	Fertilization 16 P, 84 K, kg ha <sup>-1</sup>
23-04-2013	Seedbed preparation - depth 5 cm
23-04-2013	Sowing peas - cv. Alvesta - depth 5 cm, row distance 12 cm, seeding rate 230 kg ha <sup>-1</sup> . Final plant number 82 m <sup>-2</sup>
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 <sup>-1</sup>
04-05-2013	BBCH 9 – emergence
16-05-2013	BBCH stage 12
16-05-2013	Fighter 480 (bentazone) - weeds - 1.0 L ha <sup>-1</sup>
16-05-2013	Cyperb (cypermethrin) - pests - 0.3 L ha <sup>-1</sup> (not analyzed)
22-05-2013	BBCH stage 31
27-05-2013	BBCH stage 33
27-05-2013	Biomass 42.3 g m <sup>-2</sup> - 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 <sup>-2</sup> - 100% DM
26-06-2013	BBCH stage 62

Date	Management practice and growth stages – Estrup
09-07-2013	BBCH stage 66
12-07-2013	BBCH stage 68
12-07-2013	Biomass 718.1 g m <sup>-2</sup> - 100% DM
13-07-2013	BBCH stage 68
13-07-2013	Pirimor G (pirimicarb) - pests - 0.25 kg ha <sup>-1</sup> (not analyzed)
17-07-2013	BBCH stage 79
31-07-2013	BBCH stage 83
05-08-2013	BBCH stage 83
05-08-2013	Biomass 985.3 g m <sup>-2</sup> - 100% DM
13-08-2013	BBCH stage 87
20-08-2013	BBCH stage 90
21-08-2013	Glyfonova 450 Plus (glyphosate) - weeds - 2.4 L ha <sup>-1</sup>
27-08-2013	BBCH stage 93
06-09-2013	Harvest of peas. Stubble height 10 cm, seed yield 49.8 hkg ha <sup>-1</sup> - 86% dry matter.
06-09-2013	Straw shredded at harvest - 24.38 hkg ha <sup>-1</sup> 100% DM
13-09-2013	Winter wheat sown cv. Herford. Depth 4.0 cm, row distance 12 cm, seeding rate 180 kg ha <sup>-1</sup> . Final plant number 365 m <sup>-2</sup> using a combined power harrow 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 manganese nitrate (23.5%) - 2.0 kg ha <sup>-1</sup>
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 <sup>-1</sup> + 0.24 L ha <sup>-1</sup> (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 <sup>-1</sup> (liquid fertilizer - applied 1000 L ha <sup>-1</sup> with a sprayer)
22-04-2014	BBCH stage 32
22-04-2014	Fluxyr 200 EC - (fluroxypyr) - weeds - 0.7 L ha <sup>-1</sup> (not included)
22-04-2014	Fertilization manganese nitrate (23,5%) - 2.0 kg ha <sup>-1</sup>
07-05-2014	BBCH stage 34
07-05-2014	Biomass 54.0 g m <sup>-2</sup> - 100% DM
15-05-2014	BBCH stage 36
15-05-2014	Primus (florasulam) - weeds - 50 mL ha <sup>-1</sup>
20-05-2014	BBCH stage 38
20-05-2014	Folicur 250 EC (tebuconazole) - fungi - 1.0 L ha <sup>-1</sup>
27-05-2014	BBCH stage 50
02-06-2014	BBCH stage 59
02-06-2014	Biomass 497.3 g m <sup>-2</sup> - 100% DM
02-06-2014	Amistar (azoxystrobin) - fungi - 1.0 L ha <sup>-1</sup>
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 <sup>-1</sup> (not included)
02-07-2014	BBCH stage 74
07-07-2014	BBCH stage 75
07-07-2014	Biomass 1557.7 g m <sup>-2</sup> - 100% DM
16-07-2014	BBCH stage 82
26-07-2014	BBCH stage 87
26-07-2014	Glyfonova 450 Plus (glyphosate) - weeds – 2.4 L ha <sup>-1</sup>
06-08-2014	BBCH stage 90
06-08-2014	Harvest of winter wheat. Stubble height 11 cm, grain yield 69.3 hkg ha <sup>-1</sup> - 85% DM
12-08-2014	Harrowed to 5 cm depth and sown a catch crop of oilseed radish 12 kg ha <sup>-1</sup> seed on soil surface
06-08-2014	Straw shredded at harvest - 48.7 hkg ha <sup>-1</sup> , 100% DM
12-08-2014	Liming 3.5 t ha <sup>-1</sup> magnesium limestone

Date	Management practice and growth stages – <b>Estrup</b>
29-04-2015	Pig slurry application - acidified at application from pH 7.15 to 6.82- hose applied at surface - 28.0 t ha <sup>-1</sup> - 117.3 Total-N, 76.44 NH <sub>4</sub> -N, 39.2 P, 47.9 K, kg ha <sup>-1</sup> , 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 <sup>-1</sup> (placed at sowing)
11-05-2015	Sowing maize cv. Ambition, depth 4 cm, row distance 75 cm, seed distance 12.1 cm seeding rate 11 m <sup>-2</sup> . Final plant number 10.5 m <sup>-2</sup>
13-05-2015	Fertilization 55.3 N, 8.5 P, 34.0 K, kg ha <sup>-1</sup> (applied with a field sprayer - liquid fertilizer)
27-05-2015	BBCH stage 09 - emergence
27-05-2015	Callisto (mesotrione) + Harmony SX (thifensulfuron-methyl) - weeds - (0.75 L ha <sup>-1</sup> + 5.625 g ha <sup>-1</sup> ) (i.e. 75 g a.i. ha <sup>-1</sup> + 2.813 g a.i. ha <sup>-1</sup> )
03-06-2015	BBCH stage 12
06-06-2015	BBCH stage 13
06-06-2015	Callisto (mesotrione) + MaisTer (foramsulfuron + iodosulfuron) - weeds - (0.75 L ha <sup>-1</sup> + 100 g ha <sup>-1</sup> ) (i.e. 75 g a.i. ha <sup>-1</sup> + 30 g a.i. ha <sup>-1</sup> + 1 g a.i. ha <sup>-1</sup> )
08-06-2015	BBCH stage 13
08-06-2015	Biomass 0.4 g m <sup>-2</sup> - 100% DM
18-06-2015	BBCH stage 14
23-06-2015	BBCH stage 16
30-06-2015	BBCH stage 18
30-06-2015	MaisTer (foramsulfuron + iodosulfuron) + Lodin 200 EC (fluroxypyr) - weeds - (50 g ha <sup>-1</sup> + 1.0 L ha <sup>-1</sup> ) (i.e. 15 g a.i. ha <sup>-1</sup> + 0.5 g a.i. ha <sup>-1</sup> + 180 g a.i. ha <sup>-1</sup> ) (fluroxypyr not included)
01-07-2015	BBCH stage 19
09-07-2015	BBCH stage 22
16-07-2015	BBCH stage 33
23-07-2015	BBCH stage 43
30-07-2015	BBCH stage 51
04-08-2015	BBCH stage 51
04-08-2015	Biomass 1794 g m <sup>-2</sup> - 100% DM
05-08-2015	BBCH stage 60
13-08-2015	BBCH stage 65
08-06-2015	Biomass 4159 g m <sup>-2</sup> - 100% DM
20-08-2015	BBCH stage 69
01-09-2015	BBCH stage 72
15-09-2015	BBCH stage 73
22-09-2015	BBCH stage 74
06-10-2015	BBCH stage 75
13-10-2015	BBCH stage 78
23-10-2015	BBCH stage 81
23-10-2015	Harvest of maize. Stubble height 25 cm. Total harvested yield 105.98 hkg ha <sup>-1</sup> 100% DM.
04-05-2016	Pig slurry application - acidified at application trail hose applied at surface - 21.0 t ha <sup>-1</sup> - 86.5 Total-N, 56.3 NH <sub>4</sub> -N, 11.6 P, 29.6 K, kg ha <sup>-1</sup> , 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 <sup>-1</sup> (20% thereof placed at sowing and 80% harrowed into the soil before the sowing)
06-05-2016	Sowing maize cv. Ambition, depth 4 cm, row distance 75 cm, seed distance 12.1 cm, seeding rate 11 m <sup>2</sup> . Final plant number 10.5 m <sup>2</sup>
14-05-2016	BBCH stage 09 - emergence
14-05-2016	BBCH stage 11
14-05-2016	BBCH stage 13
01-06-2016	BBCH stage 14
01-06-2016	Callisto (mesotrione) + Harmony SX (thifensulfuron-methyl) - weeds - (0.75 l ha <sup>-1</sup> + 5.625 g ha <sup>-1</sup> ) (i.e. 75 g a.i. ha <sup>-1</sup> + 2.813 g a.i. ha <sup>-1</sup> )
05-06-2016	BBCH stage 14
05-06-2015	Biomass 288.5 g m <sup>-2</sup> - 100% DM
08-06-2016	BBCH stage 16
11-06-2016	BBCH stage 17

Date	Management practice and growth stages – <b>Estrup</b>
11-06-2016	Callisto (mesotrione) + MaisTer (foramsulfuron + iodosulfuron) - weeds - (0.75 l ha <sup>-1</sup> + 100 g ha <sup>-1</sup> ) (i.e. 75 g a.i. ha <sup>-1</sup> + 30 g a.i. ha <sup>-1</sup> + 1 g a.i. ha <sup>-1</sup> )
15-06-2016	BBCH stage 18
16-06-2016	BBCH stage 18
16-06-2016	MaisTer (foramsulfuron + iodosulfuron) - weeds - (50 g ha <sup>-1</sup> ) (i.e. 15 g a.i. ha <sup>-1</sup> + 0.5 g a.i. ha <sup>-1</sup> )
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 <sup>-2</sup> - 100% DM
27-07-2016	BBCH stage 57
09-08-2016	BBCH stage 65
09-08-2016	Biomass 8118.8 g m <sup>-2</sup> - 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 <sup>-1</sup> 100% DM.
04-04-2017	Fertilization 28 P, 147 K, kg ha <sup>-1</sup>
08-04-2017	Sowing peas - cv. Mascara - depth 7 cm, row distance 13 cm seeding rate 220 kg ha <sup>-1</sup> . Final plant number 72 m <sup>2</sup>
14-04-2017	BBCH stage 09 - emergence
15-04-2017	BBCH stage 12
15-04-2017	Stomp CS (pendimethalin) - weeds - 1.0 L ha <sup>-1</sup> (i.e. 455 g a.i. ha <sup>-1</sup> ) - not included in monitoring
15-04-2017	Fighter 480 (bentazone) - weeds - 1.0 L ha <sup>-1</sup> (i.e. 480 g a.i. ha <sup>-1</sup> )
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 <sup>-2</sup> - 100% DM
08-06-2017	BBCH stage 51
12-06-2017	BBCH stage 60
12-06-2017	Biomass 162.8 g m <sup>-2</sup> - 100% DM
22-06-2017	BBCH stage 62
29-06-2017	BBCH stage 64
07-07-2017	BBCH stage 65
10-07-2017	BBCH stage 70
10-07-2017	Biomass 484.4 g m <sup>-2</sup> - 100% DM
19-07-2017	BBCH stage 70
04-08-2017	BBCH stage 82
04-08-2017	Biomass 613.2 g m <sup>-2</sup> - 100% DM
07-08-2017	BBCH stage 090
07-08-2017	Glyphomax HL (glyphosate) - weeds - 2.5 L ha <sup>-1</sup> (i.e. 1152 g a.i./ha)
10-08-2017	BBCH stage 090
15-08-2017	Harvest of peas. Stubble height 10 cm, seed yield 24.2 hkg ha <sup>-1</sup> - 86% dry matter.
15-08-2017	Straw shredded at harvest - 18.85 hkg ha <sup>-1</sup> - 100 % DM
22-09-2017	Ploughed - depth 20 cm
22-09-2017	Winter wheat sown cv. Sheriff, depth 4.0 cm row distance 12 cm seeding rate 168 kg ha <sup>-1</sup> . Final plant number 320 m <sup>-2</sup> using a combined power harrow sowing equipment
22-09-2017	Seed dressing Redigo Pro 170 FS (12.6 g prothioconazole a.i. ha <sup>-1</sup> and 1.68 g a.i. ha <sup>-1</sup> )
05-10-2017	BBCH stage 09 - emergence
16-10-2017	BBCH stage 12
16-10-2017	Lexus 50 WG (flupyrsulfuron) - weeds - 10 g ha <sup>-1</sup> (i.e. 4.63 g a.i. ha <sup>-1</sup> flupyrsulfuron)
27-03-2018	BBCH stage 20
03-04-2018	BBCH stage 21
06-04-2018	BBCH stage 24
06-04-2018	Fertilization 52.0 N kg ha <sup>-1</sup>
18-04-2018	BBCH stage 25
18-04-2018	Biomass 60.1 g m <sup>-2</sup> - 100% DM
20-04-2018	BBCH stage 28

Date	Management practice and growth stages – <b>Estrup</b>
20-04-2018	Hussar Plus OD - weeds - 0.14 L ha <sup>-1</sup> (i.e. 7.0 g a.i. ha <sup>-1</sup> iodosulfuron-methyl-Na and 1.05 g a.i. ha <sup>-1</sup> mesosulfuron-methyl)
30-04-2018	BBCH stage 30
30-04-2018	Pig slurry application (sow) - trail hose applied at surface - 41.7 t ha <sup>-1</sup> - 93.4 Total-N, 78.8 NH <sub>4</sub> -N, 5.4 P, 135.5 K, kg ha <sup>-1</sup> , DM of slurry 1.0 %
03-05-2018	BBCH stage 31
03-05-2018	Lexus 50 WG (flupyr-sulfuron) - weeds - 10 g ha <sup>-1</sup> (i.e. 4.63 g a.i. ha <sup>-1</sup> flupyr-sulfuron)
14-05-2018	BBCH stage 41
24-05-2018	BBCH stage 50
30-05-2018	BBCH stage 52
30-05-2018	Biomass 2581.7 g m <sup>-2</sup> - 100% DM
04-06-2018	BBCH stage 68-69
06-06-2018	BBCH stage 68-69
06-06-2018	Topsin WG (thiophanate-methyl) - fungi - 1.1 kg ha <sup>-1</sup> (i.e. 770 g a.i. ha <sup>-1</sup> )
13-05-2018	BBCH stage 71
21-06-2018	BBCH stage 73
21-06-2018	Karate 2.5 WG (lambda-cyhalothrin - (pests) - 0.2 kg ha <sup>-1</sup> (i.e. 10 g a.i. ha <sup>-1</sup> ) (not monitored)
22-06-2018	BBCH stage 73
09-07-2018	BBCH stage 75
10-07-2018	BBCH stage 75
10-07-2018	Biomass 2836.3 g m <sup>-2</sup> - 100% DM
17-07-2018	BBCH stage 80
25-07-2018	BBCH stage 89
27-07-2018	Harvest of winter wheat. Stubble height 13 cm, grain yield 75.2 hkg ha <sup>-1</sup> - 85% DM,
27-07-2018	Straw shredded at harvest - 37.9 hkg ha <sup>-1</sup> 100% DM
05-11-2018	Ploughed - depth 20 cm
08-04-2019	Fertilization 137 N, 26 P, 65 K, kg ha <sup>-1</sup>
08-04-2019	Spring barley sown cv. Flair. Depth 4 cm, seeding rate 165 kg ha <sup>-1</sup> , row distance 12.0 cm. Final plant number 360 m <sup>-2</sup> . Sown with combine seed drill (Amazone Drill-Star RP-AD 302)
08-04-2019	Redigo Pro 170 FS (12.38 g a.i. ha <sup>-1</sup> prothioconazole + 1.65 g a.i. ha <sup>-1</sup> tebuconazole) - seed dressing
17-04-2019	BBCH stage 09 - emergence
02-05-2019	BBCH stage 17
15-05-2019	BBCH stage 23
15-05-2019	Biomass 194.9 g m <sup>-2</sup> - 100% DM
22-05-2019	BBCH stage 31
22-05-2019	Pixxaro EC (fluroxypyr + halauxifen-methyl) - weeds - 0.35 L ha <sup>-1</sup> (i.e. 98 g a.i. ha <sup>-1</sup> fluroxypyr and 4.375 g a.i. ha <sup>-1</sup> halauxifen-methyl)
22-05-2019	Juventus 90 (metconazole) - fungi - 1.0 L ha <sup>-1</sup> (90 g metconazole a.i. ha <sup>-1</sup> )
05-06-2019	BBCH stage 41
12-06-2019	BBCH stage 50
12-06-2019	Biomass 420.8 g m <sup>-2</sup> - 100% DM
13-06-2019	BBCH stage 50
13-06-2019	Juventus 90 (metconazole) - fungi - 1.0 L ha <sup>-1</sup> (90 g metconazole a.i. ha <sup>-1</sup> )
26-06-2019	BBCH stage 62
09-07-2019	BBCH stage 75
09-07-2019	Biomass 1096.2 g m <sup>-2</sup> - 100% DM
25-07-2019	BBCH stage 83
01-08-2019	BBCH stage 87
08-08-2019	BBCH stage 89
11-08-2019	Harvest of spring barley. Stubble height 20 cm, grain yield 70.4 hkg ha <sup>-1</sup> 85% DM, straw yield 23.3 hkg ha <sup>-1</sup> 100% DM
11-08-2019	Straw shredded at harvest - 23.3 hkg ha <sup>-1</sup> 100% DM
16-09-2019	Ploughed - depth 20 cm
16-09-2019	Winter wheat sown cv. Sheriff. Depth 4.0 cm row distance 12 cm, seeding rate 178 kg ha <sup>-1</sup> , final plant number 360 g m <sup>-2</sup> using a combined power harrow sowing equipment
16-09-2019	Redigo Pro 170 FS 89 ml ha <sup>-1</sup> (13.35 g a.i. ha <sup>-1</sup> prothioconazole + 1.78 g a.i. ha <sup>-1</sup> tebuconazole) - seed dressing
26-09-2019	BBCH stage 09 – emergence
07-10-2019	BBCH stage 21
07-10-2019	Stomp CS (pendimethalin) - weeds - 1.0 L ha <sup>-1</sup> (455 g a.i. ha <sup>-1</sup> ) (not monitored)

