The Danish Pesticide Leaching Assessment Programme

Monitoring results May 1999–June 2003

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Preface

In 1998, the Danish Government initiated the Danish Pesticide Leaching Assessment Programme (PLAP), an intensive monitoring programme aimed at evaluating the leaching risk of pesticides under field conditions. The Danish Government funded the first phase of the programme from 1998 to 2001, while the Ministry of the Environment and the Ministry of Food, Agriculture and Fisheries is funding a prolongation from 2002 to 2009.

The work was conducted by the Geological Survey of Denmark and Greenland (GEUS), the Danish Institute of Agricultural Sciences (DIAS) and the National Environmental Research Institute (NERI) under the direction of a management group comprising Jeanne Kjær (GEUS), Walter Brüsch (GEUS), Svend Elsnab Olesen (DIAS), Preben Olsen (DIAS), Ruth Grant (NERI), Christian Ammitsøe (Danish Environmental Protection Agency) and Christian Deibjerg Hansen (Danish Environmental Protection Agency). During 2004, Christian Deibjerg Hansen was replaced by Steen Marker (Danish Environmental Protection Agency) and Svend Elsnab Olesen was replaced by Ole Hørbye Jacobsen (DIAS).

This report presents the results for the period May 1999–June 2003. Results covering part of the period (May 1999–June 2002) have been reported previously (Kjær *et al.*, 2002 and Kjær *et al.*, 2003). The present report should therefore be seen as a continuation of previous reports, focusing mainly on the monitoring period July 2002–June 2003.

The report was prepared jointly by Jeanne Kjær, Heidi C. Barlebo, Walter Brüsch and Rene K. Juhler, Lasse Gudmundsson (all GEUS), Preben Olsen and Finn Plauborg (DIAS) and Ruth Grant (NERI). While all authors contributed to the whole report, the aspects for which each author was mainly responsible are as follows:

- Pesticide and bromide leaching: Jeanne Kjær, Preben Olsen and Walter Brüsch
- Soil water dynamics and water balances: Heidi C. Barlebo, Finn Plauborg and Ruth Grant
- Pesticide analysis quality assurance: Rene K. Juhler

Jeanne Kjær
June 2004

Summary

In 1998, the Danish Government initiated the Pesticide Leaching Assessment Programme (PLAP), an intensive monitoring programme aimed at evaluating the leaching risk of pesticides under field conditions. The objective of the PLAP is to improve the scientific foundation for decision making in the Danish registration procedures for pesticides. The specific aim is to analyse whether pesticides applied in accordance with current regulations leach to the groundwater in unacceptable concentrations.

The PLAP includes evaluation of the leaching risk of 28 pesticides at six agricultural sites (ranging from 1.1 to 2.4 ha) representing a range of Danish soil and climate conditions. The pesticides were all applied at the maximum permitted rate. In order to describe water transport, bromide tracer was also applied to the fields. Bromide and pesticide concentrations are measured monthly in both the unsaturated and the saturated zones, and weekly in the drainage water. This report presents the monitoring results for the six agricultural sites during the monitoring period May 1999–June 2003, with the main focus on the last year of the monitoring period (July 2002–June 2003). The report must be seen as a provisional report because not all of the pesticides applied have been monitored for at least two consecutive years. The findings so far nevertheless show that:

- A quarter of the applied pesticides (7 of 28) were not leached during the current monitoring period.

- The monitoring data indicate marked leaching of four of the applied pesticides or their degradation products. Thus glyphosate and its degradation product AMPA as well as the degradation products of metribuzin, terbuthylazine and rimsulfuron leached from the root zone (1 m b.g.s.) in average concentrations exceeding the maximum allowable concentration of 0.1 µg/l.
- At the two sandy sites, previous application of pesticides has caused marked groundwater contamination with degradation products of metribuzin. These appear to be relatively stable, and both leached throughout the entire monitoring period, thus indicating continuation of leaching as long as four years after application. There was evidence that the degradation products may persist in the groundwater several years after application.

- Finally, the monitoring data indicate leaching of a further 17 pesticides. The levels of leaching hitherto detected were not unacceptable, however. Although the concentration in several samples exceeded 0.1 µg/l, the average concentration did not.

The monitoring data was supported by hydrological modelling (MACRO version 4.2) providing an overall water balance for each of the six sites. The models were parameterized using measured data as well as literature/default values. Subsequently the model was thoroughly calibrated to the sandy soils whereas a more simple calibration was done on the loamy soils. During the calibration period May 1999–June 2002 the models generally per

formed well when comparing simulated and observed time series for groundwater table, soil water content and drainage flow in the loamy soils, and for bromide concentration in the sandy soils. The latest year of the monitoring period, July 2002–June 2003, is considered a validation period and no further model calibration has therefore been performed. The model validation results confirmed the previous results indicating that all models generally performed well as regards predicting the above-mentioned time series.

The overall quality of the pesticide analysis was considered satisfactory. The QA system showed that:

- Reproducibility of the pesticide analyses was good, total standard deviation being in the range 0.001–0.053 µg/l.
- No differences in reproducibility were observed between pesticides and degradation products
- Recovery was generally good (70–125%) in external spiked samples. Low recovery of the pesticides desmedipham, fluroxypyr and phenmedipham was observed at single sites. High recovery was observed for bentazone and the degradation products triazinamin-methyl and triazinamin at single sites.
- Variation in recovery of the same compound in spiked samples from different field sites indicate that uncertainties in analysis are partly attributable to differences in matrix composition.
- Contamination of samples was not observed during collection, storage and analysis.

Dansk sammendrag

I 1998 iværksatte Folketingen projektet ”Varslingssystem for udvaskning af pesticider til grundvandet” (VAP), et omfattende moniteringsprogram, der undersøger udvaskning af pesticider under reelle markforhold. Programmet har til formål at undersøge, om godkendte pesticider eller deres nedbrydningsprodukter - ved regelret brug - udvaskes til grundvandet i uacceptable koncentrationer for herigennem at forbedre det videnskabelige grundlag for danske myndigheders (Miljøstyrelsens) procedurer for registrering af sprøjtemidler.

28 stoffers udvaskningsrisiko undersøges således på 6 marker af en størrelse mellem 1,1 og 2,6 ha. Markerne er placeret så de repræsenterer forskellige typer af geologi, og er tillige placeret så der tages hensyn til de klimatiske variationer i Danmark, specielt hvad angår nedbørsforhold. De anvendte pesticider bliver udbragt i maximalt tilladte doseringer. Til brug for beskrivelsen af vandtransport anvendes bromid som sporstof. Bromid- og pesticidkoncentrationer bliver analyseret månedligt i prøver udtaget i den umættede og mættede zone, og i ugentligt prøver af drænvand. I denne rapport præsenteres moniteringsresultaterne for de seks områder for perioden Maj 1999 – Juni 2003, primært med fokus på det sidste moniteringsår (juli 2002 – juni 2003). En del af stofferne har kun været inkluderet i moniteringsprogrammet i en udvaskningssæson og for disse er det derfor for tidligt at konkludere noget endeligt. De hidtidige resultater viser imidlertid at:

- En fjerdedel af de udbragte pesticider (7 ud af 28) blev ikke udvasket i løbet af indeværende moniteringsperiode.

- Fire af de udbragte stoffer, eller nedbrydningsprodukter heraf, gav anledning til en markant udvaskning. Glyphosat, dettes nedbrydningsprodukt AMPA, samt nedbrydningsprodukter fra henholdsvis metribuzin, terbuthylazin og rimsulfuron blev udvasket fra rodzonen (1 m.u.t.), i gennemsnitskoncentrationer, over grænseværdien på 0.1 µg/l.

- På de to sandede lokaliteter har tidligere metribuzinbehandlinger givet anledning til en markant grundvandsforurening med stoffets nedbrydningsprodukter. Nedbrydningsprodukterne er relativt stabile, og selv 4 år efter anvendelse ses en stadig at foregå en udvaskning til grundvandet.

- Andre 17 stoffer gav anledning til udvaskning. Selv om flere af disse stoffer ofte blev fundet i koncentrationer over 0.1 µg/l, var der ikke tale om at udvaskningen, som årsmiddel, oversteg grænseværdien på 0.1 µg/l.