Date	Management practice and growth stages – <b>Estrup</b>
07-04-2020	BBCH stage 21
07-04-2020	136.5 N, 26 P, 65 K, kg ha <sup>-1</sup>
15-04-2020	BBCH stage 22
15-04-2020	73.5 N, 14P, 35 K, kg ha <sup>-1</sup>
21-04-2020	BBCH stage 22
21-04-2020	Biomass 27.3 g m <sup>-2</sup> - 100% DM
03-05-2020	BBCH stage 31
03-05-2020	Broadway (pyroxsulam + florasulam) - weeds - 165 g ha <sup>-1</sup> (11.27 g a.i. ha <sup>-1</sup> pyroxsulam and 3.76 g a.i. ha <sup>-1</sup> florasulam)
14-05-2020	BBCH stage 35
24-05-2020	BBCH stage 41
29-05-2020	BBCH stage 49
29-05-2020	Biomass 450 g m <sup>-2</sup> - 100% DM
15-06-2020	BBCH stage 52
26-06-2020	BBCH stage 65

**Table A3.2.** Management practice at **Faardrup** during the 2012 to 2020 growing seasons. The active ingredients of the various pesticides are indicated in parentheses.

Date	Management practice and growth stages – <b>Faardrup</b>
26-03-2012	Fertilization 112 N, 9 P, 30 K, kg ha <sup>-1</sup>
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 <sup>-1</sup> . Final plant number 200 m <sup>-2</sup> . Under sown white clover cv. Liflex, seeding rate 2.0 kg ha <sup>-1</sup> , depth 2-3 cm, row distance 13 cm
04-04-2012	Tracer (potassium bromide) 30 kg ha <sup>-1</sup>
19-04-2012	BBCH stage 09 - emergence of spring barley
23-04-2012	BBCH stage 10
24-04-2012	BBCH stage 09 - 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 <sup>-1</sup>
23-05-2012	BBCH stage 29-31
23-05-2012	Biomass 112.7 g m <sup>-2</sup> - 100% DM
01-06-2012	BBCH stage 33-37
06-06-2012	BBCH stage 39
06-06-2012	Flexity (metrafenone) - fungi - 0.5 L ha <sup>-1</sup>
11-06-2012	BBCH stage 45-51
11-06-2012	Biomass 592.5 g m <sup>-2</sup> - 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 <sup>-2</sup> - 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 <sup>-1</sup> - 85% DM
12-08-2012	Straw removed. Straw yield 27.62 hkg ha <sup>-1</sup> - 100% DM
27-08-2012	BBCH stage 22-29 clover vegetative growth - formation of side shots
29-08-2012	Trimming of stubble
26-01-2013	Kerb 400 SC (propyzamide) - fungi - 1.0 L ha <sup>-1</sup>
13-05-2013	Biomass 298.2 g m <sup>-2</sup> - 100% DM
14-05-2013	Fighter 480 (bentazone) - weeds - 3.0 L ha <sup>-1</sup>
22-05-2013	Rolled with a concrete roller
29-05-2013	Biomass 402.9 g m <sup>-2</sup> - 100% DM
31-05-2013	Karate (Lambda-cyhalothrin) - pest - 0.3 L ha <sup>-1</sup> (not monitored)
12-06-2013	Karate (Lambda-cyhalothrin) - pest - 0.3 L ha <sup>-1</sup> (not monitored)
25-06-2013	Biomass 698.3 g m <sup>-2</sup> - 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 <sup>-1</sup> . Straw yield fresh 0.96 hkg ha <sup>-1</sup>
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 <sup>-1</sup> - final plant number 320 m <sup>-2</sup>
18-10-2013	BBCH stage 09 – emergence
13-03-2014	BBCH stage 23
13-03-2014	Fertilization 81 N, 16 P, 61 K, kg ha <sup>-1</sup>
09-04-2014	Fertilization 81 N, 16 P, 61 K, kg ha <sup>-1</sup>
09-04-2014	BBCH stage 25
15-04-2014	BBCH stage 24
28-04-2014	Briotril (ioxynil + bromoxynil) - weeds - 0.6 L ha <sup>-1</sup> + Tomahawk 180 EC (fluroxypyr) - weeds - 0.8 L ha <sup>-1</sup> (neither monitored)
28-04-2014	BBCH stage 24
30-04-2014	BBCH stage 30
15-05-2014	BBCH stage 32
15-05-2014	Amistar (azoxystrobin) - fungi - 1.0 L ha <sup>-1</sup> (not monitored)
04-06-2014	Biomass 1321 g m <sup>-2</sup> - 100% DM
04-06-2014	BBCH stage 55



Date	Management practice and growth stages – <b>Faardrup</b>
12-06-2014	BBCH stage 59
20-07-2014	BBCH stage 83
20-07-2014	Biomass 1995 g m <sup>-2</sup> - 100% DM
25-07-2014	BBCH stage 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 <sup>-1</sup> (not monitored)
23-09-2014	Ploughing - 14 cm depth - straw 70 hkg ha <sup>-1</sup> (fresh weight) incorporated
23-09-2014	Sowing winter wheat cv. Mariboss. Depth 3.5 cm, seeding rate 180 kg ha <sup>-1</sup> , row distance 13.0 cm. Final plant number 375 m <sup>-2</sup>
01-10-2014	BBCH stage 09 – emergence
20-11-2014	BBCH stage 23
20-11-2014	Folicur 250 (tebuconazole) - fungi - 1.0 L ha <sup>-1</sup> (i.e. 250g a.i. ha <sup>-1</sup> )
30-11-2014	BBCH stage 23
30-11-2014	Lexus 50 WG (flupyrsulfuron) - weeds - 10 g ha <sup>-1</sup> (i.e. 4.6 g a.i. ha <sup>-1</sup> )
30-11-2014	Boxer (prosulfocarb) - weeds - 3.0 L ha <sup>-1</sup> (i.e. 2400 g a.i. ha <sup>-1</sup> ) (not monitored)
10-03-2015	BBCH stage 25
10-03-2015	Biomass 44 g m <sup>-2</sup> - 100% DM
13-03-2015	BBCH stage 25
13-03-2015	Fertilization 80 N, 18 P, 63 K, kg ha <sup>-1</sup>
21-04-2015	BBCH stage 30
21-04-2015	Fertilization 94 N, 21 P, 74 K, kg ha <sup>-1</sup>
22-04-2015	BBCH stage 30
22-04-2015	Lexus 50 WG (flupyrsulfuron) - weeds - 10 g ha <sup>-1</sup> (i.e. 4.6 g a.i. ha <sup>-1</sup> )
08-05-2015	BBCH stage 37
12-05-2015	BBCH stage 37
12-05-2015	Starane XL (fluroxypyr+ florasulam) - weeds - 1.2 L ha <sup>-1</sup> (i.e. 120 g a.i. ha <sup>-1</sup> + 3 g a.i. ha <sup>-1</sup> ) (florasulam not monitored)
12-05-2015	Proline 250 EC (prothioconazole) - fungi - 0.8 L ha <sup>-1</sup> (i.e. 200 g a.i. ha <sup>-1</sup> ) (not monitored)
12-06-2015	BBCH stage 53
23-06-2015	BBCH stage 55
23-06-2015	Biomass 356.5 g m <sup>-2</sup> - 100% DM
12-08-2015	BBCH stage 55
12-08-2015	Biomass 443.7 g m <sup>-2</sup> – 100 % DM
28-08-2015	BBCH stage 89
02-09-2015	Harvest of winter wheat. Grain yield 79.7 hkg ha <sup>-1</sup> 85% DM, straw yield 71.5 hkg ha <sup>-1</sup> 100% DM, stubble height 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 <sup>-1</sup> , row distance 12.0 cm. Final plant number 315 m <sup>-2</sup>
11-04-2016	Fertilization 130 N, 26 P, 98 K, kg ha <sup>-1</sup>
20-04-2016	BBCH stage 09 – emergence
02-05-2016	BBCH stage 15
13-05-2016	BBCH stage 16-21
13-05-2016	Biomass 60.7 g m <sup>-2</sup> – 100% DM
27-05-2016	BBCH stage 27
27-05-2016	Starane 180 S + Oxitril (fluroxypyr + bromoxynil and ioxynil) - weeds - 0.8 L ha <sup>-1</sup> + 0.2 L ha <sup>-1</sup> (i.e. 144 + 48 + 32 g a.i. ha <sup>-1</sup> – (bromoxynil and ioxynil not monitored)
01-06-2016	BBCH stage 31
08-06-2016	BBCH stage 39
16-06-2016	BBCH stage 47
16-06-2016	Bumper 25 EC (propiconazole) - fungi - 0.5 L ha <sup>-1</sup> (i.e. 125 g a.i. ha <sup>-1</sup> )
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 <sup>-2</sup> - 100% DM
11-08-2016	BBCH stage 87
11-08-2016	Roundup PowerMax (glyphosate) - weeds - 2.0 kg ha <sup>-1</sup> (i.e. 1440 g a.i. ha <sup>-1</sup> - not monitored)
22-08-2016	BBCH stage 87
26-08-2016	Harvest of spring barley. Grain yield 57.7 hkg ha <sup>-1</sup> - 85% DM – stubble height 13 cm.
26-08-2016	Biomass 369.3 g m <sup>-2</sup> - 100% DM

Date	Management practice and growth stages – <b>Faardrup</b>
27-08-2016	Straw removed from the field - yield 54.0 hkg ha <sup>-1</sup> fresh weight.
20-12-2016	Ploughing - depth 24 cm
07-04-2017	Fertilization 132 N, 17 P, 61 K, kg ha <sup>-1</sup>
02-05-2017	Rotor harrowed at the time of sowing the spring barley. CV Quench. Depth 4 cm, seeding rate 180 kg ha <sup>-1</sup> , row distance 13.0 cm. Final plant number 365 m <sup>-2</sup> . Seed coated with Fungazil A (imazalil - not monitored)
10-05-2017	BBCH stage 09 - emergence
11-05-2017	BBCH stage 10-11
18-05-2017	BBCH stage 12-13
02-06-2017	BBCH stage 22
02-06-2017	Hussar Plus OD (iodosulfuron-methyl-Na and mesosulfuron -methyl) - weeds - 0.035 L ha <sup>-1</sup> (i.e. 1.75 g a.i. ha <sup>-1</sup> iodosulfuron-methyl-Na and 0.27 g a.i. ha <sup>-1</sup> mesosulfuron-methyl) (not monitored)
14-06-2017	BBCH stage 43
19-06-2017	BBCH stage 45
19-06-2017	Biomass 115.8 g m <sup>-2</sup> - 100% DM
19-06-2017	Bumper 25 EC (propiconazole) - fungi - 0.5 L ha <sup>-1</sup> (i.e. 125 g ai ha <sup>-1</sup> )
19-06-2017	Zypar (halauxifen-methyl + florasulam) - weeds - 0.5 L ha <sup>-1</sup> (i.e. 3.125 g a.i. ha <sup>-1</sup> halauxifen-methyl and 2.5 g a.i. ha <sup>-1</sup> florasulam)
07-07-2017	BBCH stage 65
07-07-2017	Bumper 25 EC (propiconazole) - fungi - 0.5 L ha <sup>-1</sup> (i.e. 125 g a.i. ha <sup>-1</sup> )
15-08-2017	BBCH stage 85
15-08-2017	Biomass 317.2 g m <sup>-2</sup> - 100% DM
22-08-2017	Harvest of spring barley. Grain yield 62.3 hkg ha <sup>-1</sup> fresh weight and 35.5 hkg ha <sup>-1</sup> straw fresh weight – stubble height 9 cm.
20-10-2017	Glyphomax (glyphosate) - weeds - 2.5 L ha <sup>-1</sup> (i.e. 900 g a.i ha <sup>-1</sup> ) (not monitored)
03-12-2017	Ploughing - depth 22 cm
20-04-2018	Seed bed preparation - depth 10 cm
20-04-2018	Sowing sugar beet cv. SMART JANNINKA KWS. depth 2.0 cm row distance 50.0 cm plant distance 25cm. seeding rate 100.000 seeds ha <sup>-1</sup> , seed bed rather uneven, Final plant number 9 m <sup>-2</sup>
20-04-2018	Seed dressing Gaucho WS70 (60 g a.i. ha <sup>-1</sup> imidacloprid) and Tachigaren WP (14-18 g a.i. ha <sup>-1</sup> hymexazol) (not monitored). Fertilization 140 N, 24.5 P, 65.3 K, kg ha <sup>-1</sup> , done together with sowing
20-04-2018	BBCH stage 09 – emergence
07-05-2018	BBCH stage 11
18-05-2018	BBCH stage 11
22-05-2018	BBCH stage 12
25-05-2018	BBCH stage 12
29-05-2018	2.0 L ha <sup>-1</sup> Betanal (phenmedipham) - weeds (i.e. 320 g a.i. ha <sup>-1</sup> phenmedipham) (not monitored)
29-05-2018	1.0 L ha <sup>-1</sup> Goltix (metamitron) - weeds (i.e. 700 g a.i. ha <sup>-1</sup> )
	0.16 L ha <sup>-1</sup> Conviso One (foramsulfuron + thien carbazone-methyl) - weeds (i.e. 4.8 g a.i. ha <sup>-1</sup> foramsulfuron and 8.0 g a.i. ha <sup>-1</sup> thien carbazone-methyl)
	0.07 L ha <sup>-1</sup> Nortron SC (ethofumesat) - weeds (i.e. 35 g a.i. ha <sup>-1</sup> ) (not monitored)
08-06-2018	BBCH stage 15
08-06-2018	Mechanical weeding between rows - depth 3 cm
12-06-2018	BBCH stage 15
12-06-2018	2.0 L ha <sup>-1</sup> Betanal (phenmedipham) - weeds (i.e. 320 g a.i. ha <sup>-1</sup> phenmedipham) (not monitored)
	1.0 L ha <sup>-1</sup> Goltix (metamitron) - weeds (i.e. 700 g a.i. ha <sup>-1</sup> )
	0.07 L ha <sup>-1</sup> Nortron SC (ethofumesat) - weeds (i.e. 35 g a.i. ha <sup>-1</sup> ) (not monitored)
27-06-2018	BBCH stage 15
27-06-2018	2.0 L ha <sup>-1</sup> Betanal (phenmedipham) - weeds (i.e. 320 g a.i. ha <sup>-1</sup> phenmedipham) (not monitored)
	1.0 L ha <sup>-1</sup> Goltix (metamitron) - weeds (i.e. 700 g a.i. ha <sup>-1</sup> )
	0.07 L ha <sup>-1</sup> Nortron SC (ethofumesat) - weeds (i.e. 35 g a.i. ha <sup>-1</sup> ) (not monitored)
	0.2 kg ha <sup>-1</sup> Karate 2,5 WG (lambda-cyhalothrin) - pests (i.e. 10 g a.i. ha <sup>-1</sup> ) (not monitored)
01-07-2018	BBCH stage 15
09-07-2018	BBCH stage 19
09-07-2018	Biomass 1248.1 g m <sup>-2</sup> – sugar beet top only - 100% DM
28-09-2018	BBCH stage 49
28-09-2018	Harvest of sugar beets 79.8 hkg ha <sup>-1</sup> root - 100% DM Top 32.0 hkg ha <sup>-1</sup> - 100% DM
18-12-2018	Ploughing - depth 22 cm
05-04-2019	Seed bed preparation, depth 3 cm
08-04-2019	Sowing spring barley cv. IKWS Irina - seed coated with Redigo Pro. Depth 3 cm, seeding rate 170 kg ha <sup>-1</sup> , row distance 12.5 cm. Final plant number 365 m <sup>-2</sup>

Date	Management practice and growth stages – <b>Faardrup</b>
08-04-2019	Redigo Pro 170 FS (12.75 g a.i. ha <sup>-1</sup> prothioconazole + 1.70 g a.i. ha <sup>-1</sup> tebuconazole) - seed dressing
09-04-2019	Fertilization 113. 3 N, 19.8 P, 52.8 K, kg ha <sup>-1</sup>
11-04-2019	Rolled with a ring roller
15-04-2019	BBCH stage 09
23-04-2019	BBCH stage 10
26-04-2019	BBCH stage 12
26-04-2019	DFF (diflufenican) - weeds - 0.15 L ha <sup>-1</sup> (75 g a.i. ha <sup>-1</sup> ) (not monitored)
29-04-2019	BBCH stage 20
15-05-2019	BBCH stage 20
15-05-2019	Biomass 50.1 g m <sup>-2</sup> - 100% DM
03-06-2019	BBCH stage 32
03-06-2019	Talius (proquinazid) - fungi - 0.125 L ha <sup>-1</sup> (25 g a.i. ha <sup>-1</sup> )
17-06-2019	BBCH stage 45
17-06-2019	Talius (proquinazid) - fungi - 0.125 L ha <sup>-1</sup> (25 g a.i. ha <sup>-1</sup> )
01-07-2019	BBCH stage 51
01-07-2019	Biomass 341.9 g m <sup>-2</sup> - 100% DM
18-07-2019	BBCH stage 75
18-07-2019	Biomass 1188.9 g m <sup>-2</sup> - 100% DM
12-08-2019	BBCH stage 89
12-08-2019	Harvest of spring barley. Grain yield 82.0 hkg ha <sup>-1</sup> - 85% DM – stubble height 13 cm. Straw yield 35.5 hkg ha <sup>-1</sup> (DM not measured)
15-11-2019	Ploughing, depth 24 cm
20-03-2020	Seed bed preparation - depth 4.0 cm
26-03-2020	Sowing spring wheat cv. Cornette - seed coated with Celest Formula M (fludioxonil). Sowing depth 4 cm, seeding rate 200 kg/ha, row distance 12.0 cm. Final plant number 364 m <sup>-2</sup>
02-04-2020	Fertilization 134.0 N, 26.0 P, 65.0 K, kg ha <sup>-1</sup>
06-04-2020	BBCH stage 09 - emergence
15-04-2020	BBCH stage 10-12
16-04-2020	Rolled with a ring roller
20-04-2020	Buctril EC 225 (bromoxynil) - weeds - 0.4 L ha <sup>-1</sup> (90 g a.i. ha <sup>-1</sup> ) (not monitored)
04-05-2020	BBCH stage 20
12-05-2020	BBCH stage 20
12-05-2020	Biomass 16.9 g m <sup>-2</sup> - 100% DM
12-06-2020	BBCH stage 51
12-06-2020	Biomass 22.0 g m <sup>-2</sup> - 100% DM

**Table A3.2.** Management practice at **Lund** during the 2012 to 2020 growing seasons. The active ingredients of the various pesticides are indicated in parentheses.

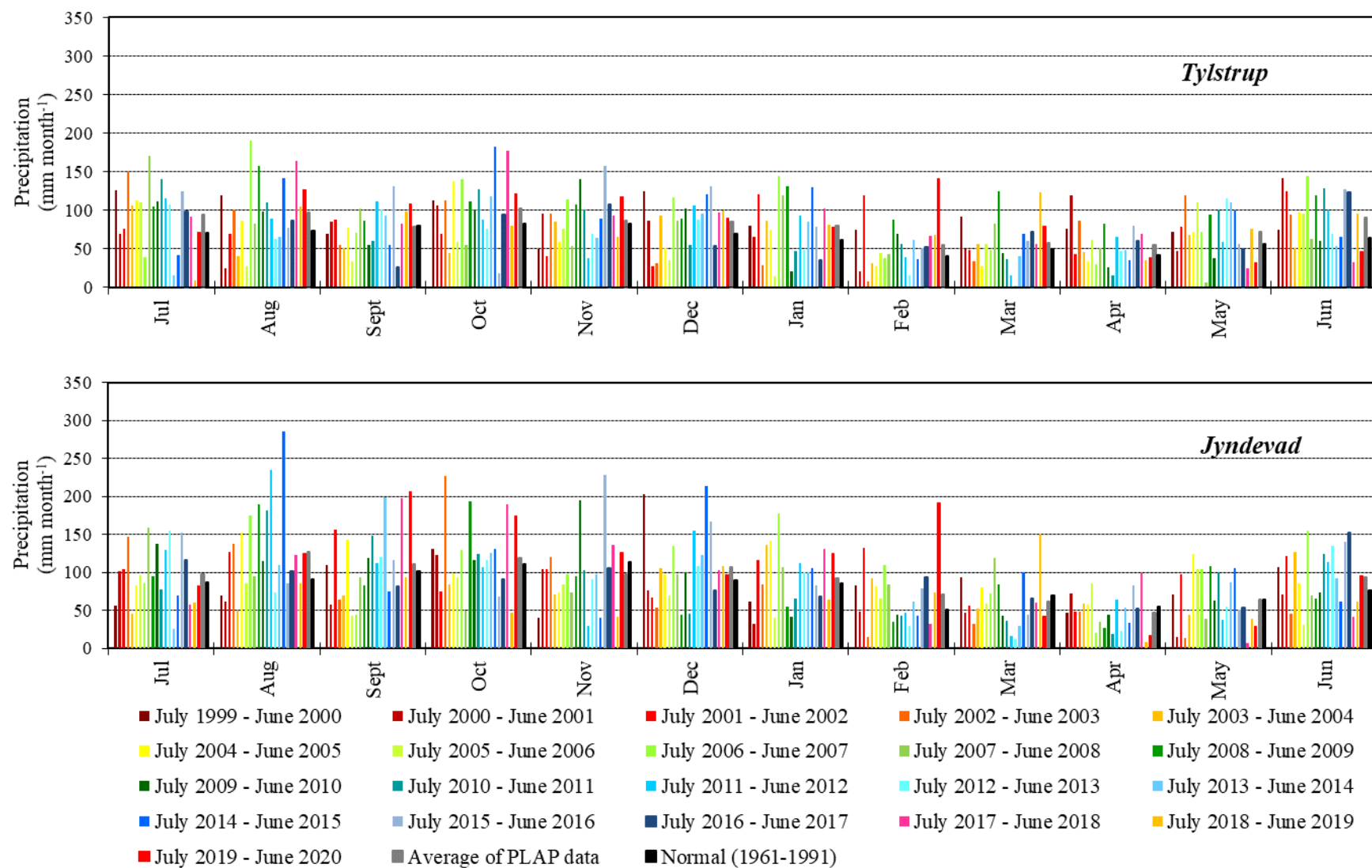
Date	Management practice and growth stages – <b>Lund</b>
22-03-2017	Ploughing - 25 cm depth
02-04-2017	Fertilization 123.6 N, 15.6 P, 57.6 K, kg ha <sup>-1</sup>
03-04-2017	Seed bed preparation - 8 cm depth
03-04-2017	Sowing spring barley cv. Irina. Depth 3.5 cm, seeding rate 175 kg ha <sup>-1</sup> , row distance 12 cm, final plant number 245 m <sup>-2</sup>
03-04-2017	Seed dressing Fungazil A (imazalil 87.5 g a.i. ha <sup>-1</sup> ) (not monitored)
03-04-2017	Clover grass sown (white clover and smooth meadow-grass). Depth 1.5 cm, seeding rate 28 kg ha <sup>-1</sup>
20-04-2017	BBCH stage 09 - emergence
08-05-2017	BBCH stage 12 to 14
09-05-2017	BBCH stage 20
09-05-2017	Fighter 480 (bentazone) - weeds - 1.5 L ha <sup>-1</sup> (i.e. 720 g a.i. ha <sup>-1</sup> )
09-05-2017	Stomp CS (pendimethalin) - weeds - 0.9 L ha <sup>-1</sup> (i.e. 410 g a.i. ha <sup>-1</sup> ) (not monitored)
17-05-2017	BBCH stage 22
17-05-2017	Biomass 14.6 g m <sup>-2</sup> - 100% DM
07-06-2017	BBCH stage 39
15-06-2017	BBCH stage 51
15-06-2017	Amistar (azoxystrobin) - fungi - 1.0 L ha <sup>-1</sup> (i.e. 250 g a.i. ha <sup>-1</sup> )
04-07-2017	BBCH stage 59
04-07-2017	Biomass 329.9 g m <sup>-2</sup> - 100% DM
11-08-2017	BBCH stage 85
11-08-2017	Biomass 359 g m <sup>-2</sup> - 100% DM
13-08-2017	Harvest of spring barley. Grain yield 71.0 hkg ha <sup>-1</sup> 85% DM, straw yield 85.2 hkg ha <sup>-1</sup> fresh weight, stubble height 8 cm
06-10-2017	Biomass 54.5 g m <sup>-2</sup> - 100% DM (catch crop of clover and grass)
19-10-2017	Glyphomax HL (glyphosate) - weeds - 3.2 L ha <sup>-1</sup> (i.e. 1536 g a.i. ha <sup>-1</sup> ) (killing of the clover grass)
31-10-2017	Tracer (potassium bromide), 30 kg ha <sup>-1</sup>
04-01-2018	Ploughing - 25 cm depth
12-04-2018	Seed bed preparation - 3 cm depth
19-04-2018	Pig slurry application - trail hose applied and subsequent harrowed - 50.0 t ha <sup>-1</sup> - 131.5 Total-N, 113.5 NH <sub>4</sub> -N, 3.0 P, 72.5 K, 1.5 Mg and 0.1 Cu, kg ha <sup>-1</sup>
20-04-2018	Sowing spring barley cv. Quench. Depth 3.5 cm, seeding rate 170 kg ha <sup>-1</sup> , row distance 12 cm, final plant number 325 m <sup>-2</sup>
20-04-2018	Seed dressing Redigo Pro 170 FS (12.75 g prothioconazole a.i. ha <sup>-1</sup> and 1.70 g tebuconazole a.i. ha <sup>-1</sup> )
01-05-2018	BBCH stage 09 - emergence
30-05-2018	BBCH stage 20
30-05-2018	BBCH stage 31
30-05-2018	Proline 250 EC (prothioconazole) - fungi - 0.8 L ha <sup>-1</sup> (i.e. 200 g a.i. ha <sup>-1</sup> )
30-05-2018	Zypar (halauxifen-methyl + florasulam) - weeds - 1.0 L ha <sup>-1</sup> (i.e. 6.25 g halauxifen-methyl and 5.0 g florasulam a.i. ha <sup>-1</sup> )
12-06-2018	BBCH stage 42
12-06-2018	Proline 250 EC (prothioconazole) - fungi - 0.8 L ha <sup>-1</sup> (i.e. 200 g a.i. ha <sup>-1</sup> )
06-08-2018	BBCH stage 89
06-08-2018	Harvest of spring barley. Grain yield 55.5 hkg ha <sup>-1</sup> . Total-N 1.87% and total-C 43.83% - 85 % DM- Straw yield 22.35 hkg ha <sup>-1</sup> , Total-N 0.69% and total-C 43.78% - 100% DM, stubble height 10 cm.
18-09-2018	Ploughing - 25 cm depth
19-09-2018	Seed bed preparation - 5 cm depth
19-09-2018	Sowing winter barley cv. Menento. Depth 3.0 cm, seeding rate 160 kg ha <sup>-1</sup> , row distance 12.5 cm, final plant number 300 m <sup>-2</sup>
19-09-2018	Redigo Pro 170 FS (12.00 g a.i. ha <sup>-1</sup> prothioconazole + 1.60 g a.i. ha <sup>-1</sup> tebuconazole) - seed dressing
19-09-2018	Rolled with a ring roller
28-09-2018	BBCH stage 09 – emergence
15-10-2018	BBCH stage 12
08-11-2018	BBCH stage 20
08-11-2018	DFF + Boxer (diflufenican + prosulfocarb) - weeds - 0.15 L ha <sup>-1</sup> + 1,0 L ha <sup>-1</sup> (75 g + 800 g a.i. ha <sup>-1</sup> ) (not monitored)
05-04-2019	BBCH stage 20-23
05-04-2019	Biomass 168.0 g m <sup>-2</sup> - 100% DM

Date	Management practice and growth stages – <b>Lund</b>
25-04-2019	BBCH stage 30
30-04-2019	BBCH stage 32
02-05-2019	BBCH stage 32
02-05-2019	Fertilization 150 N 26,3 P 70 K, kg ha <sup>-1</sup>
04-05-2019	BBCH stage 49
09-05-2019	BBCH stage 49
09-05-2019	Flurostar 180 (fluroxypyr) - weeds - 0.8 L ha <sup>-1</sup> (144 g a.i. ha <sup>-1</sup> ) (not monitored)
11-05-2019	BBCH stage 49
11-05-2019	Zypar (halauxifen-methyl + florasulam) - weeds - 1.0 L ha <sup>-1</sup> (i.e. 6.25 g halauxifen-methyl and 5.0 g florasulam a.i. ha <sup>-1</sup> )
13-05-2019	BBCH stage 50
13-05-2019	Biomass 247.6 g m <sup>-2</sup> - 100% DM
27-05-2019	BBCH stage 51
03-07-2019	BBCH stage 71
03-07-2019	Biomass 297.2 g m <sup>-2</sup> - 100% DM
12-07-2019	BBCH stage 89
13-07-2019	Harvest winter barley - grain yield 66.4 hkg ha <sup>-1</sup> - 100% DM, Straw yield 35.9 hkg ha <sup>-1</sup> DM not determined, stubble height 15 cm
25-08-2019	Rotor harrow sowing tillage depth 6 cm
25-08-2019	Direct drilling with deep loosening. Sowing winter rape cv. InVigor 1030. Depth 2.0 cm row distance 15 cm seeding rate 2.5 kg/ha, final plant number 25 m <sup>-2</sup> Seed dressing - Bacillus amyloliquefaciens MBI 600
28-08-2019	Glyphomax HL (glyphosate) and Clomate (clomazone) - weeds - 0.5 L ha <sup>-1</sup> + 0.25 L ha <sup>-1</sup> (i.e. 240 g + 90 g a.i. ha <sup>-1</sup> ) (not monitored)
30-08-2019	BBCH stage 09 - emergence
05-09-2019	Fertilization 19.2 N, 7.4 P kg ha <sup>-1</sup>
17-12-2019	BBCH stage 13
17-12-2019	Kerb 400 SC (propyzamide) - weeds - 1.25 L ha <sup>-1</sup> (500 g a.i. ha <sup>-1</sup> )
17-12-2019	Belkar (picloram + halauxifen-methyl) - weeds - 0.5 L ha <sup>-1</sup> - (i.e. 24 + 2,5 g a.i. ha <sup>-1</sup> )
23-03-2020	Fertilization 97.9 N, 19.0 P, 47.5 K kg ha <sup>-1</sup>
24-04-2020	Fertilization 80.3 N, 15.6 P, 39.0 K kg ha <sup>-1</sup>