Moniteringsresultaterne blev understøttet af hydrologisk modellering (MACRO version 4.2) som gav en overordnet vandbalance for hver af de seks områder. Parameteriseringen af modellen blev foretaget udfra såvel målte data som litteratur/default værdier. Modellen er blevet grundigt kalibreret på de sandede lokaliteter, mens en grovere kalibreringsprocedure er blevet anvendt på de lerede lokaliteter. For kalibreringsperioden Maj 1999 - Juni 2002 gav modellen en tilfredsstillende beskrivelse af grundvandsspejlets beliggenhed, jordvandsind hold, drænvandsafstrømning (lerede lokaliteter) samt bromidkoncentrationer (sandende lokaliteter). Det sidste år (Juli 2002 - Juni 2003) blev anvendt til validering af modellen, dvs. uden yderligere kalibrering af modellen. Resultater fra valideringsperioden bekræfter tidligere fundne resultater, idet modellen generelt leverede en tilfredsstillende beskrivelse af ovennævnte tidsserier.

Kvaliteten af de udførte pesticidanalyser blev fundet at være tilfredsstillende idet:

- Reproducerbarheden var god med en total standardafvigelse på mellem 0.001 - 0.053 µg/l.
- Genfindingen var generelt god (70% - 125%) i de eksternt spikede kontrolprøver. På enkelte lokaliteter blev der dog konstateret lav genfinding af desmedipham, fluroxypyr og phenmedipham. Enkelte steder var der desuden høje genfindingsprocenter for bentazon, triazinaminmethyl og triazinamin.
- Der blev ikke konstateret kontaminering ved prøvehåndtering, transport og efterfølgende analyse.
- Variationen i genfinding af det samme stof i spikede prøver fra de forskellige lokaliteter kunne tyde på at usikkerheden på analyserne til dels kan henføres til forskelle i matricen; vandprøvernes kemiske sammensætning.

1 Introduction

There is growing public concern in Denmark about pesticide contamination of our surface waters and groundwater. Pesticides and their degradation products have increasingly been detected in the groundwater during the past decade and are now present in much of the Danish groundwater. Under the Danish National Groundwater Monitoring Programme (GRUMO), pesticides and their degradation products have so far been detected in 40% of all screens monitored (Jørgensen, 2003).

The increasing detection of pesticides in groundwater over the past 10 years has raised doubts as to the adequacy of the existing approval procedure for pesticides. A main issue in this respect is that the EU assessment and hence also the Danish assessment of the risk of pesticide leaching to the groundwater is largely based on data from laboratory or lysimeter studies. However, these types of data may not suffice to adequately characterize the leaching that may occur under actual field conditions. A major limitation is that the laboratory and lysimeter studies do not include the spatial variability of the soil parameters (hydraulic, chemical and microbiological soil properties) affecting pesticide leaching. This is of particular importance for silty and loamy soils, where preferential transport may have a major impact on pesticide leaching. In fact, various field studies suggest that considerable preferential transport of several pesticides occurs to a depth of 1 m under conditions comparable to those pertaining in Denmark (Kördel, 1997).

The inclusion of field studies, i.e. test plots exceeding 1 ha, in risk assessment of pesticide leaching to the groundwater is considered an important improvement in risk assessment procedures. For example, the US Environmental Protection Agency (US-EPA) has included field-scale studies in its risk assessments since 1987. Pesticides that may potentially leach to the groundwater are required to be included in field studies as part of the registration procedure. Over the past decade the US-EPA has therefore conducted field studies of more than 50 pesticides (US Environmental Protection Agency, 1998). A similar concept has also been adopted within the European Union (EU), where Directive 91/414/EEC, Annexe VI (Council Directive 97/57/EC of 22 September 1997) enables field study results to be included in the risk assessments.

1.1 Objective

In 1998, the Danish Government initiated the Pesticide Leaching Assessment Programme (PLAP), an intensive monitoring programme aimed at evaluating the leaching risk of pesticides under field conditions. The PLAP is intended to serve as an early warning system providing decision makers with advance warning if approved pesticides leach in unacceptable concentrations. The programme focuses on pesticides used in arable farming, and monitors leaching at six agricultural test sites representative of Danish conditions.

The objective of the PLAP is to improve the scientific foundation for decision making in the Danish registration and approval procedures for pesticides. The specific aim is to analyse whether pesticides applied in accordance with current regulations leach at levels exceeding the maximum allowable concentration of 0.1 µg/l.

1.2 Structure of the PLAP

The pesticides included in the PLAP were selected by the Danish Environmental Protection Agency on the basis of expert judgement. At present, 28 pesticides and several of their degradation products are included in the PLAP. All the compounds analysed are listed in Appendix 1. The reasons for selecting the specific pesticides are detailed in Lindhardt *et al.* (2001).

Soil type and climatic conditions are considered to be some of the most important parameters controlling pesticide leaching. The PLAP therefore encompasses six test sites representative of the dominant soil types and the climatic conditions in Denmark (Figure 1). The groundwater table at all six sites is shallow, thereby enabling a rapid groundwater response

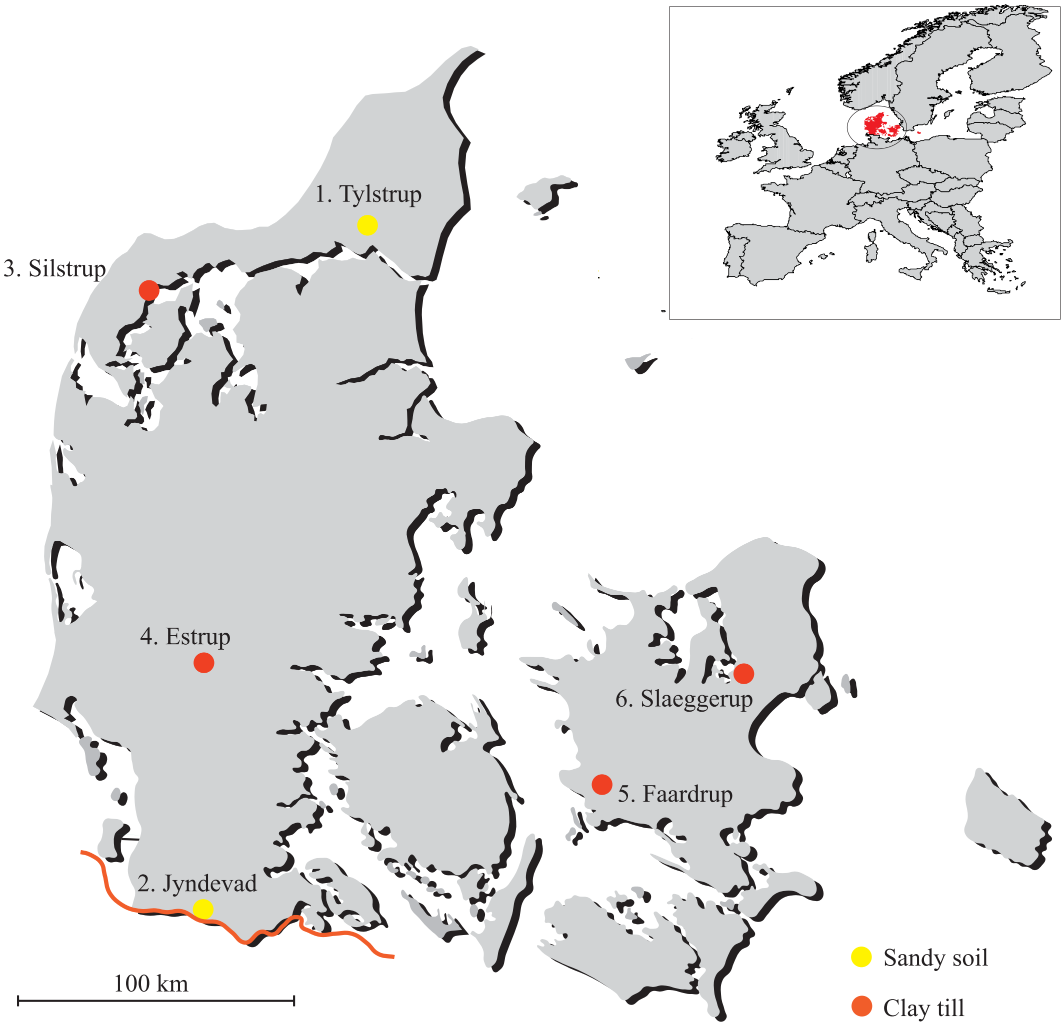

Figure 1. Location of the six PLAP sites Tylstrup, Jyndevad, Silstrup, Estrup, Faardrup and Slaeggerup.

to pesticide leaching (Table 1). Cultivation of the PLAP sites is in line with conventional agricultural practices in the vicinity. The pesticides are applied in the maximum permitted dosage and in the manner specified in the regulations. Hence any occurrence of pesticides or degradation products in the groundwater downstream of the sites can be related to the current approval conditions pertaining for the individual pesticides. The PLAP was initiated in autumn 1998. The six test sites were selected and established during 1999. Monitoring was initiated in 1999 at Tylstrup, Jyndevad and Faardrup, and in 2000 at Silstrup, Estrup and Slaeggerup (Table 1).