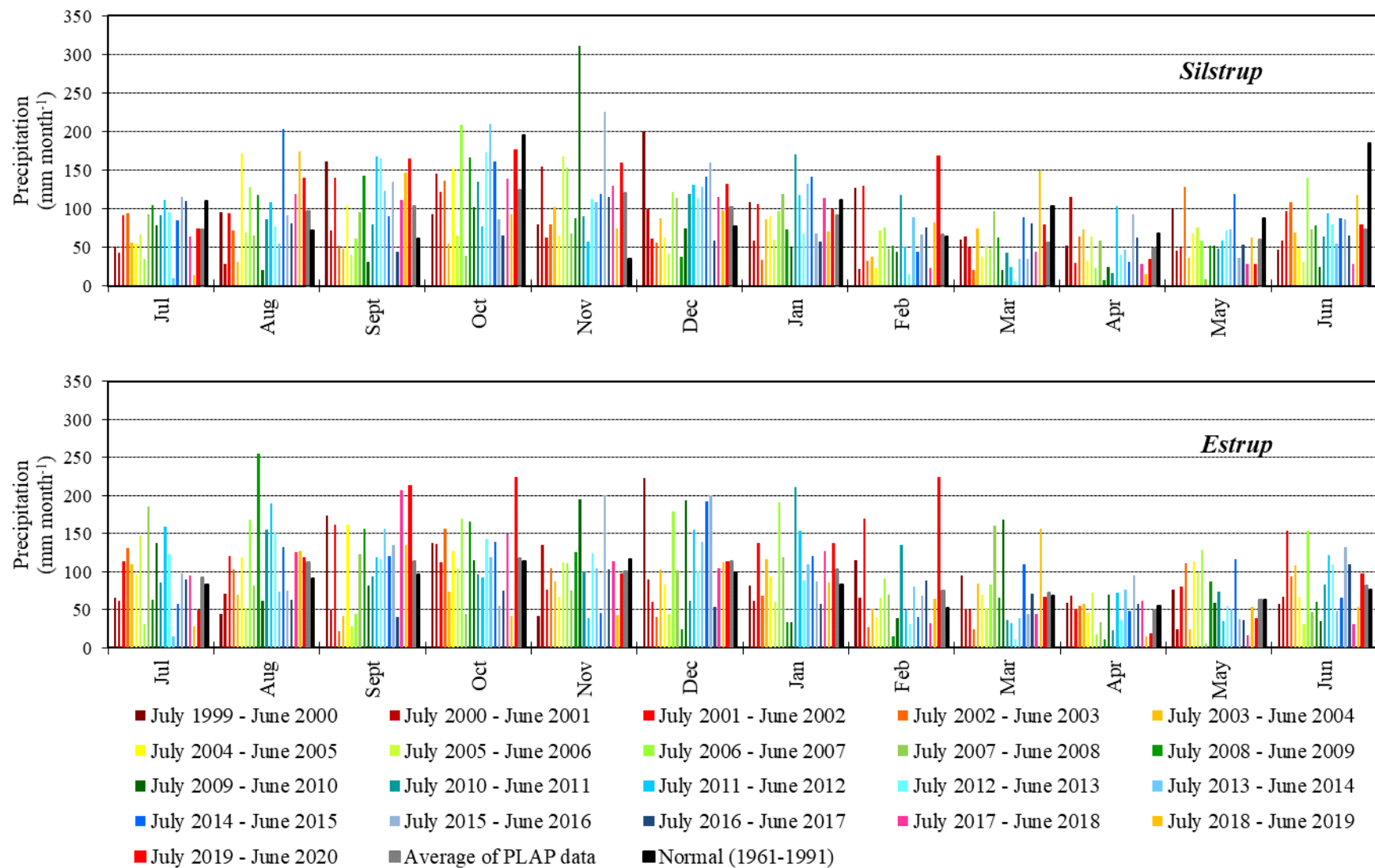
## **Appendix 4**

*Precipitation at the PLAP fields*

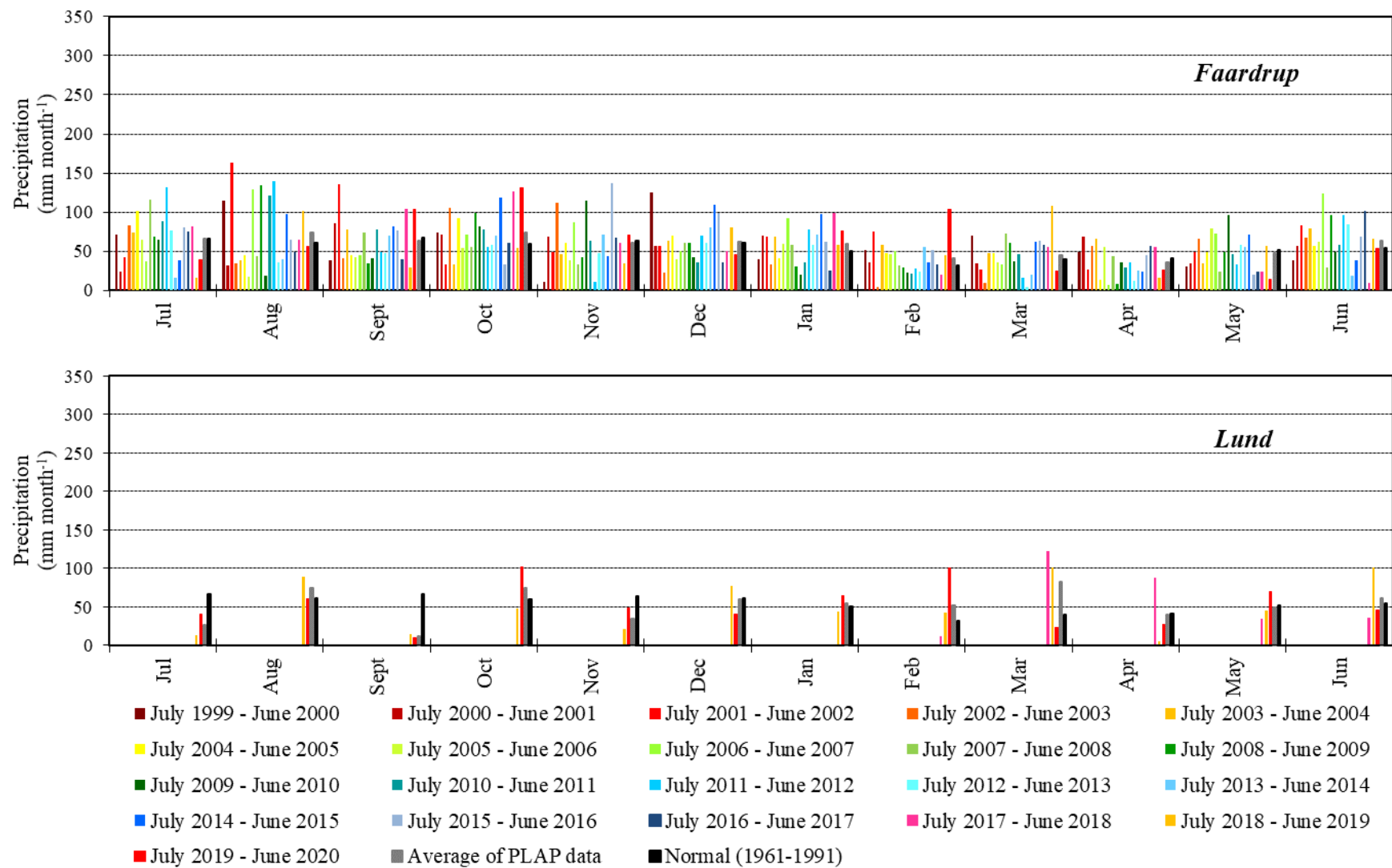


**Figure A4.1.** Monthly precipitation at all PLAP fields for the monitoring period July 2000–June 2020. Regional normal values (1961–1990) are included for comparison.

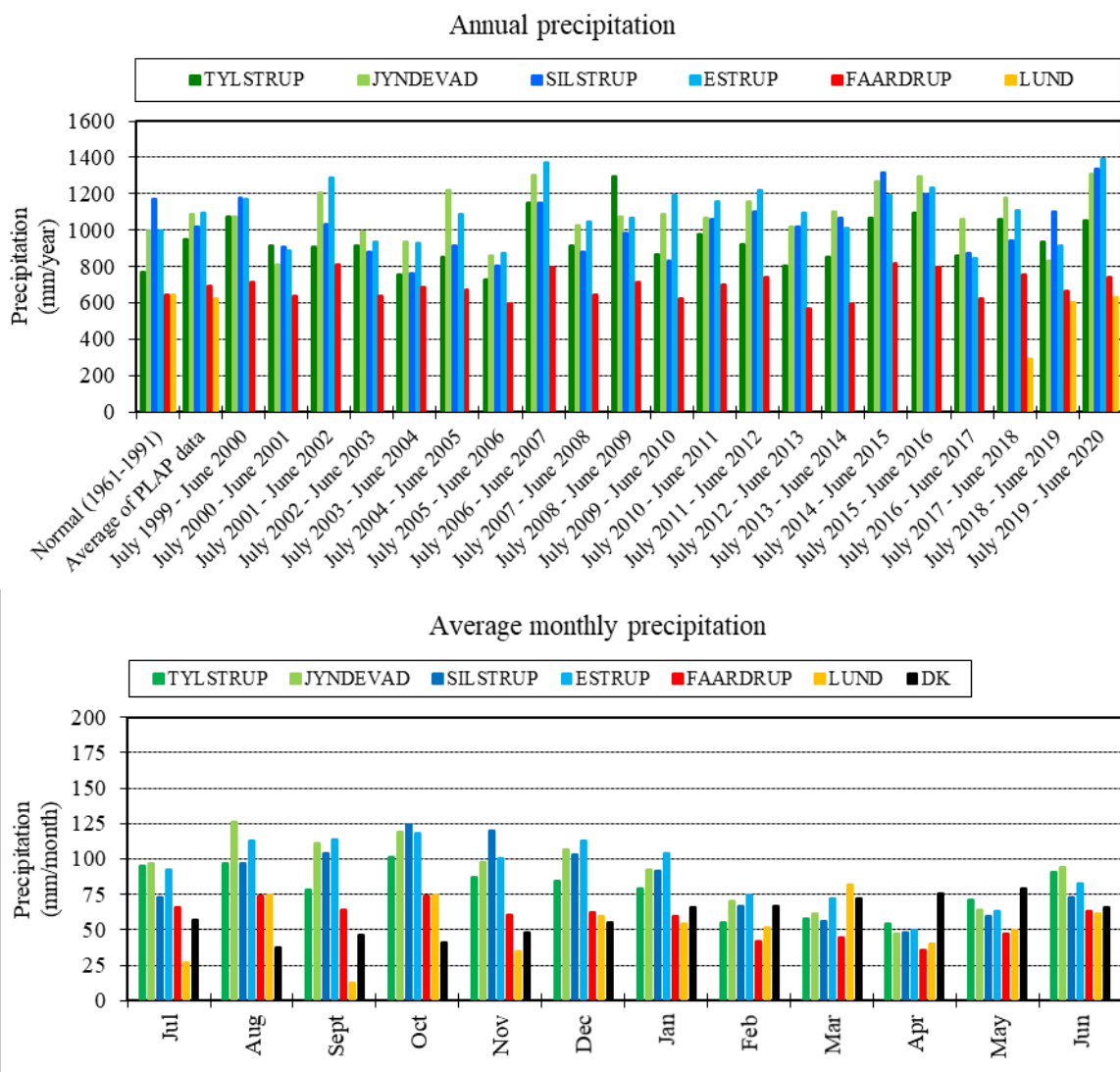




**Figure A4.1 (continued).** Monthly precipitation at all PLAP fields for the monitoring period July 2000–June 2020. Regional normal values (1961–1990) are included for comparison.



**Figure A4.1 (continued).** Monthly precipitation at all PLAP fields for the monitoring period July 2000–June 2020. Regional normal values (1961–1990) are included for comparison.



**Figure A4.2.** Top: Annual precipitation at the PLAP fields during the period July 1999 – June 2020. Note that data from 2017-2018 for Lund only covers February-June 2018. Bottom: Average monthly precipitation for each PLAP field during the period July 1999 – June 2020.



## **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  $\leq 0.1 \mu\text{g L}^{-1}$  or detected in concentrations  $> 0.1 \mu\text{g L}^{-1}$  at **Tylstrup**. Monitoring at the field was suspended 1 January 2019, why numbers are accumulated until that date. All samples included.

<b>Tylstrup</b>		Horizontal screens			Vertical screens			Suction cups		
Parent	Compound	nd	$\leq 0.1$	$> 0.1$	nd	$\leq 0.1$	$> 0.1$	nd	$\leq 0.1$	$> 0.1$
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	24	-	-	156	-	-	65	-	-
	8-hydroxy-bentazone	24	-	-	156	-	-	65	-	-
	Bentazone	24	-	-	486	-	-	198	4	-
	N-methyl-bentazone	24	-	-	156	-	-	65	-	-
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	-
Mesosulfuron-methyl	AE-F099095	16	-	-	128	-	-	54	-	-
	AE-F160459	16	-	-	128	-	-	54	-	-
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				72	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	-	-
Tebuconazole	1,2,4-triazole	6	30	-	149	81	-	78	18	2
	Tebuconazole				195	1	-	77	-	-

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

**Table A5.2.** Number of samples where pesticides were either not detected (nd), detected in concentrations  $\leq 0.1 \mu\text{g L}^{-1}$  or detected in concentrations  $> 0.1 \mu\text{g L}^{-1}$  at **Jynde vad**. Numbers are accumulated for the monitoring period up to July 2020. All samples included.

<b>Jynde vad</b>		Horizontal screens			Vertical screens			Suction cups		
Parent	Compound	nd	$\leq 0.1$	$> 0.1$	nd	$\leq 0.1$	$> 0.1$	nd	$\leq 0.1$	$> 0.1$
Acetamiprid	IM-1-4*	3	-	-	23	-	-	6	-	-
	IM-1-5*	3	-	-	23	-	-	6	-	-
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	22	-	-	207	-	-	43	-	-
	8-hydroxy-bentazone	22	-	-	207	-	-	43	-	-
	Bentazone	50	2	-	849	1	-	121	92	17
	N-methyl-bentazone	22	-	-	207	-	-	43	-	-
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	CCIM*	3	-	-	23	-	-	6	-	-
	CTCA*	3	-	-	23	-	-	6	-	-
	Cyazofamid	4	-	-	131	-	-	32	-	-
	DMSA*	3	-	-	23	-	-	6	-	-
	N,N-DMS*	1	2	-	22	1	-	6	-	-
Cycloxydim	BH 517-T2SO2	12	-	-	188	-	-	39	-	-
	E/Z BH 517-TSO	10	2	-	188	-	-	28	8	3
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	-	-
Flupyr-sulfuron-methyl	Flupyr-sulfuron-methyl	28	-	-	201	-	-	30	-	-
	IN-JE127	8	-	-	142	-	-	31	-	-
	IN-JV460	28	-	-	201	-	-	30	-	-
	IN-KC576	28	-	-	201	-	-	30	-	-
	IN-KF311	8	-	-	142	-	-	31	-	-
	IN-KY374	28	-	-	201	-	-	26	1	3
	Fluroxypyr				193	-	-	55	-	-
Foramsulfuron	AE-F092944	2	-	-	12	-	-	4	-	-
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	AE-F099095	10	-	-	179	-	-	43	-	-
	AE-F147447	8	2	-	179	-	-	46	-	-
	AE-F160459	10	-	-	179	-	-	43	-	-
	Mesosulfuron				12	-	-	45	-	-
	Mesosulfuron-methyl				285	-	-	78	-	-



Jynde vad		Horizontal screens			Vertical screens			Suction cups		
Parent	Compound	nd	≤ 0.1	>0.1	nd	≤0.1	>0.1	nd	≤0.1	>0.1
Mesotrione	AMBA	30	-	-	207	-	-	67	-	-
	MNBA	30	-	-	207	-	-	67	-	-
Metalaxyl-M	Mesotrione	30	-	-	207	-	-	67	-	-
	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	-	-
	Pirimicarb-desmethyl				251	-	-	68	1	-
	Pirimicarb-desmethyl-formamido				251	-	-	69	-	-
	Propiconazole				291	-	-	87	-	-
Proquinazid	IN-MM671	10	-	-	109	-	-	30	-	-
	IN-MM991	10	-	-	109	-	-	30	-	-
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	21	38	-	215	345	8	50	68	9
	Tebuconazole				213	1	-	58	-	-
Terbuthylazine	Desethyl-terbuthylazine				490	27	-	130	20	-
	Terbuthylazine				260	-	-	79	-	-
Tribenuron-methyl	Triazinamin-methyl				252	-	-	77	-	-

\* Parent compound was applied in spring 2020. Data evaluation is not included in this report but will be discussed in next year's report covering 2019-2021.

**Table A5.3.** Number of samples where pesticides were either not detected (nd), detected in concentrations  $\leq 0.1 \mu\text{g L}^{-1}$  or detected in concentrations  $> 0.1 \mu\text{g L}^{-1}$  at **Silstrup**. Numbers are accumulated for the monitoring period up to July 2020. All samples included.

<b>Silstrup</b>		Drainage			Horizontal screens			Vertical screens			Suction cups		
Parent	Compound	nd	$\leq 0.1$	$> 0.1$	nd	$\leq 0.1$	$> 0.1$	nd	$\leq 0.1$	$> 0.1$	nd	$\leq 0.1$	$> 0.1$
Amidosulfuron	Amidosulfuron	1	-	-									
	Desmethyl-amidosulfuron	1	-	-									
Azoxystrobin	Azoxystrobin	165	22	1	231	3	-	405	5	-			
	CyPM	59	128	24	227	41	6	438	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	-	-			
Cycloxydim	BH 517-T2SO2	40	-	-	34	-	-	80	-	-			
	E/Z BH 517-TSO	31	8	1	23	11	-	62	18	-			
Desmedipham	Desmedipham	101	-	-	107	1	-	240	-	-	58	-	-
	EHPC	74	-	-	68	-	-	139	-	-	26	-	-
Diffenican	AE-05422291	66	-	-	83	-	-	118	-	-			
	AE-B107137	56	4	1	82	1	-	118	-	-			
	Diffenican	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	-	-
Florasulam	TSA	58	-	-	53	-	-	129	-	-			
	5-OH-florasulam*	2	-	-	4	-	-	14	-	-			
	DFP-TSA*	2	-	-	4	-	-	14	-	-			
	DFP-ASTCA*	2	-	-	4	-	-	14	-	-			
Fluazifop-P-butyl	Fluazifop-P	116	-	-	140	1	-	301	-	-	59	-	-
	TFMP	79	30	23	137	23	2	211	48	14			
Flupyrifos-methyl	IN-JE127	41	-	-	26	-	-	60	-	-			
	IN-KF311	69	-	-	44	-	-	100	-	-			
Fluroxypyr	Fluroxypyr	50	-	-	74	-	-	142	-	-			
Foramsulfuron	AE-F092944	75	-	-	74	-	-	146	-	-			
	AE-F130619	65	10	-	66	6	-	140	3	-			
	Foramsulfuron	65	8	2	69	3	-	141	2	-			
Glyphosate	AMPA	47	185	18	227	14	-	380	26	-	8	-	-
	Glyphosate	141	86	22	236	5	-	371	35	-	8	-	-
Haloxifen-methyl	X-757	53	-	-	45	-	-	105	-	-			
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	-	-			
Mesosulfuron-methyl	AE-F099095	51	-	-	40	-	-	91	-	-			
	AE-F147447	51	-	-	38	-	-	86	-	-			
	AE-F160459	51	-	-	40	-	-	91	-	-			
Mesotrione	AMBA	76	-	-	76	-	-	147	-	-			
	MNBA	68	8	-	76	-	-	147	-	-			
	Mesotrione	63	6	7	76	-	-	147	-	-			

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
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	-	-
Picloram	Picloram	1	-	-									
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	76	26	12	103	10	1	216	11	5			
	RH-24580	64	2	-	78	-	-	149	-	-			
	RH-24644	51	15	-	77	1	-	148	1	-			
	RH-24655	66	-	-	78	-	-	149	-	-			
Proquinazid	IN-MM671	1	-	-									
	IN-MM991	1	-	-									
Prosulfocarb	Prosulfocarb	69	4	1	78	1	-	147	-	-			
Pyridate	PHCP	62	-	4	66	2	-	109	8	4			
Pyroxsulam	5-OH-XDE-742*	2	-	-	4	-	-	14	-	-			
	6-Cl-7-OH-XDE-742*	2	-	-	4	-	-	14	-	-			
	7-OH-XDE-742*	2	-	-	4	-	-	14	-	-			
	PSA*	2	-	-	4	-	-	14	-	-			
	Pyridine-sulfonamide*	2	-	-	4	-	-	14	-	-			
	Amitrol**	3	-	-	6	-	-	17	-	-			
Rimsulfuron	PPU	1	-	-									
	PPU-desamino	1	-	-									
Tebuconazole	1,2,4-triazole	1	75	6	19	44	2	96	59	2			
	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			
	Triazinamin	88	-	-	113	-	-	228	-	-			
	Triazinamin-methyl	82	-	-	74	-	-	148	-	-	27	-	-
Triasulfuron-methyl	IN-D8526	32	-	-	56	-	-	102	-	-			
	IN-E7710	27	5	-	56	-	-	102	-	-			
	IN-M7222	32	-	-	55	1	-	102	-	-			
	Triflusulfuron-methyl	32	-	-	56	-	-	102	-	-			

\* Parent compound was applied in spring 2020. Data evaluation is not included in this report but will be discussed in next year's report covering 2019-2021.

\*\* Amitrol was included in the monitoring of pyroxsulam as it was suspected to be a groundwater pollutant in the Danish groundwater monitoring programme (GRUMO) in relation to the yearly screenings in 2019. Pyroxsulam was therefore tested as a theoretical source of origin to amitrol. The findings of amitrol in the groundwater screening was later shown to be an analytical artefact and the monitoring of amitrol in VAP was thus suspended.

**Table A5.4.** Number of samples where pesticides were either not detected (nd), detected in concentrations  $\leq 0.1 \mu\text{g L}^{-1}$  or detected in concentrations  $> 0.1 \mu\text{g L}^{-1}$  at **Estrup**. Numbers are accumulated for the monitoring period up to July 2020. All samples included.

<b>Estrup</b>		Drainage			Horizontal screens			Vertical screens			Suction cups		
Parent	Compound	nd	$\leq 0.1$	$> 0.1$	nd	$\leq 0.1$	$> 0.1$	nd	$\leq 0.1$	$> 0.1$	nd	$\leq 0.1$	$> 0.1$
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	-	-
Carbendazim	Carbendazim	19	3	-	12	-	-	21	-	-			
Chlormequat	Chlormequat	45	1	-	18	-	-	56	-	-			
Clomazone	Clomazone	60	-	-	47	-	-	51	-	-			
	FMC 65317	60	-	-	47	-	-	51	-	-			
Clopyralid	Clopyralid	1	-	-									
Diffenican	AE-05422291	57	-	-	26	-	-	45	-	-			
	AE-B107137	40	18	-	38	2	-	49	-	-			
	Diffenican	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	-	-			
	TSA				3	-	-	9	-	-			
	5-OH-florasulam*				3	-	-	9	-	-			
	DFP-TSA*				3	-	-	9	-	-			
	DFP-ASTCA*				3	-	-	9	-	-			
Flupyr-sulfuron-methyl	IN-JE127				1	-	-	3	-	-			
	IN-KF311				1	-	-	3	-	-			
Fluroxypyr	Fluroxypyr	87	1	2	34	-	-	120	1	-			
Foramsulfuron	AE-F092944	90	1	-	65	-	-	88	-	-	1		
	AE-F130619	85	6	-	65	-	-	88	-	-	1		
	Foramsulfuron	71	17	3	65	-	-	88	-	-	1		
Glyphosate	AMPA	79	379	120	291	1	-	719	7	-	23	-	-
	Glyphosate	235	234	109	284	6	1	680	41	5	23	-	-
Halauxifen-methyl	X-729	30	-	-	25	-	-	39	-	-			
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	AE-F099095	48	-	-	39	-	-	50	-	-			
	AE-F147447	19	-	-	16	-	-	19	-	-	1	-	-
	AE-F160459	48	-	-	39	-	-	50	-	-			
	Mesosulfuron	74	-	-	24	-	-	83	-	-			
	Mesosulfuron-methyl	62	13	-	27	-	-	99	-	-			
Mesotrione	AMBA	88	4	-	67	-	-	90			1		
	MNBA	81	10	1	67	-	-	87	1	-	1		
	Mesotrione	52	30	10	64	2	1	88	2	-	1		
Metamitron	Desamino-metamitron	76	38	11	46	-	-	157	-	-			
	Metamitron	81	27	15	46	-	-	158	-	-			

Estrup		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
Metconazole	Metconazole	30	-	-	25	-	-	39	-	-	7	-	-
Metrafenone	Metrafenone	100	20	-	69	-	-	119	1	-			
Pendimethalin	Pendimethalin	119	4	-	41	-	-	147	-	-			
Picolinafen	CL 153815	50	20	11	40	-	-	118	-	-			
	Picolinafen	64	17	-	40	-	-	118	-	-	6	-	-
Pirimicarb	Pirimicarb	159	40	-	67	-	-	225	1	-			
	Pirimicarb-desmethyl	192	-	-	66	-	-	223	-	-			
	Pirimicarb-desmethyl-formamido	199	13	13	76	-	-	261	-	-			
Propiconazole	Propiconazole	192	23	3	86	-	-	309	2	-	23	-	-
Propyzamide	Propyzamide	5	-	-	4	-	-	3	-	-			
Pyroxsulam	5-OH-XDE-742*				3	-	-	9	-	-			
	6-Cl-7-OH-XDE-742*				3	-	-	9	-	-			
	7-OH-XDE-742*				3	-	-	9	-	-			
	PSA*				3	-	-	9	-	-			
	Pyridine-sulfonamide				3	-	-	9	-	-	1	-	-
Tebuconazole	Amitrol**				3	-	-	9	-	-			
	1,2,4-triazole	1	10	175	2	115	13	33	84	60			
Terbuthylazine	Tebuconazole	40	24	17	39	-	-	118	3	2			
	2-hydroxy-desethyl-terbuthylazine	44	63	24	50	-	-	180	-	-	22	-	-
	Desethyl-terbuthylazine	18	111	35	59	7	-	232	-	-			
	Desisopropyltriazine	90	70	1	62	1	-	197	26	-			
	Hydroxy-terbuthylazine	43	72	16	50	-	-	180	-	-			
	Terbuthylazine	49	78	34	63	-	-	222	1	-			
Thiacloprid	M34	55	-	-	34	-	-	66	-	-	70	-	-
	Thiacloprid	47	-	-	34	-	-	66	-	-			
	Thiacloprid sulfonic acid	56	-	-	34	-	-	66	-	-			
	Thiacloprid-amide	46	1	-	34	-	-	66	-	-			
Triasulfuron	Triazinamin	188	-	-	90	-	-	255	1	-	1	-	-
Tribenuron-methyl	Triazinamin-methyl	52	2	-	37	-	-	70	-	-			

\* Active ingredient was applied in spring 2020. Data evaluation is not included in this report but will be discussed in next year's report covering 2019-2021.

\*\* Amitrol was included in the monitoring of pyroxsulam as it was suspected to be a groundwater pollutant in the Danish groundwater monitoring programme (GRUMO) in relation to the yearly screenings in 2019. Pyroxsulam was therefore tested as a theoretical source of origin to amitrol. The findings of amitrol in the groundwater screening was later shown to be an analytical artefact and the monitoring of amitrol in VAP was thus suspended.

**Table A5.5.** Number of samples where pesticides were either not detected (nd), detected in concentrations  $\leq 0.1 \mu\text{g L}^{-1}$  or detected in concentrations  $> 0.1 \mu\text{g L}^{-1}$  at **Faardrup**. Numbers are accumulated for the monitoring period up to July 2020. All samples included.

<b>Faardrup</b>		Drainage			Horizontal screens			Vertical screens			Suction cups		
Parent	Compound	nd	$\leq 0.1$	$> 0.1$	nd	$\leq 0.1$	$> 0.1$	nd	$\leq 0.1$	$> 0.1$	nd	$\leq 0.1$	$> 0.1$
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	-	-			
Florasulam	TSA	35	-	-	26	-	-	115	-	-			
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	-	-			
Flupyr-sulfuron-methyl	Flupyr-sulfuron-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	29	-	-	31	-	-	115	-	-			
	Fluroxypyr-pyridinol	29	-	-	31	-	-	115	-	-			
Glyphosate	AMPA	163	9	1	128	-	-	321	2	-	58	5	-
	Glyphosate	169	4	-	127	1	-	319	4	-	62	1	-
Halauxifen-methyl	X-729	1	-	-	1	-	-	3	-	-			
	X-757	34	-	-	25	-	-	111	-	-			
Ioxynil	Ioxynil	99	1	-	81	-	-	224	1	-	73	-	-
MCPA	2-methyl-4-chlorophenol	142	-	1	109	-	-	256	-	-			
	MCPA	141	1	1	109	-	-	256	-	-			
Mesosulfuron-methyl	AE-F099095							1	-	-			
	AE-F160459							1	-	-			
Metamitron	Desamino-metamitron	198	12	4	133	-	-	329	36	12	29	-	-
	MTM-126-AMT	48	-	-	28	-	-	112	-	-			
	Metamitron	168	10	2	115	-	-	293	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	-	-
Picloram	Picloram	1	-	-	1	-	-	3	-	-			
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	121	2	2	114	1	-	250	-	-			
	RH-24580	125	-	-	115	-	-	249	-	-			
	RH-24644	121	4	-	115	-	-	249	-	-			
	RH-24655	123	1	-	114	-	-	246	-	-			
Proquinazid	IN-MM671	40	-	-	20	-	-	68	-	-			
	IN-MM991	40	-	-	20	-	-	68	-	-			
Prosulfocarb	Prosulfocarb	78	-	-	61	-	-	126	-	-			

<b>Faardrup</b>		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
Tebuconazole	1,2,4-triazole	3	112	5	82	18	-	324	18	-			
	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	-	-			
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	-	-			

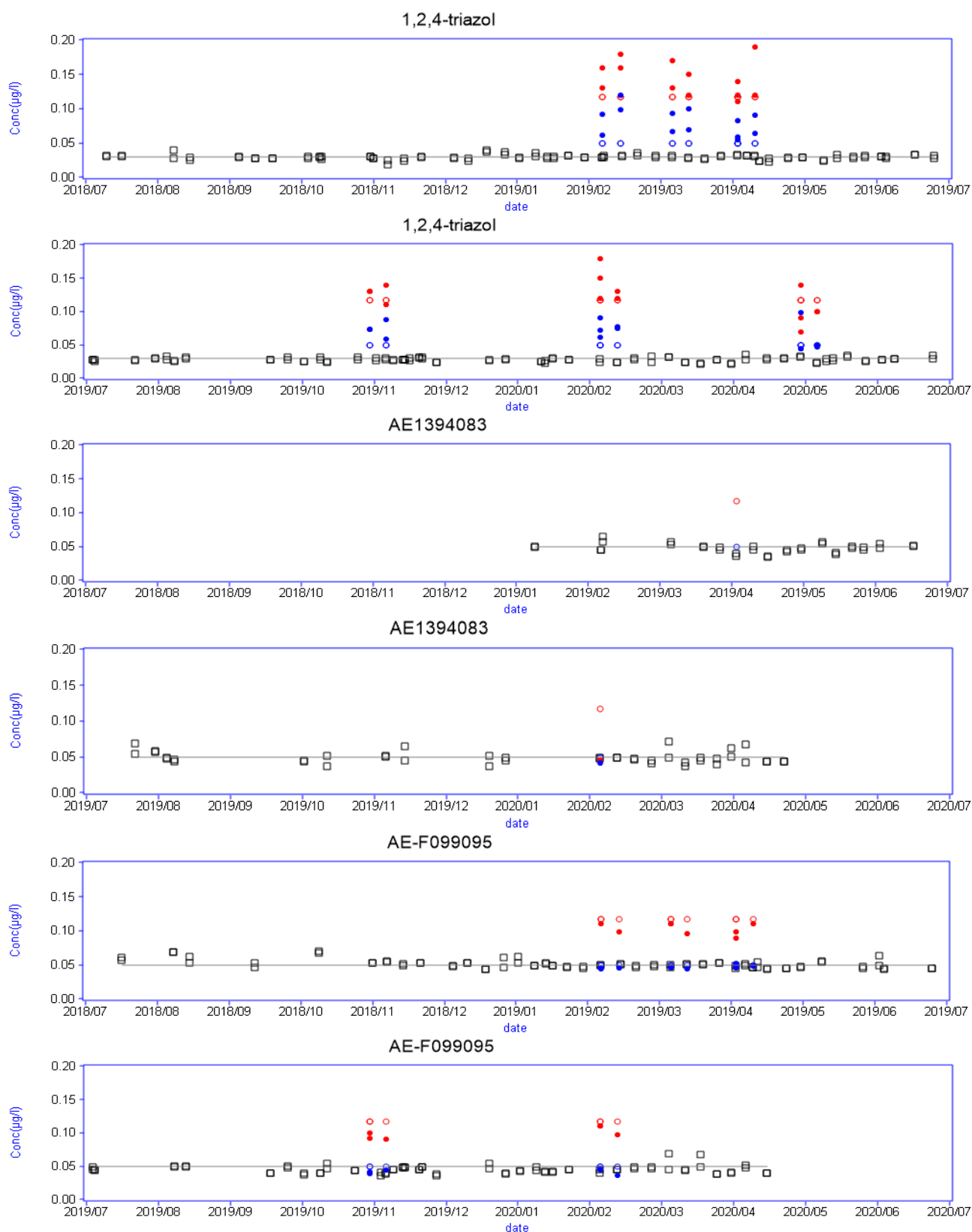
**Table A5.6.** Number of samples where pesticides were either not detected (nd), detected in concentrations  $\leq 0.1 \mu\text{g L}^{-1}$  or detected in concentrations  $>0.1 \mu\text{g L}^{-1}$  at **Lund**. Numbers are accumulated for the monitoring period up to July 2020. All samples included.