Table 1. Characteristics of the six PLAP sites (modified from Lindhardt *et al.,* 2001).

	Tylstrup	**Jyndevad**	**Silstrup**	**Estrup**	**Faardrup**	**Slaeggerup**
Location	Brønderslev	Tinglev	Thisted	Vejen	Slagelse	Roskilde
Precipitation 1) (mm/y)	668	858	866	862	558	585
Pot. evapotransp.1) (mm/y)	552	555	564	543	585	572
W x L (m)	70 x 166	135 x 184	91 x 185	105 x 120	150 x 160	130 x 165
Area (ha)	1.1	2.4	1.7	1.3	2.3	2.2
Tile drain	No	No	Yes	Yes	Yes	Yes
Monitoring initiated	May 1999	Sep 1999	Apr 2000	Apr 2000	Sep 1999	Apr 2000
Geological characteristics						
– 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 b.g.s.)	6	5–9	1.3	1–4 2)	1.5	0.7
– Depth to the reduced matrix (m b.g.s.)	>12	10–12	5	>5 2)	4.2	3.7
– Max. fracture depth 3) (m)	–	–	4	>6.5	8	4.7
– Fracture intensity 3–4 m depth (fractures m^{-1})	–	–	<1	11	4	11
– Ks in C horizon (m/s)	$2.0\cdot10^{-5}$	$1.3\cdot10^{-4}$	$3.4\cdot10^{-6}$	$8.0\cdot10^{-8}$	$7.2\cdot10^{-6}$	$3.1\cdot10^{-6}$
Topsoil characteristics						
– DK classification	JB2	JB1	JB7	JB5/6	JB5/6	JB7
– Classification	Loamy sand	Sand	Sandy clay loam/ sandy loam	Sandy loam	Sandy loam	Loam/ sandy loam
– Clay content (%)	6	5	18–26	10–20	14–15	20–24
– Silt content (%)	13	4	27	20–27	25	25–33
– Sand content (%)	78	88	8	50–65	57	41–54
– pH	4–4.5	5.6–6.2	6.7–7	6.5–7.8	6.4–6.6	6–6.3
– TOC (%)	2.0	1.8	2.2	1.7–7.3	1.4	1.4

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

2) Large variation within the field

3) Maximum fracture depth refers to the maximum fracture depth found in excavations and wells

Site characterization and monitoring design are described in detail in Lindhardt *et al.* (2001). This report presents the results of the monitoring period May 1999–June 2003. Results covering part of the monitoring period (May 1999–June 2002) have been published previously (Kjær *et al.*, 2002; Kjær *et al.*, 2003). The present report should therefore be seen as a continuation of the latter report, with the main focus on the last year of the monitoring period (July 2002–June 2003). For detailed description of the first part of the monitoring period (May 1999–June 2002), see Kjær *et al*. (2002) and Kjær *et al*. (2003).

Within the PLAP, the evaluation of pesticide leaching risk is based upon at least two years of monitoring data. For some pesticides the present report must be considered preliminary because they have been monitored for an insufficient period of time.

Hydrological modelling of the unsaturated zone at each PLAP site supports the monitoring data. The MACRO model (version 4.2) is used to describe the soil water dynamics at each site during the full monitoring period July 1999–June 2003. In addition, bromide transport is simulated at the two sandy sites Tylstrup and Jyndevad. The latest year of the monitoring period, July 2002–June 2003, is considered a validation period and no further model calibration has therefore been performed. The model set-up is thus identical to that reported in Kjær *et al.* (2003), although with the precipitation, evapotranspiration and plant data having been prolonged by one year.

Scientifically valid methods of analysis are essential for the integrity of the PLAP. The field monitoring work has therefore been supported by intensive quality assurance entailing continuous evaluation of the analyses employed. The quality assurance methodology and results are presented in Section 8.

2 Pesticide leaching at Tylstrup

2.1 Materials and methods

2.1.1 Site description and monitoring design

Tylstrup is located in northern Jutland (Figure 1). The test field covers a cultivated area of 1.1 ha (70 x 166 m) and is practically flat, with a windbreak 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 characterized as loamy sand with 6% clay and 2.0% total organic carbon (Table 1). The aquifer material consists of about 20 metres of marine sand sediment deposited in the Yoldia Sea. The southern part is rather homogeneous, consisting entirely of fine-grained sand, whereas the northern part is more heterogeneous due to the intrusion of several silt and clay lenses (Lindhardt *et al.,* 2001). During the monitoring period the groundwater table was 3–4.5 m b.g.s. The overall direction of groundwater flow was towards the west (Figure 2). A brief description of the sampling procedure is provided in Appendix 2. The monitoring design and test site are described in detail in Lindhardt *et al.* (2001) and the analysis methods in Kjær *et al.* (2002).

2.1.2 Agricultural management

Management practice during the two most recent growing seasons is briefly summarised below and detailed in Appendix 3 (Table A3.1). For information about management practice during the first two monitoring periods see Kjær *et al*. (2003).

The 2002 crop was winter rape (cv. Artus). Due to the rainy conditions in August 2001, sowing had to be postponed until the 3 September, more than 2 weeks later than normal. Clomazone was sprayed to combat weeds 2 days after sowing, i.e. before the crop emerged. On 16 October, when the crop had 4 unfolded leaves, weeds were sprayed with clopyralid (this substance was not included in the monitoring, however). Due to the unusually warm weather in October, the rape was well developed at the onset of winter. At the end of 2001, temperatures dropped below zero, and on 1 January the field was covered with approx. 15 cm of snow. At the beginning of January, temperatures rose above zero and on 8 January there was 1–2 cm of standing meltwater at both ends of the field. One week later, all of the water had infiltrated. The rape was fertilized once on the 22 March using commercial fertilizer. The crop was irrigated three times between 24 April and 31 May. The yield of rapeseed was just 26 hkg/ha at 91% dry mater, the low yield being attributable to the late sowing time.

On 19 September 2002 the field was sown with winter wheat (cv. Solist). On 9 October, when the crop had 2 unfolded leaves, weeds were sprayed with a mixture of prosulfocarb, ioxynil and bromoxynil. Prosulfocarb was not included in the monitoring programme, however. Potassium bromide tracer was applied on 27 May, the second application since the start of the monitoring program. On 8 May, when the first joint of the wheat was detectable, the herbicide fluroxypyr was applied. Seven days later, when the second joint was detectable, an additional herbicide, flamprop-M-isopropyl, was applied. The fungicide propiconazole was applied on 28 May and 17 June and the pesticide dimethoate was applied on 8 July. Irrigation was performed once on 24 June using 23 mm/ha. The yield of grain was disappointingly low – 54.5 hkg/ha (85% dry matter). In field trials conducted this year on sandy soils by the Danish Farmers association the average yield was 74.5 hkg/ha. The low yield at Tylstrup may be attributable to the local conditions. Considering the time of sowing, a plant density of 270 plants/m^2 was too low. Furthermore, due to heavy sand drift in the spring the plants suffered mechanical damage.