<b>Faardrup</b>		Drainage			Vertical screens		
Parent	Compound	nd	$\leq 0.1$	$>0.1$	nd	$\leq 0.1$	$>0.1$
Azoxystrobin	Azoxystrobin	24	3	0	240	0	0
	CyPM	6	16	3	229	11	0
Bentazone	6-hydroxy-bentazone	22	0	0	146	0	0
	8-hydroxy-bentazone	22	0	0	146	0	0
	Bentazone	21	6	0	235	5	0
	N-methyl-bentazone	21	1	0	146	0	0
Florasulam	TSA	30	0	0	176	0	0
Glyphosate	Glyphosate	12	13	8	216	2	0
	AMPA	7	21	5	213	4	0
Halauxifen-methyl	X-729	22	0	0	80	0	0
Picloram	Picloram	18	1	0	42	0	0
Propyzamide	Propyzamide	12	6	3	45	2	0
	RH-24580	21	0	0	47	0	0
	RH-24644	19	1	1	47	0	0
Prothioconazole	1,2,4-triazole	1	31	0	41	147	1

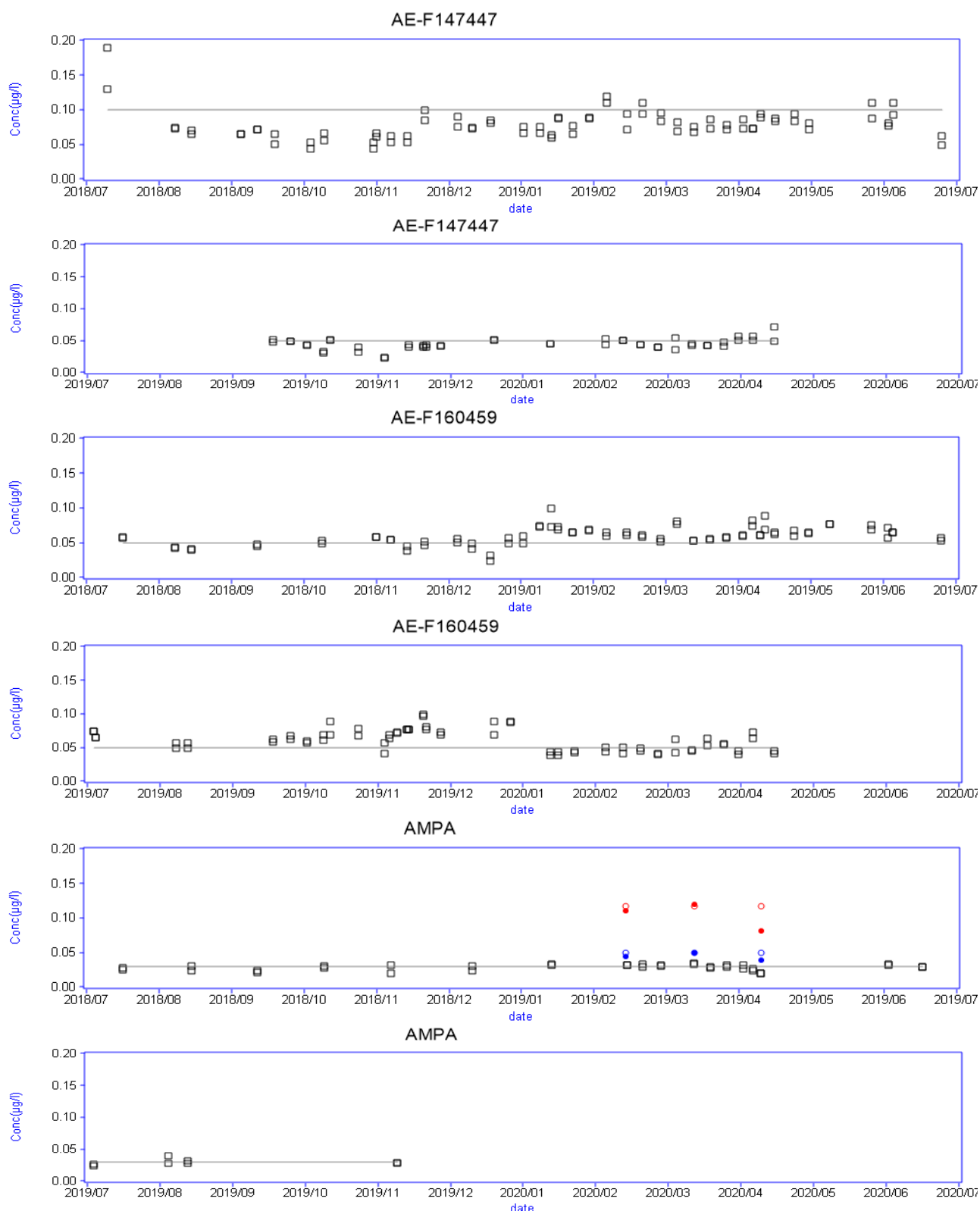


## **Appendix 6**

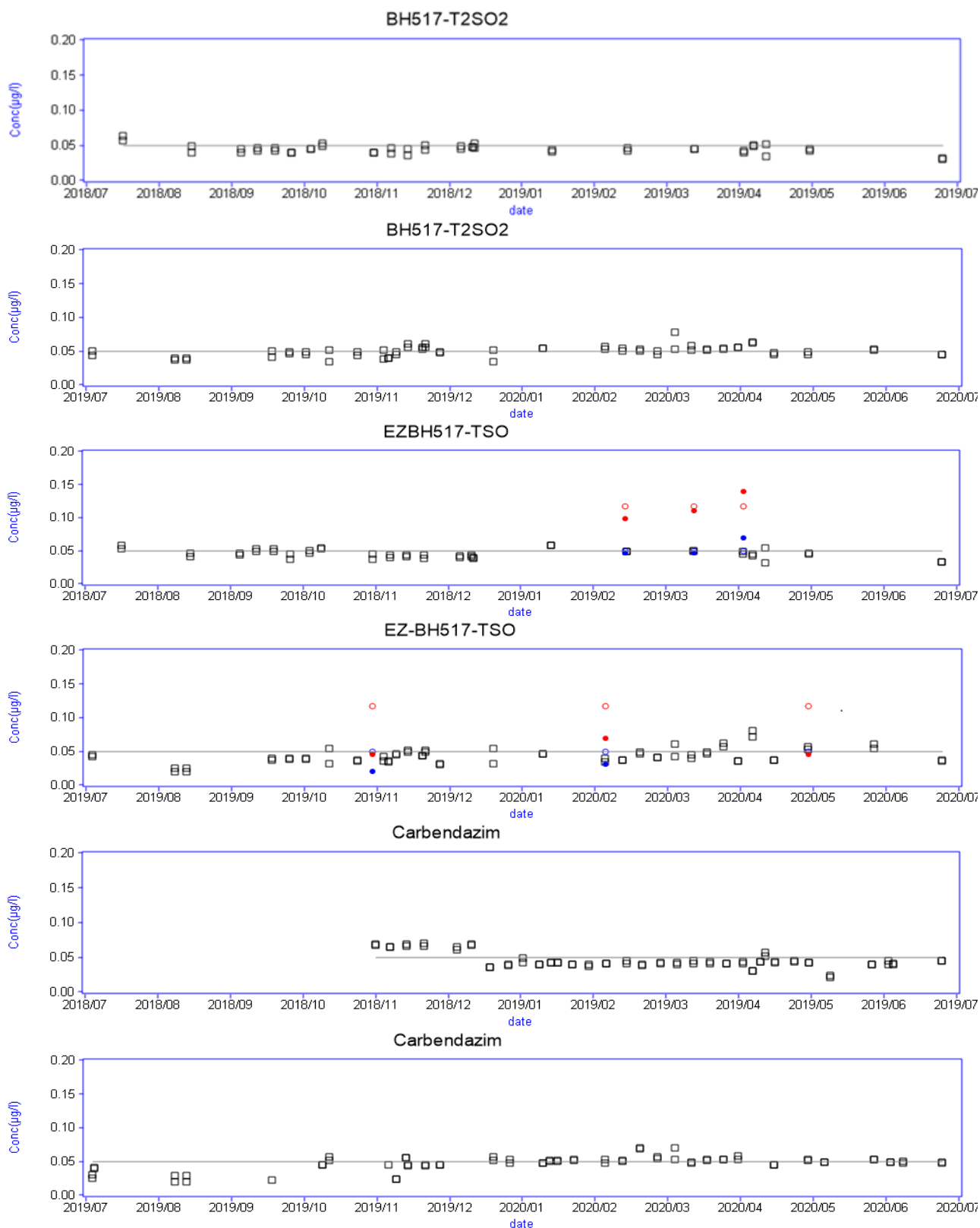
*Internal- and external control sample plots for July 2018 to June 2020*



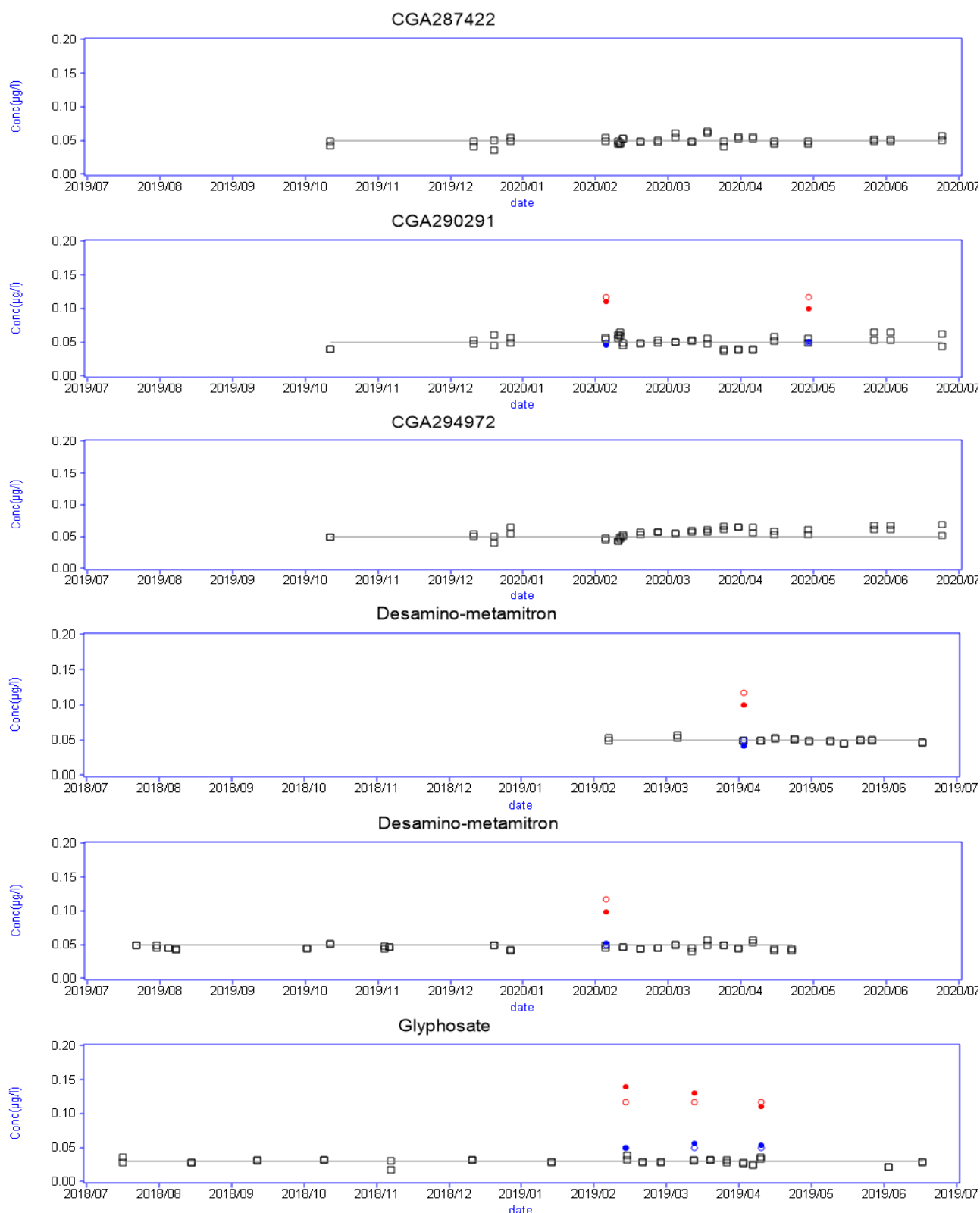
**Figure A6.1.** Quality control data for pesticide analysis by the commercial laboratory. Internal laboratory control (IQ) samples are indicated by square symbols and the nominal level is indicated by the solid grey line ( $\square$  IQ measured, — IQ nominal concentration). External control (EQ) samples are indicated by circles. Open circles indicate the nominal level ( $\circ$  EQ nominal low,  $\circ$  EQ nominal high), and closed circles the measured concentration ( $\bullet$  EQ measured low,  $\bullet$  EQ measured high). AE1394083 was not stable in the ampoule solution resulting in erroneously low recoveries.



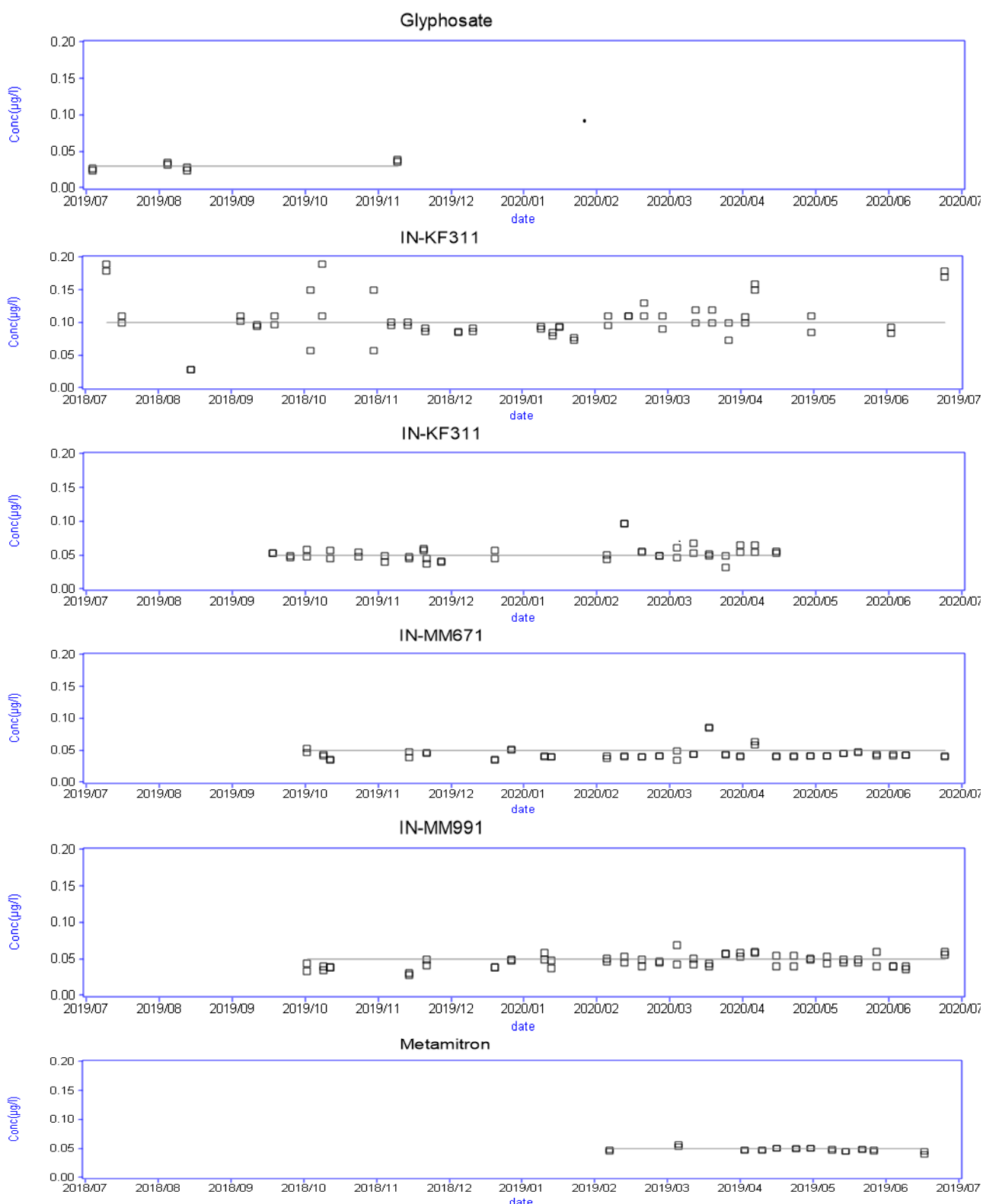
**Figure A6.2.** Quality control data for pesticide analysis by the commercial laboratory. Internal laboratory control (IQ) samples are indicated by square symbols and the nominal level is indicated by the solid grey line ( $\square$  IQ measured, — IQ nominal concentration). External control (EQ) samples are indicated by circles. Open circles indicate the nominal level ( $\circ$  EQ nominal low,  $\circ$  EQ nominal high), and closed circles the measured concentration ( $\bullet$  EQ measured low,  $\bullet$  EQ measured high). During the reporting period, the control concentration of AE-F147447 was changed from  $0.1 \mu\text{g L}^{-1}$  (upper graph) to  $0.05 \mu\text{g L}^{-1}$  (lower graph).



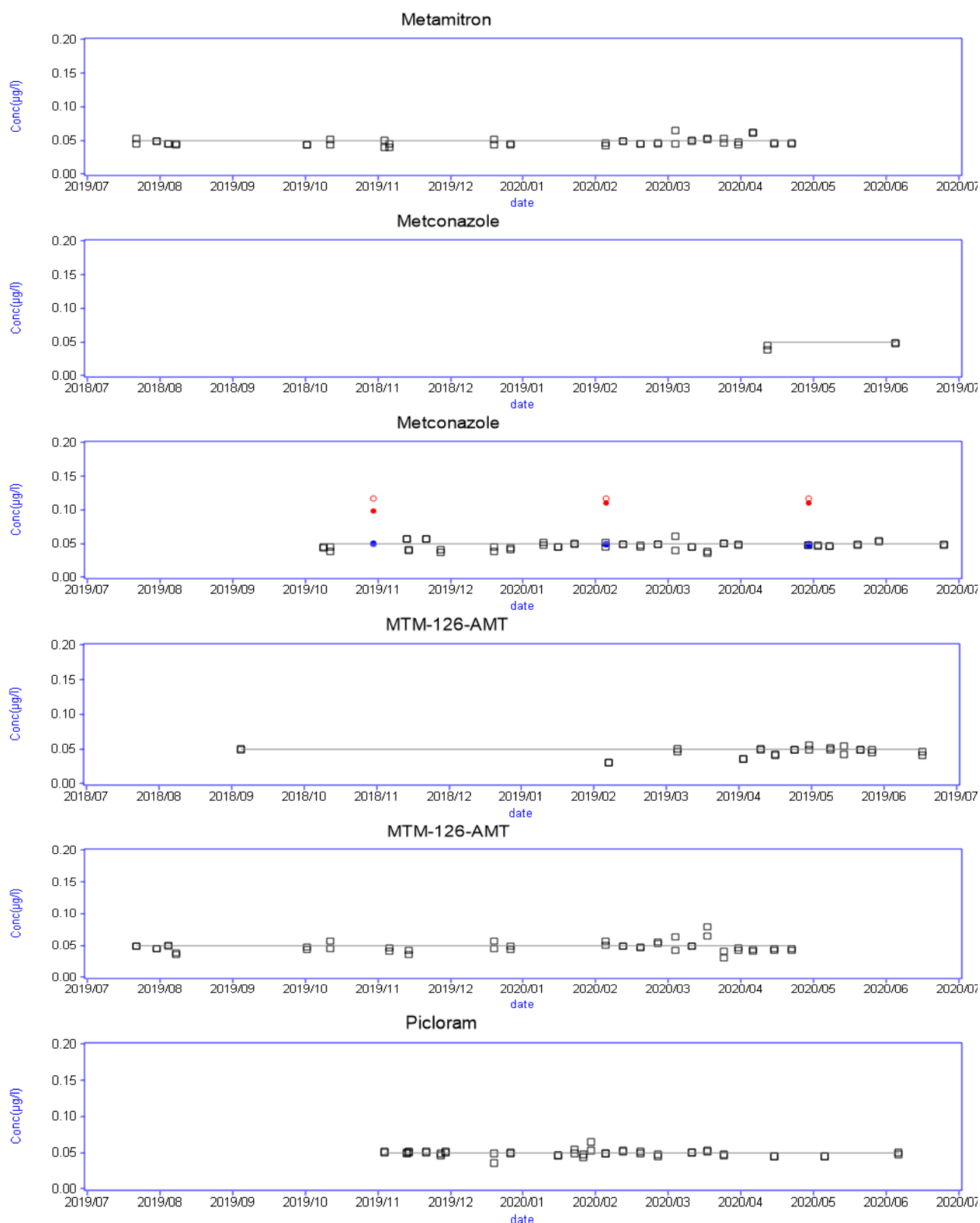
**Figure A6.3.** Quality control data for pesticide analysis by the commercial laboratory. Internal laboratory control (IQ) samples are indicated by square symbols and the nominal level is indicated by the solid grey line ( $\square$  IQ measured, — IQ nominal concentration). External control (EQ) samples are indicated by circles. Open circles indicate the nominal level ( $\circ$  EQ nominal low,  $\circ$  EQ nominal high), and closed circles the measured concentration ( $\bullet$  EQ measured low,  $\bullet$  EQ measured high). E/Z BH 517-TSO was not stable in the ampoule solution resulting in erroneously low recoveries.



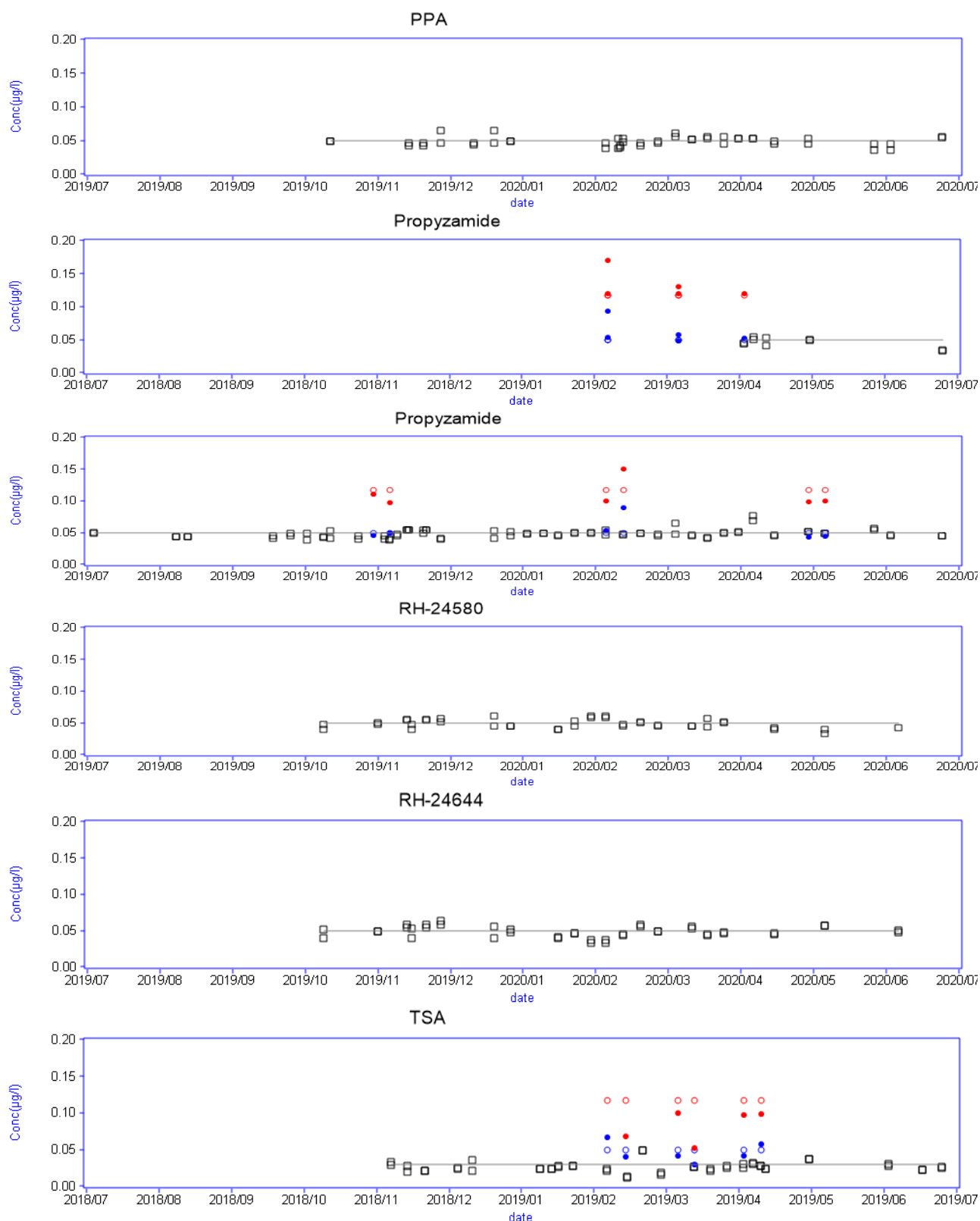
**Figure A6.4.** Quality control data for pesticide analysis by the commercial laboratory. Internal laboratory control (IQ) samples are indicated by square symbols and the nominal level is indicated by the solid grey line (□ IQ measured, — IQ nominal concentration). External control (EQ) samples are 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). Samples for analysis of CGA287422, CGA290291, and CGA294972 were stored from March 2019 to October 2019 due to lacking analytical methods. Hence, no internal control data are available for this period. In February 2019, the control concentration of desamino-metamitron was changed from 0.03 µg L<sup>-1</sup> to 0.05 µg L<sup>-1</sup> (only data for 0.05 µg L<sup>-1</sup> is shown here).



**Figure A6.5.** Quality control data for pesticide analysis by the commercial laboratory. Internal laboratory control (IQ) samples are indicated by square symbols and the nominal level is indicated by the solid grey line ( $\square$  IQ measured, — IQ nominal concentration). External control (EQ) samples are indicated by circles. Open circles indicate the nominal level ( $\circ$  EQ nominal low,  $\circ$  EQ nominal high), and closed circles the measured concentration ( $\bullet$  EQ measured low,  $\bullet$  EQ measured high). In 2019/07 the control concentration of IN-KF311 was changed from  $0.1 \mu\text{g L}^{-1}$  to  $0.05 \mu\text{g L}^{-1}$  in September 2019 (only data for  $0.05 \mu\text{g L}^{-1}$  shown in the lower plot). In February 2019, the control concentration of metamitron was changed from  $0.03 \mu\text{g L}^{-1}$  to  $0.05 \mu\text{g L}^{-1}$  (only data for  $0.05 \mu\text{g L}^{-1}$  is shown here).

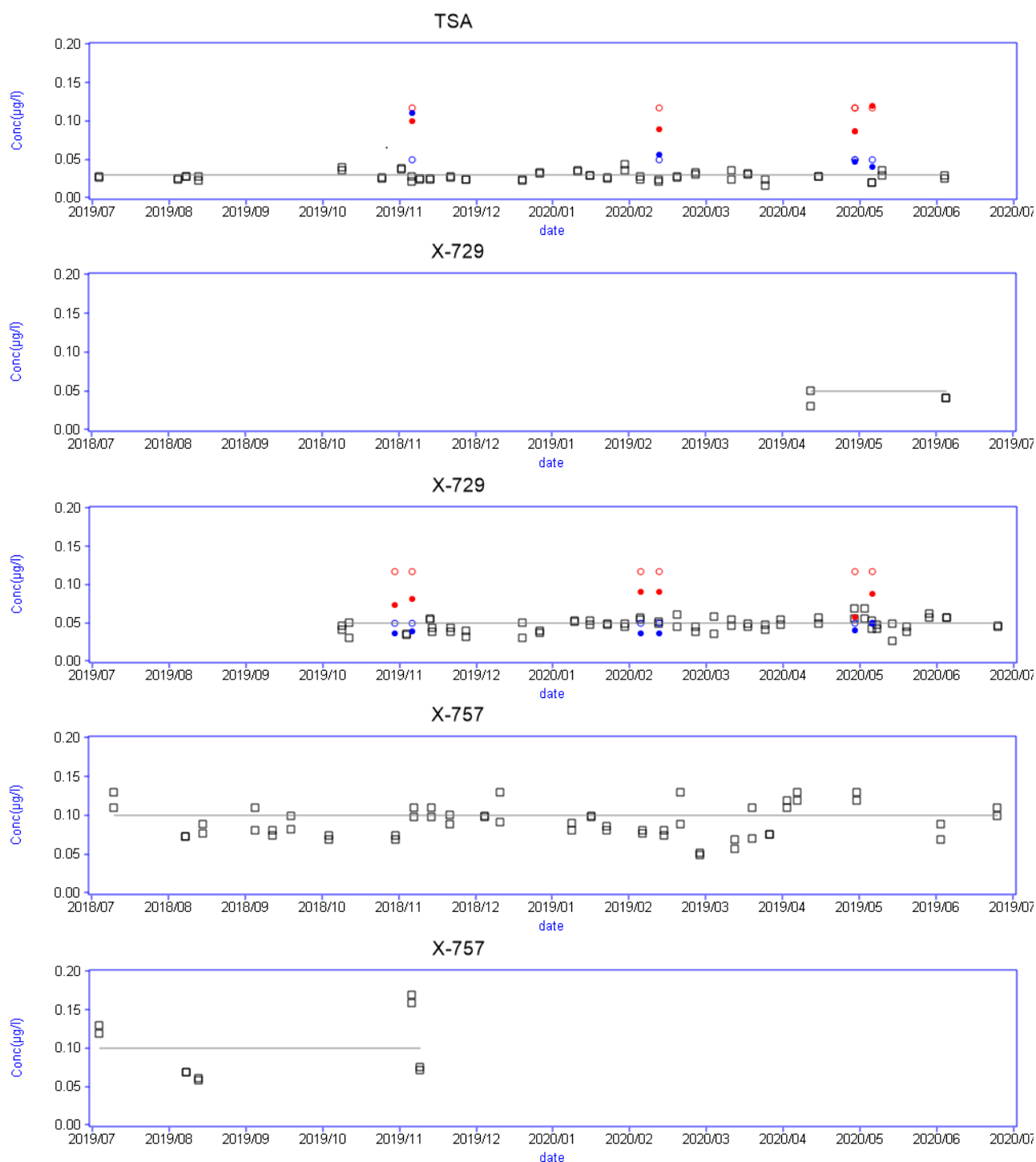


**Figure A6.6.** Quality control data for pesticide analysis by the commercial laboratory. Internal laboratory control (IQ) samples are indicated by square symbols and the nominal level is indicated by the solid grey line (□ IQ measured, — IQ nominal concentration). External control (EQ) samples are 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). Samples for analysis of metconazole and picloram were stored from June 2019 to October 2019 due to the implementation of new compounds in the analytical method package. Hence, no internal control data are available for this period.



**Figure A6.7.** Quality control data for pesticide analysis by the commercial laboratory. Internal laboratory control (IQ) samples are indicated by square symbols and the nominal level is indicated by the solid grey line ( $\square$  IQ measured, — IQ nominal concentration). External control (EQ) samples are indicated by circles. Open circles indicate the nominal level ( $\circ$  EQ nominal low,  $\circ$  EQ nominal high), and closed circles the measured concentration ( $\bullet$  EQ measured low,  $\bullet$  EQ measured high). Samples for analysis of PPA were stored from April 2019 to October 2019 due to lack of an analytical method. In April 2019, the control concentration of propyzamide was changed from  $0.03 \mu\text{g L}^{-1}$  to  $0.05 \mu\text{g L}^{-1}$  (only data for  $0.05 \mu\text{g L}^{-1}$  is shown here).





**Figure A6.8.** Quality control data for pesticide analysis by the commercial laboratory. Internal laboratory control (IQ) samples are indicated by square symbols and the nominal level is indicated by the solid grey line ( $\square$  IQ measured, — IQ nominal concentration). External control (EQ) samples are indicated by circles. Open circles indicate the nominal level ( $\circ$  EQ nominal low,  $\circ$  EQ nominal high), and closed circles the measured concentration ( $\bullet$  EQ measured low,  $\bullet$  EQ measured high). Samples for analysis of X-729 were stored from June 2019 to October 2019 due to the implementation of new compounds in the analytical method package. Hence no internal control data is available for this period. X-729 was not stable in the ampoule solution resulting in erroneously low recoveries.



## **Appendix 7**

*Pesticides analysed at five PLAP fields in the period up to 2014/2015/2016*

**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. 1<sup>st</sup> month perc. refers to accumulated percolation within the first month after the application. C<sub>mean</sub> refers to average leachate concentration at 1 mbgs the first year after application. (See Appendix 2 for calculation method).

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

<sup>1)</sup> Degradation product of mancozeb. The parent compound degrades too rapidly to be detected by monitoring.

<sup>2)</sup> Degradation product of tribenuron-methyl. The parent compound degrades too rapidly to be detected by monitoring.

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

<sup>4)</sup> Degradation product of rimsulfuron. The parent compound degrades too rapidly to be detected by monitoring.

<sup>5)</sup> Leaching increased the second and third year after application.

<sup>6)</sup> Leaching increased during the second year after application but measured concentrations did not exceed 0.042 µg L<sup>-1</sup> (see Kjær et al., 2008).

<sup>7)</sup> 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 1<sup>st</sup> Precip, Y 1<sup>st</sup> Percol) and first month (M 1<sup>st</sup> Precip, M 1<sup>st</sup> Percol) after the first application. C<sub>mean</sub> refers to average leachate concentration [ $\mu\text{g L}^{-1}$ ] at 1 mbgs 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 /degradation product	Appl. date	End mon.	Y 1 <sup>st</sup> precip.	Y 1 <sup>st</sup> percol.	M 1 <sup>st</sup> precip.	M 1 <sup>st</sup> percol.	C <sub>mean</sub>
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
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
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 2013	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

\*Difference between S1 and S2.