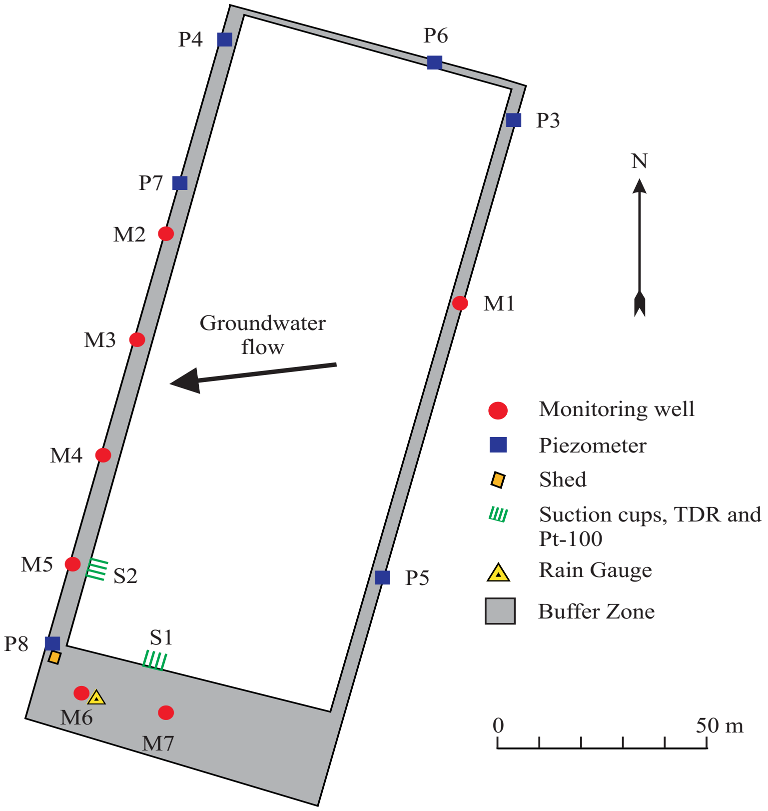

Figure 2. Overview of the Tylstrup test site. The innermost white area indicates the cultivated land, while the grey area indicates the surrounding buffer zone. The positions of the various installations are indicated, as is the direction of groundwater flow (by an arrow).

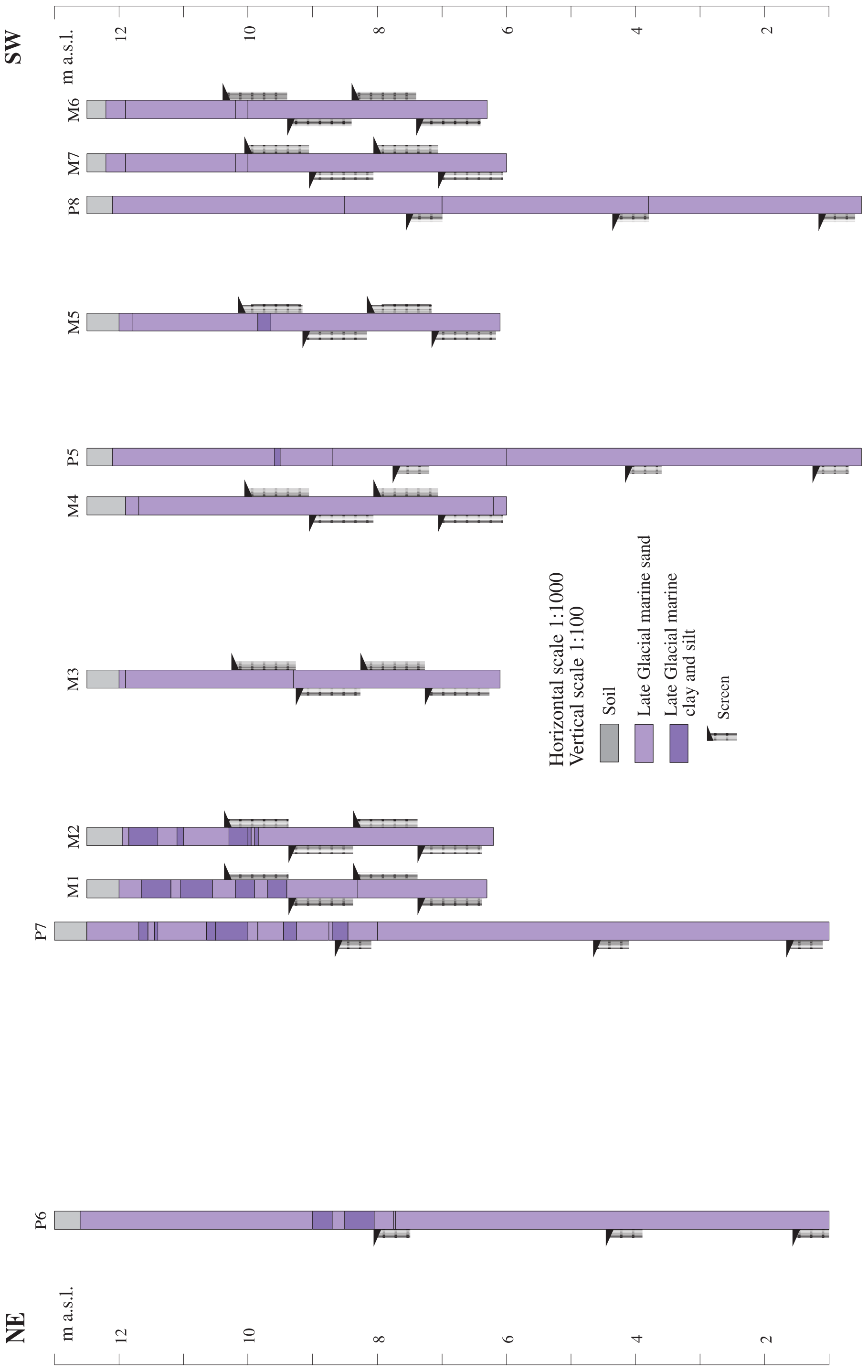

Figure 3. NE-SW cross section based on wells at the Tylstrup site (Lindhardt *et al.*, 2001). The location of the wells is indicated in Figure 2.

2.1.3 Model set-up and calibration

The MACRO model is applied to the Tylstrup site covering the soil profile to a depth of 5 m b.g.s., always including the groundwater table. The model is used to simulate water and bromide transport in the unsaturated zone during the full monitoring period May 1999–June 2003 and to establish an annual water balance.

For the simulation period May 1999–June 2002 the model was calibrated to the observed groundwater table measured in the piezometers located in the buffer zone, as well as to measured time series of soil water content at three different depths (25, 60 and 110 cm b.g.s.) from the two profiles S1 and S2 (see Figure 2) and to the bromide concentration measured in the suction cups located 1 and 2 m b.g.s. The latest year of the monitoring period, July 2002–June 2003, is considered a validation period and no further model calibration has therefore been performed. The model set-up is thus identical to that reported in Kjær *et al.* (2003), although with the precipitation, evapotranspiration and plant data having been prolonged by one year. For a detailed description of data acquisition, model set-up and calibration procedures see Kjær *et al.* (2002) and (2003).

2.2 Results and discussion

2.2.1 Soil water dynamics and water balances

In general the model validation shows that the latest model simulations, July 2002–June 2003, are consistent with the observed data, thus indicating a good model description of the overall soil water dynamics in the unsaturated zone. As for previous years (Kjær *et al.*, 2003), the model provides a good simulation of the measured fluctuations in the groundwater table (Figure 4B). The dynamics is captured, whereas the amplitude of the fluctuations is less well described. The overall trends in soil water content are modelled successfully, with the model capturing soil water dynamics at all depths (Figure 4C-E).

The resulting annual water balance is shown for each monitoring period (July–June) in Table 2. Precipitation in the latest monitoring year, July 2002–June 2003, was greater than “normal”, as was the case at Tylstrup in the previous four years. Precipitation in summer 2002 was particularly high (Appendix 4), resulting in continuous percolation 1 m b.g.s. throughout the latest monitoring period and percolation peaks of up till 10 mm/d during the summer. Precipitation was lower than normal during the period December to March, which is reflected in a lower than normal groundwater table for this time of the year as well as in low percolation. The annual water balance for the latest monitoring period is similar to that for the monitoring period July 2000–June 2001, although the lower irrigation is reflected in lower groundwater recharge. For information about the water balance in previous monitoring periods see Kjær *et al.* (2003).