**Table A7.2A.** Pesticides analysed at **Jyndeved** 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. 1<sup>st</sup> month perc. refers to accumulated percolation within the first month after application. C<sub>mean</sub> refers to average leachate concentration 1 mbgsthe first year after application. (See Appendix 2 for calculation method).

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

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

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

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

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

<sup>4)</sup> Leaching increased the second year after application.

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

**Table A7.2B.** Pesticides analysed at **Jynde vad**. 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 1<sup>st</sup> Precip, Y 1<sup>st</sup> Percol) and first month (M 1<sup>st</sup> Precip, M 1<sup>st</sup> Percol) after the first application. C<sub>mean</sub> refers to average leachate concentration [ $\mu\text{g L}^{-1}$ ] at 1 mbgs 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 /degradation product	Appl. date	End mon.	Y 1 <sup>st</sup> precip.	Y 1 <sup>st</sup> percol.	M 1 <sup>st</sup> precip.	M 1 <sup>st</sup> percol.	C <sub>mean</sub>
<b>Triticale 2007</b>	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
<b>Winter wheat 2008</b>	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
<b>Spring barley 2009</b>	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
<b>Potatoes 2010</b>	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**
<b>Spring barley 2011</b>	DFF	Diiflufenican(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
<b>Maize 2012</b>	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 <sup>1</sup>
<b>Peas 2013</b>	Fighter 480	Bentazone(P) <sup>2</sup>	May 13	Mar 15	1175	703	84	0.2	0.02-0.16 <sup>1</sup>
<b>Potatoes 2014</b>	Command CS Clomazone	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	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	EBIS (M)	Jun 14	Mar 15	1407	844	138	37	<0.02

<sup>1)</sup>Difference between S1 and S2. <sup>2)</sup> Bentazone applied on 7 May and 16 May 2013.

**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. 1<sup>st</sup> month perc. refers to accumulated percolation within the first month after application. C<sub>mean</sub> refers to average leachate concentration in the drainage water within the first drainage season after application. (See Appendix 2 for calculation methods).

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



**Table A7.3A 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. 1<sup>st</sup> month perc. refers to accumulated percolation within the first month after application. C<sub>mean</sub> refers to average leachate concentration in the drainage water within the first drainage season after application. (See Appendix 2 for calculation methods).

Crop and analysed pesticides	Application date	End of monitoring	Prec. (mm)	Perc. (mm)	1 <sup>st</sup> month perc.	C <sub>mean</sub> (µg L <sup>-1</sup> )
<b>Winter rape 2006</b>						
Propyzamide (Kerb 500 SC)	Nov 05	Apr 08	2345	1115	75	0.22 <sup>1)</sup>
- <i>RH-24644</i>						0.01 <sup>1)</sup>
- <i>RH-24580</i>						<0.01 <sup>1)</sup>
- <i>RH-24655</i>						<0.01 <sup>1)</sup>
Clopyralid (Matrigan)	Apr 06	Apr 08	2009	859	8	<0.01
<b>Winter wheat 2007</b>						
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
<b>Fodder beet 2008</b>						
- <i>Fluazifop-P</i> (Fusilade Max)	Jul 08	Jun 12	985	494	21	<0.01
- <i>TFMP</i> (Fusilade Max)	Jul 08	Jun 12	985	494	21	0.24
Metamitron (Goliath)	May 08	Dec 10	969	498	4	0.01
- <i>Desamino-metamitron</i>	May 08	Dec 10	969	498	4	0.02
Triflurosulfuron-methyl (Safari)	May 08	Jun 10	969	498	4	<0.01
- <i>IN-D8526</i>	May 08	Jun 10	969	498	4	<0.01
- <i>IN-E7710</i>	May 08	Jun 10	969	498	4	<0.01
- <i>IN-M7222</i>	May 08	Jun 10	969	498	4	<0.02
Ethofumesate (Tramat 500 SC)	May 08	May 10	969	497	3	<0.01

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

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

<sup>3)</sup> 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.

<sup>4)</sup> 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 1<sup>st</sup> Precip, Y 1<sup>st</sup> Percol) and first month (M 1<sup>st</sup> Precip, M 1<sup>st</sup> Percol) after the first application. C<sub>mean</sub> refers to average leachate concentration [µg L<sup>-1</sup>] at 1 mbgs 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 /degradation product	Appl. date	End mon.	Y 1 <sup>st</sup> Precip.	Y 1 <sup>st</sup> Percol.	M 1 <sup>st</sup> Precip	M 1 <sup>st</sup> Percol	C <sub>mean</sub>
<b>Spring barley 2009</b>	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
<b>Red fescue 2010</b>	Fighter 480	Bentazone(P)	May 09	Jun 11	876	391	85	1	0.03
	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
<b>Red fescue 2011</b>	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

**Table A7.4B continued.** 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 1<sup>st</sup> Precip, Y 1<sup>st</sup> Percol) and first month (M 1<sup>st</sup> Precip, M 1<sup>st</sup> Percol) after the first application. C<sub>mean</sub> refers to average leachate concentration [ $\mu\text{g L}^{-1}$ ] at 1 mbgs 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 /degradation product	Appl. date	End mon.	Y 1 <sup>st</sup> Precip.	Y 1 <sup>st</sup> Percol	M 1 <sup>st</sup> Precip	M 1 <sup>st</sup> Percol	C <sub>mean</sub>
<b>Red fescue 2012</b>	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
<b>Winter wheat 2013</b>	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
<b>Spring barley 2013</b>	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
<b>Winter wheat 2014</b>	Oxitril CM	Ioxynil (P)	Oct 13	Mar 15	804	542	222	189	<0.01
		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
<b>Maize 2015</b>	Callisto	Mesotrione (P)	May 15	May 18	1219	783	117	52	0.05
		AMBA (M)	May 15	May 18	1219	783	117	52	<0.01
		MNBA (M)	May 15	May 18	1219	783	117	52	<0.01
	MaisTer	Foramsulfuron (P)	Jun 15	May 18	1257	791	100	37	<0.01
		AE-F130619 (M)	Jun 15	May 18	1257	791	100	37	<0.01
		AE-F092944 (M)	Jun 15	May 18	1257	791	100	37	<0.01
<b>Maize 2016</b>	Callisto	Mesotrione (P)	Jun 16	May 18	562	826	77	26	0.1
		AMBA (M)	Jun 16	May 18	562	826	77	26	<0.01
		MNBA (M)	Jun 16	May 18	562	826	77	26	0.01
	MaisTer	Foramsulfuron (P)	Jun 16	May 18	514	881	82	121	0.03
		AE-F130619 (M)	Jun 16	May 18	514	881	82	121	<0.01
		AE-F092944 (M)	Jun 16	May 18	514	881	82	121	<0.01
	Iodosulfuron (P)	Triazinamine (M)	Jun 16	Mar 18	514	881	82	121	<0.01
	Harmony SX								
	Thifensulfuron-methyl (P)	Triazinamine (M)	Jun 16	Mar 18	562	826	77	26	<0.01

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

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

**Table A7.4A 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. 1<sup>st</sup> month perc. refers to accumulated percolation within the first month after application. C<sub>mean</sub> refers to average leachate concentration in the drainage water within the first drainage season after application. (See Appendix 2 for calculation methods).

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

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

*The values for prec. and perc. are accumulated up to July 2006.*

<sup>1)</sup> *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 1<sup>st</sup> Precip, Y 1<sup>st</sup> Percol) and first month (M 1<sup>st</sup> Precip, M 1<sup>st</sup> Percol) after the first application. C<sub>mean</sub> refers to average leachate concentration [µg L<sup>-1</sup>] at 1 mbgs 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 /degradation product	Appl. date	End mon.	Y 1 <sup>st</sup> precip	Y 1 <sup>st</sup> percol	M 1 <sup>st</sup> precip	M 1 <sup>st</sup> percol	C <sub>mean</sub>
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
	Roundup Max	CL 153815(M)	Oct 07	Mar 10	1253	267	76	24	0.24
		Glyphosate(P)	Sep 07	Jun 12	1200	261	113	29	0.19
		AMPA(M)	Sep 07	Jun 12	1200	261	113	29	0.13
Spring barley 2009	Amistar	Azoxystrobin(P)	Jun 09	Jun 12	1215	235	60	0	0.04
		CyPM(M)	Jun 09	Jun 12	1215	235	60	0	0.41
	Basagran M75	Bentazone(P)	May 09	Jun 12	1222	238	83	4	0.05
	Fox 480 SC	Bifenox(P)	May 09	Jun 12	1243	246	87	16	<0.02
		Bifenox acid(M)	May 09	Jun 12	1243	246	87	16	0.16
		Nitrofen(M)	May 09	Jun 12	1243	246	87	16	<0.01
Winter rape 2010	Biscaya OD 240	Thiacloprid(P)	May 10	Mar 12	1083	196	43	0	<0.01
		M34(M)	May 10	Mar 12	1083	196	43	0	<0.02
		Thiacloprid sulfonic acid(M)	May 10	Mar 12	1083	196	43	0	<0.1
		Thiacloprid-amide(M)	May 10	Mar 12	1083	196	43	0	<0.01
		Triazinamin-methyl(M)	Sep 10	Aug 12	823	176	97	31	0.01
Winter wheat 2011	Express ST								
	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
	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
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
Glyphonova 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

**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. 1<sup>st</sup> month perc. refers to accumulated percolation within the first month after application. C<sub>mean</sub> refers to average leachate concentration in the drainage water the first drainage season after application. (See Appendix 2 for calculation methods).

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

<sup>1)</sup> 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 1<sup>st</sup> Precip, Y 1<sup>st</sup> Percol) and first month (M 1<sup>st</sup> Precip, M 1<sup>st</sup> Percol) after the first application. C<sub>mean</sub> refers to average leachate concentration [ $\mu\text{g L}^{-1}$ ] at 1 mbgs 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 /degradation product	Appl. date	End mon.	Y 1 <sup>st</sup> Precip.	Y 1 <sup>st</sup> Percol.	M 1 <sup>st</sup> Precip.	M 1 <sup>st</sup> Percol	C <sub>mean</sub>
<b>Spring barley 2006</b>	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
<b>Winter rape 2007</b>	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
<b>Winter wheat 2008</b>	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
<b>Sugar beet 2009</b>	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
		Triflurosulfuron-methyl(P)	Apr 09	Jun 11	609	146	50	2	<0.01
	Safari	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
			Apr 09	Jun 11	609	146	50	2	<0.02
<b>Spring barley and</b>	Fighter 480	Bentazone(P)	Jun 10	Jun 15*	693	327	49	29	<0.01
	Bentazone(P)								
<b>Red fescue 2010</b>	Fox 480 SC	Bifenox(P)	Oct 10	Jun 12	351	190	75	72	0.02
	Bifenox(P)	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
<b>Red fescue 2011</b>	Fusilade Max Fluazifop-P-butyl (P)	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
<b>Spring barley and</b>	Glyphogan	Glyphosate(P)	Oct 11	Aug 12	425	17	56	17	<0.01
<b>White clover 2012</b>	Glyphosate(P)	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
	Bentazone(P)								
	Flexity	Metrafenone(P)	Jun 12	Apr 15	580	215	96	14	<0.01
	Metrafenone(P)								
<b>White clover 2013</b>	Fighter 480	Bentazone(P)	May 13	Sept 15	711	213	82	0	0.02
	Bentazone(P)								
	Kerb 400 SC	Propyzamid(P)	Jan 13	Apr 15	640	213	64	51	<0.01
	Propyzamid(P)	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

## Appendix 8

### *Horizontal wells*

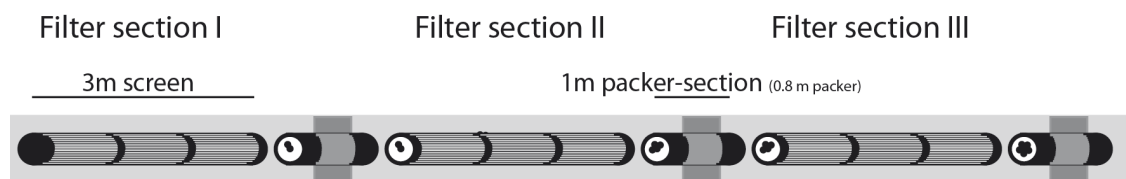
At all PLAP-fields (except Lund), additional horizontal wells with three horizontal screens, were established in September 2011.

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 to optimize monitoring of the fields both in time and space.

At the sandy fields (Tylstrup and Jyndevad), the wells were installed to improve sampling of the upper fluctuating groundwater. The location and horizontal extent of the well screens enables collection of spatially representative samples of the pore water, just reaching the groundwater zone. The wells (labelled H1) were installed at 4.5 m depth at Tylstrup and 2.5 m depth at Jyndevad.

At the clayey till fields (Silstrup “H3”, Estrup “H2”, and Faardrup “H3”), the wells were installed to improve spatial representability of the water sampled in the variably saturated zone below drain-depth. To ensure this, the wells were installed at 2 m depth and oriented such that they are orthogonal to the orientation of the dominating fracture system and crossing underneath a drain-line with one of the three filter sections/screens. Also, the wells were installed so they are 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/filter sections are installed in boreholes of 9 cm in diameter. These boreholes are drilled by applying the directional drilling system Rotamole™, which uses a dry percussion-hammer air pressure technique causing minimal disturbances of the soil medium.



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

Water sampling for pesticide analysis from the horizontal screens started April 2012 (half a year after installation) and is only conducted when the soil media surrounding the screens is saturated.

The design of the wells facilitates the possibility of collecting water from six points along the 12 m long well, but this option is currently not used.





## 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 net precipitation 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 age dating of young groundwater are based on natural or anthropogenic tracers include tritium-helium ( $^3\text{H}/^3\text{He}$ ), chlorofluorocarbons (CFCs) and sulphurhexafluoride ( $\text{SF}_6$ ). 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 because of:

- Low pumping rate excluded sampling for dissolved gases in clamped copper tubes and
- the piston flow model cannot be expected to be valid for the glacial 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 A9.1. 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 filter sections 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 filter sections, 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).

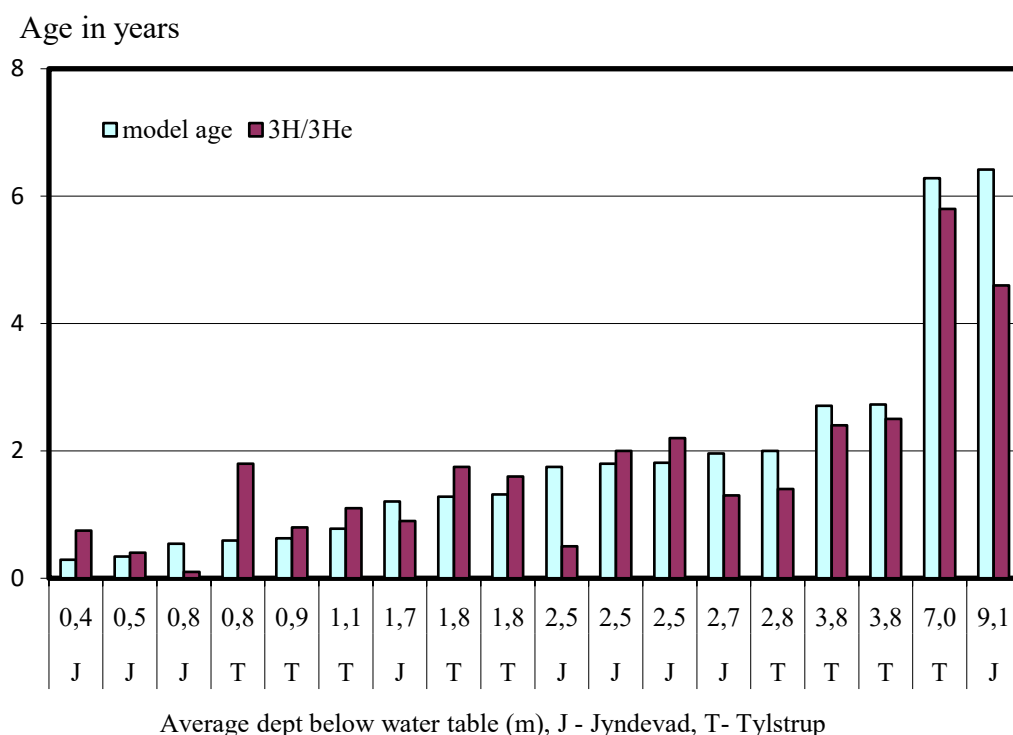
**Table A9.1.** Average recharge 2000-2009, water velocity and groundwater age.

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 ( $^3\text{H}$ ), half-life 12.5 years, and its daughter product helium-3 ( $^3\text{He}$ ) 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 Jydevad and Tylstrup. Recharge model age assumes water velocity of 1.4 m per year, except for the deep filter section 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 consistent.