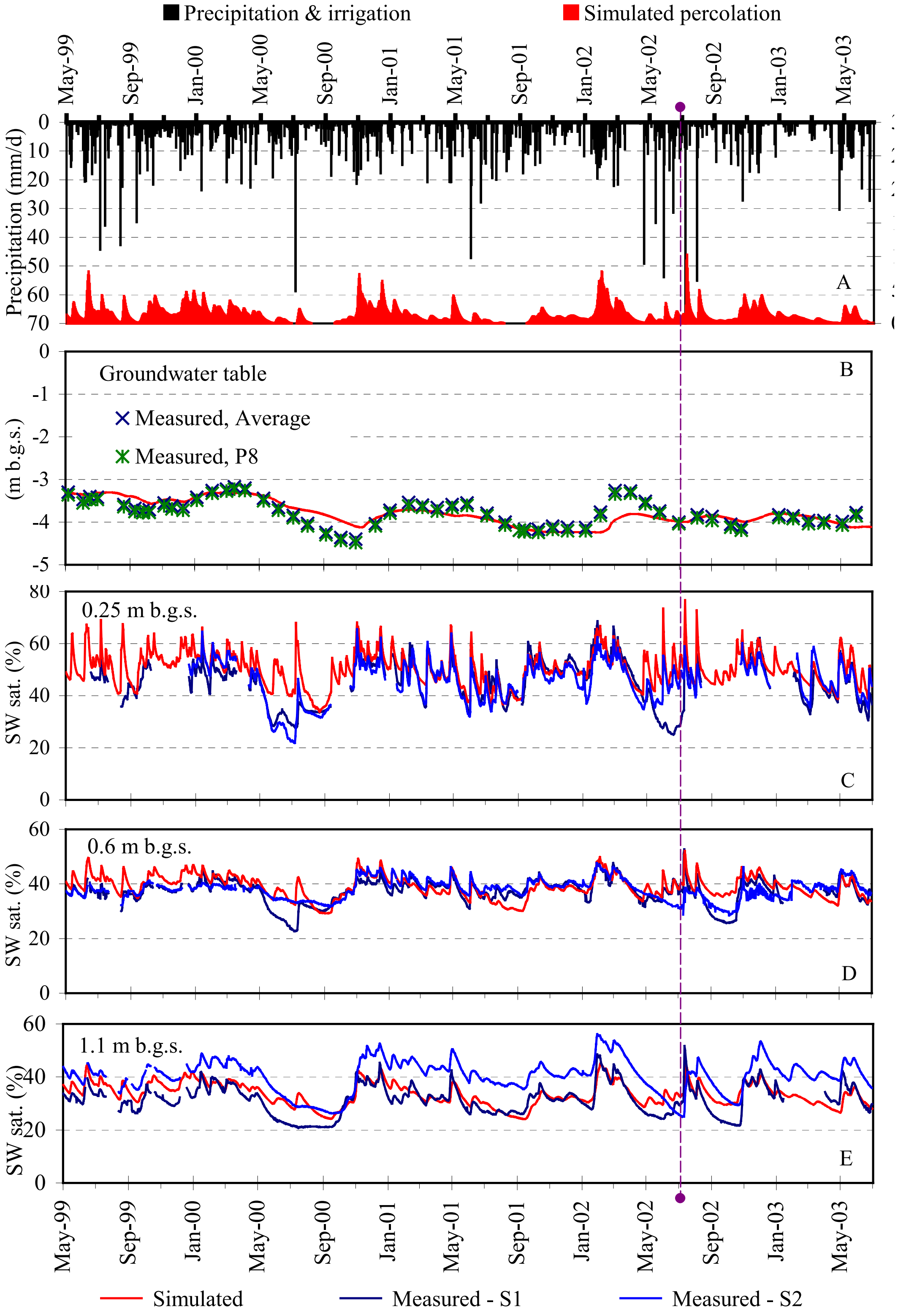

Figure 4. Soil water dynamics at Tylstrup: Measured precipitation, irrigation and simulated percolation 1 m b.g.s. (A), simulated and measured groundwater level (B), and simulated and measured soil water saturation (SW sat.) at three different soil depths (C, D and E). The measured data in B derive from piezometers located in the buffer zone. The measured data in C, D and E derive from TDR probes installed at S1 and S2 (Figure 2). The broken vertical line indicates the beginning of the validation period (July 2002–June 2003).

Table 2. Annual water balance for Tylstrup (mm/y). Precipitation is corrected to the soil surface according to the method of Allerup and Madsen (1979).

	Normal precipitation [2)]	Precipitation	Irrigation	Actual evapotranspiration	Groundwater recharge [3)]
1.5.99–30.6.99 [1)]	120	269	0	124	145
1.7.99–30.6.00	773	1073	33	511	595
1.7.00–30.6.01	773	891	75	486	480
1.7.01–30.6.02	773	906	80	550	436
1.7.02–30.6.03	773	895	23	485	433

[1)] *Accumulated for a two-month period*

[2)] *Normal values based on time series for 1961–1990*

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

2.2.2 Bromide leaching

Bromide has now been applied twice at Tylstrup. The bromide concentrations shown in Figure 5 and Figure 6 relate to the bromide applied in autumn 1999, as described further in Kjær *et al.* (2003). Leaching of the bromide applied in March 2003 will be evaluated in due course as the results become available.

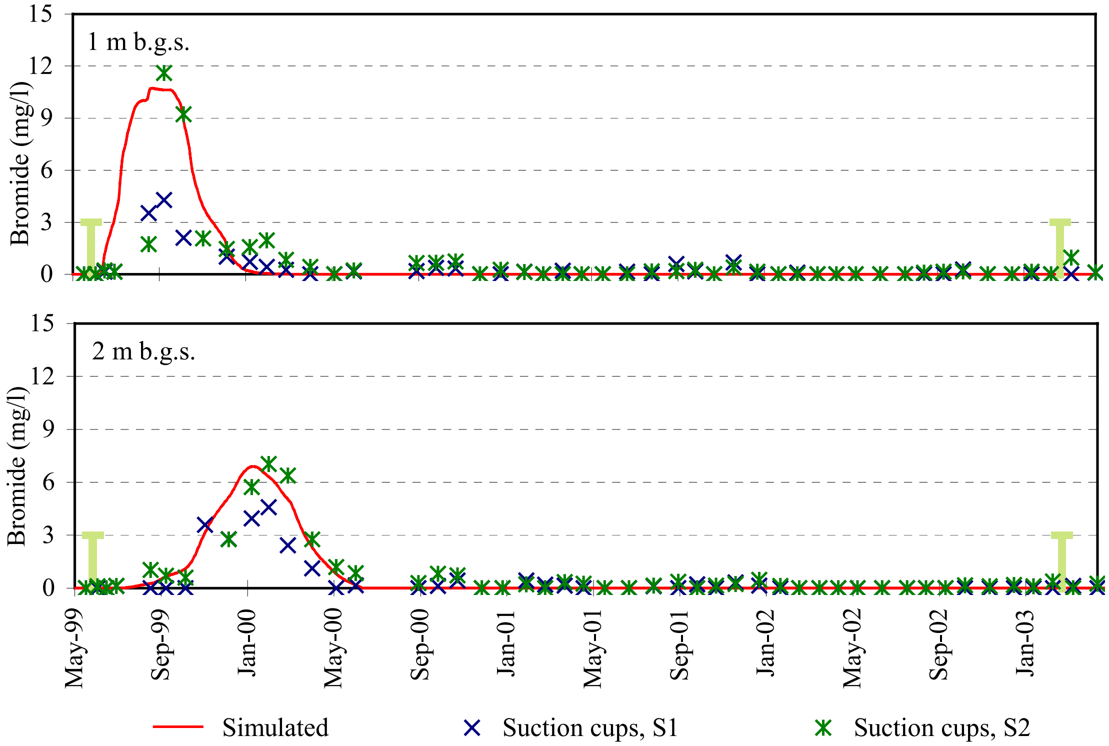

Figure 5. Simulated and measured bromide concentration in the unsaturated zone at Tylstrup. The measured data derive from suction cups installed 1 m b.g.s. and 2 m b.g.s. at locations S1 and S2 indicated in Figure 2. The green vertical lines indicate the dates of bromide application.

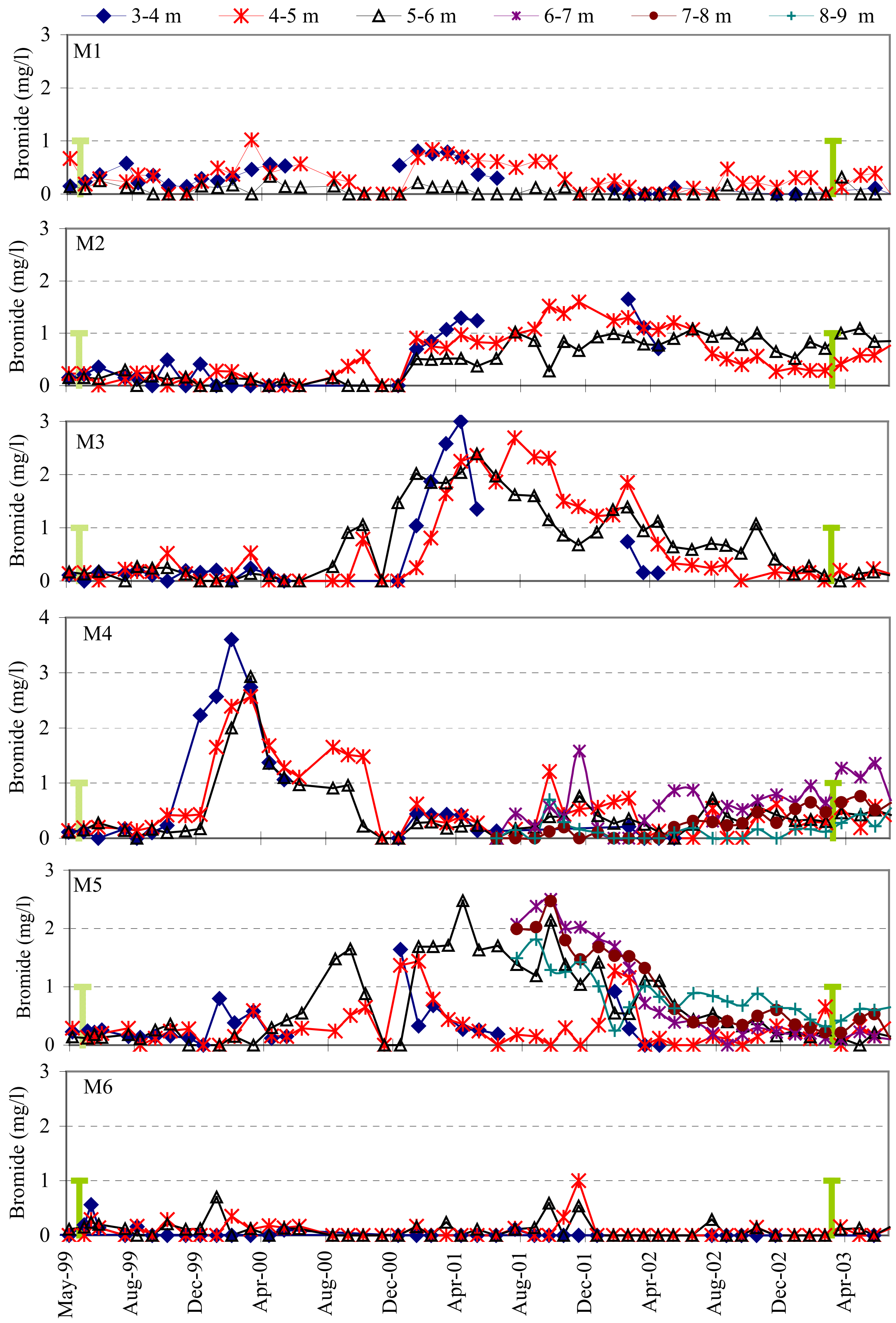

Figure 6. Bromide concentration in the groundwater at Tylstrup. The data derive from monitoring wells M1–M7. Screen depth is indicated in m b.g.s. The green vertical lines indicate the dates of bromide application.

2.2.3 Pesticide leaching

The monitoring at Tylstrup encompassed 11 different pesticides and several degradation products applied throughout four growing seasons, as indicated in Table 3, Figure 7 and Figure 8. It should be noted that precipitation in Table 3 is corrected to the soil surface according to Allerup and Madsen (1979), whereas percolation (1 m b.g.s.) refers to accumulated percolation as simulated with the MACRO model. It should also be noted that as mancozeb (applied here as Dithane DG) and tribenuron methyl (applied here as Express) degrade rapidly, the leaching risk is more associated with their respective degradation products, ETU and triazinamin-methyl. For the same reasons it is the degradation products and not the parent compounds that are monitored in the PLAP (Table 3). Pesticides applied later than April 2003 are not evaluated in this report and hence are not included in Table 3.

Table 3. Pesticides analysed at Tylstrup with the products used shown in parentheses. Degradation products are in italics. Precipitation (prec.) and percolation (perc.) are accumulated from date of first application until the end of monitoring . 1st month perc. refers to accumulated percolation within the first month after the application. C_{mean} refers to average leachate concentration at 1 m b.g.s. the first year after application. The number of pesticide-positive samples is indicated in parentheses.

Crop and analysed pesticides	Application date	End of Monitoring	Prec. (mm)	Perc. (mm)	1st month perc. (mm)	C_{mean} (µg/l)
Potatoes 1999						
Linuron (Afalon)	May 99	Jul 01	2527	1208	81	<0.01 (0)
- *ETU* (Dithane DG)	Jun 99	Oct 01	2358	1129	66	<0.01(9)
Metribuzin (Sencor WG)	Jun 99	Jul 03	4177	2083	80	<0.01 (3)
- metribuzin-diketo						0.05-0.36 (505)
- metribuzin-desamino						<0.02 (0)
- metribuzin-desamino-diketo						0.14-0.97 (305)
Spring barley 2000						
Triasulfuron (Logran 20 WG)	May 00	Apr 03	2717	1299	7	<0.02 (0)
- triazinamin						<0.02 (0)
Propiconazole (Tilt Top)	Jun 00	Jul 03	2902	1353	13	<0.01 (0)
Fenpropimorph (Tilt Top)	Jun 00	Jul 03	2902	1353	13	<0.01 (0)
- fenpropimorphic acid						<0.02 (0)
Pirimicarb (Pirimor G)	Jun 00	Apr 03	2599	1282	19	<0.01 (0)
- pirimicarb-desmethyl						<0.02 (0)
- pirimicarb-desmethyl-formamido						<0.02 (0)
Winter rye 2001						
Pendimethalin (Stomp SC)	Nov 00	Apr 03	2248	1231	114	<0.01 (0)
Triazinamin-methyl2) (Express)	Nov 00	Apr 03	2248	1231	114	<0.02 (0)
Propiconazole (Tilt Top)	May 01	Jul 03	2101	923	18	<0.01 (0)
Fenpropimorph (Tilt Top)	May 01	Jul 03	2101	923	18	<0.01 (0)
- fenpropimorphic acid						<0.01 (0)
Winter rape 2002						
Clomazone (Command CS)	Sep 01	Jul 03†	1752	889	13	<0.01 (0)
- propanamide-clomazone						<0.02 (0)
Winter wheat 2003						
Bromoxynil (Oxitril CM)	Oct 02	Jul 03†	1641	871	41	<0.01 (0)
Ioxynil (Oxitril CM)	Oct 02	Jul 03†	1641	871	41	<0.01(0)

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

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

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

†) Monitoring will continue during the following year. The values for prec. and perc. are accumulated up to July 2003

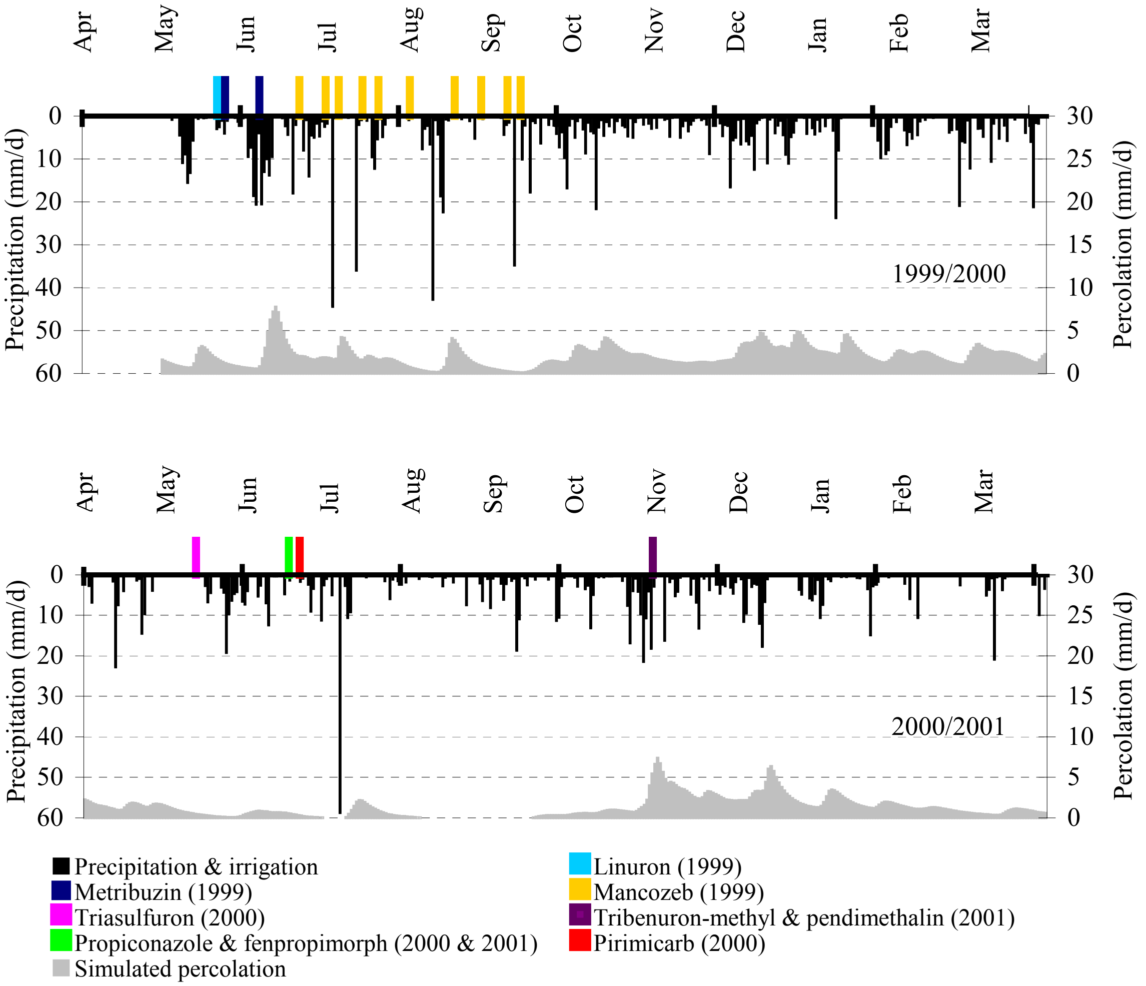

Figure 7. Pesticide application, precipitation and irrigation (primary axis) together with simulated percolation 1 m b.g.s. (secondary axis) at Tylstrup in 1999/2000 (upper) and 2000/2001 (lower). As mancozeb and tribenuron methyl degrade rapidly it is their respective degradation products, ETU and triazinamin-methyl, that are monitored.

The leaching risk of **clomazone** applied in 2002 will not be evaluated until the 2004 monitoring results become available, i.e. when two years of monitoring data have been collated. It should be noted, though, that neither clomazone nor its degradation product clomazone-propanamide have yet been detected in any of the water samples analysed.

The leaching risk of the pesticides applied to the 2001 winter rye crop e.g. ***pendimethalin***, ***triazinamin-methyl*** (degradation product of tribenuron methyl), ***propiconazole*** and ***fenpropimorph*** was found to be negligible at the Tylstrup site. Thus none of these pesticides or their degradation products listed in Table 3 were detected in any of the water samples analysed. The leaching risk of pendimethalin, triazinamin-methyl should be viewed in relation to the late autumn application, with percolation reaching 114 mm (Table 3) within the first month after application. In contrast, propiconazole and fenpropimorph were applied during spring/summer 2001. Despite June being wetter than normal, precipitation input was almost counterbalanced by actual evapotranspiration such that only 18 mm percolated during the first month after pesticide application (Table 3 and Figure 8).

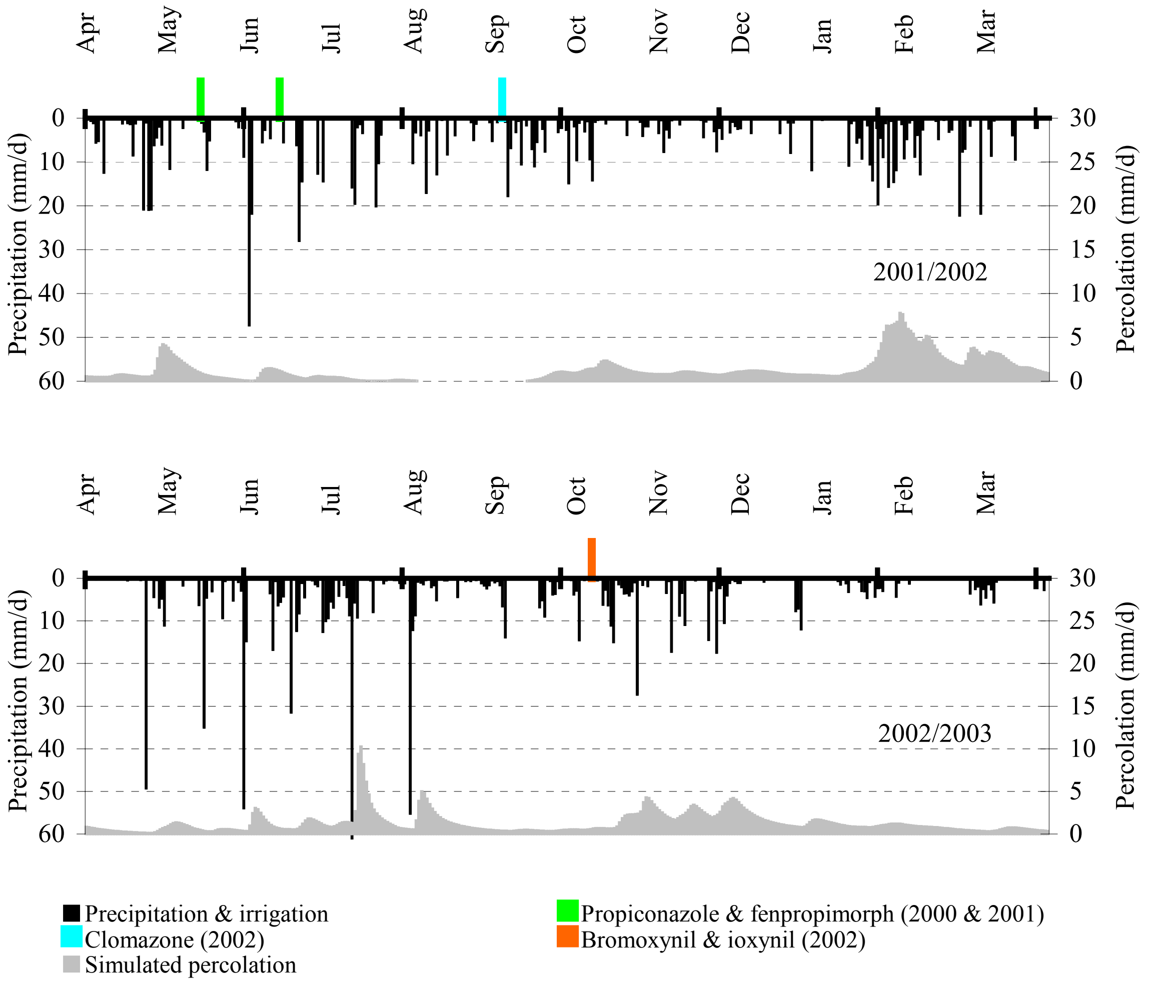

Figure 8. Pesticide application, precipitation and irrigation (primary axis) together with simulated percolation 1 m b.g.s. (secondary axis) at Tylstrup in 2001/2002 (upper) and 2002/2003 (lower).

The leaching risk of pesticides applied during 1999 and 2000 has already been evaluated in Kjær *et al.* (2002) and Kjær *et al.* (2003). The findings regarding the degradation products of metribuzin, which are still included in the monitoring programme, are briefly summarized below, however:

Metribuzin was only detected in three water samples in concentrations of 0.01–0.02 µg/l. However, two degradation products of metribuzin (***metribuzin-desamino-diketo*** and ***metribuzin-diketo***) leached from the root zone (1 m b.g.s.) in average concentrations exceeding 0.1 µg/l. Leaching was most pronounced with metribuzin-desamino-diketo, reaching an annual, average concentration of 0.9 µg/l in suction cups at S1. Metribuzin-diketo also leached, in this case reaching an average concentration of 0.3 µg/l. Both compounds were characterised by continuous leaching over a long period of time. Average concentrations exceeding 0.1 µg/l were detected as long as three years after application. Over the 4-year period as much as 2.2–3.8% and 0.96–1.5% of the applied dosage leached as metribuzin-desamino-diketo and metribuzin-diketo, respectively (Table 4 and Figure 9). The fact that root zone leaching (1 m b.g.s.) occurred as long as four year after the latest application may indicate that the compounds can be retained within the soil and gradually released over a very long period of time. The possibility thus cannot be excluded that applica-

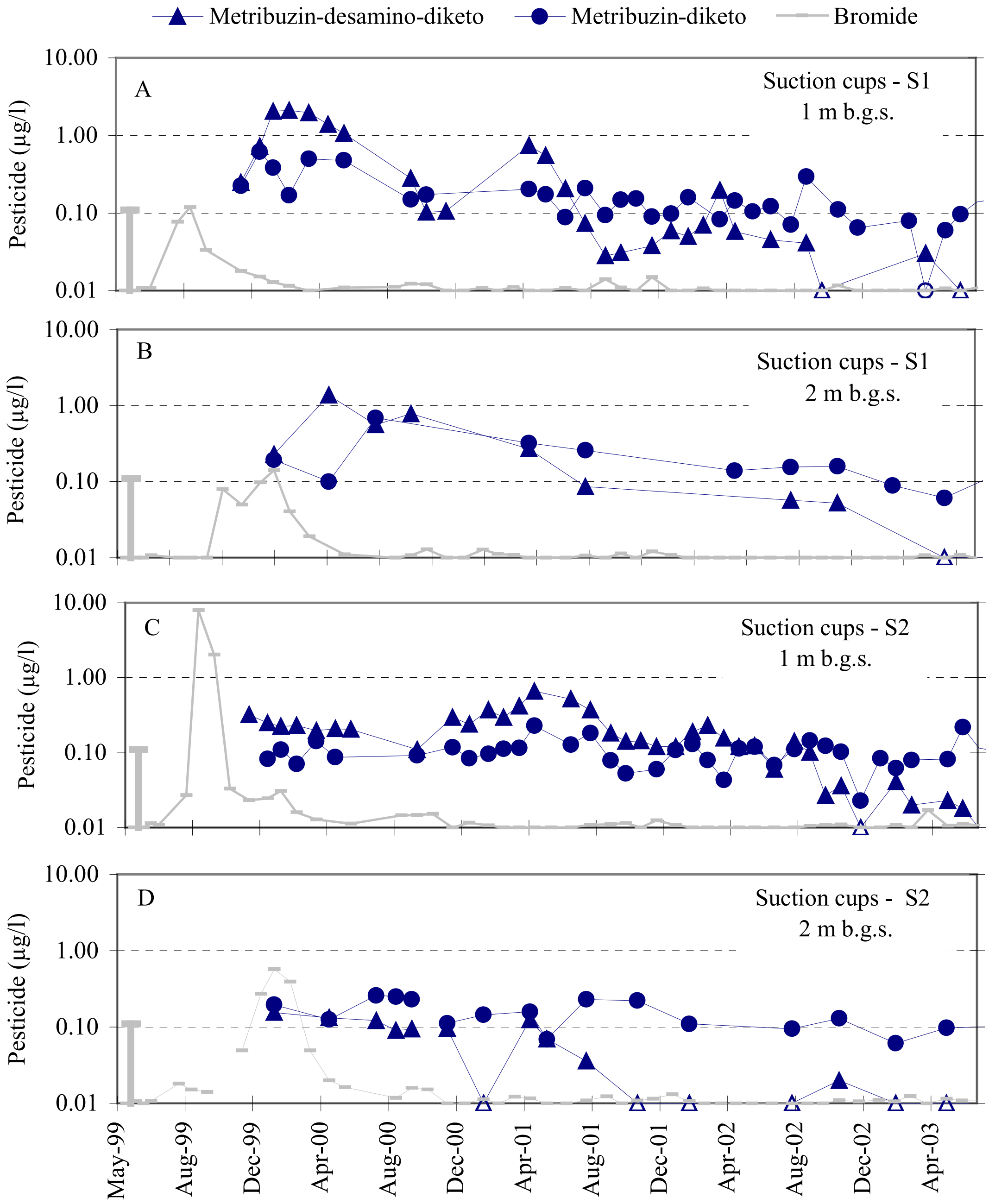

Figure 9. Bromide and pesticide concentrations in the unsaturated zone at Tylstrup. The measured data derive from suction cups installed 1 m b.g.s. and 2 m b.g.s. at locations S1 and S2 indicated in Figure 2. The grey vertical line indicates the date of bromide application. Samples with pesticides concentrations below the detection limit of 0.02 µg/l are indicated by open circles and triangles.

tions prior to the initiation of the PLAP programme may have contributed to the observed root zone leaching. The average concentration of pesticides (Table 4) was estimated using the measured pesticide concentration and estimated percolation on a monthly basis. Measured pesticide concentrations were thus assumed to be representative for each sample period, and accumulated percolation rates calculated using the MACRO model were assumed to be representative for both suction cups S1 and S2. It should also be noted that for some years the average concentration is given as a range due to the high level of uncertainty that characterized some of the analyses. The primary data and further information concerning the calculation methods are given in Appendix 5.

Table 4. Estimated average concentration (µg/l) of metribuzin-desamino-diketo and metribuzin-diketo 1 m b.g.s. at Tylstrup. Leached mass refers to the total mass (% of applied metribuzin) leached during the entire monitoring period (1.7.99–30.6.03). The primary data and calculation methods are detailed in Appendix 5.

	Metribuzin-desamino-diketo		Metribuzin-diketo	
	Suction cup – S1	Suction cup – S2	Suction cup – S1	Suction cup – S2
1.7.99–30.6.00	0.87-0.97	0.19-0.31	0.26–0.36	0.05–0.11
1.7.00–30.6.01	0.33	0.33	0.13-0.23	0.12
1.7.01–30.6.02	0.06	0.19	0.11-0.13	0.09
1.7.02–30.6.03	<0.05	0.04- 0.05	0.073-0.087	0.08
Leached mass[1)]	3.8-4.2%	1.8-2.2%	1.5-2.0%	0.8-0.9%

[1)] *Expressed as metribuzin equivalent. The discrepancy between this data and the data in last year's report is due to a printing error in that report.*

In the saturated zone, elevated concentrations of metribuzin-diketo were detected in M1, M3 and M4, while the pesticide concentration in the other wells (M5, M6) could not be distinguished from the background level (Figure 10–Figure 13). As previously reported, pesticide application prior to the monitoring period must thus have resulted in marked groundwater contamination with the degradation products of metribuzin (Kjær *et al.,* 2002; Kjær *et al.,* 2003). The high background concentration found in all monitoring wells makes it difficult to determine whether the elevated concentrations observed in downstream monitoring wells are due to the metribuzin applied during the PLAP or to metribuzin applied on the test site or on the "upstream" fields prior to the PLAP. Consequently, it is not possible to fully verify the impact of the metribuzin applied during the PLAP on the quality of the groundwater. The leaching patterns illustrated in Figure 10–Figure 13 are discussed in Kjær *et al.* (2002) and Kjær *et al.* (2003).

It should be noted, though, that the average concentration of metribuzin-diketo in the Tylstrup groundwater was 0.15 µg/l, and that the average concentration exceeded the maximum allowable concentration (0.1 µg/l) at 76% of the screens analysed. Metribuzin-desamino-diketo was also detected in 48% of the analysed groundwater samples. Apart from three samples from monitoring well M1 (Figure 10C), the concentration never exceeded 0.1 µg/l.

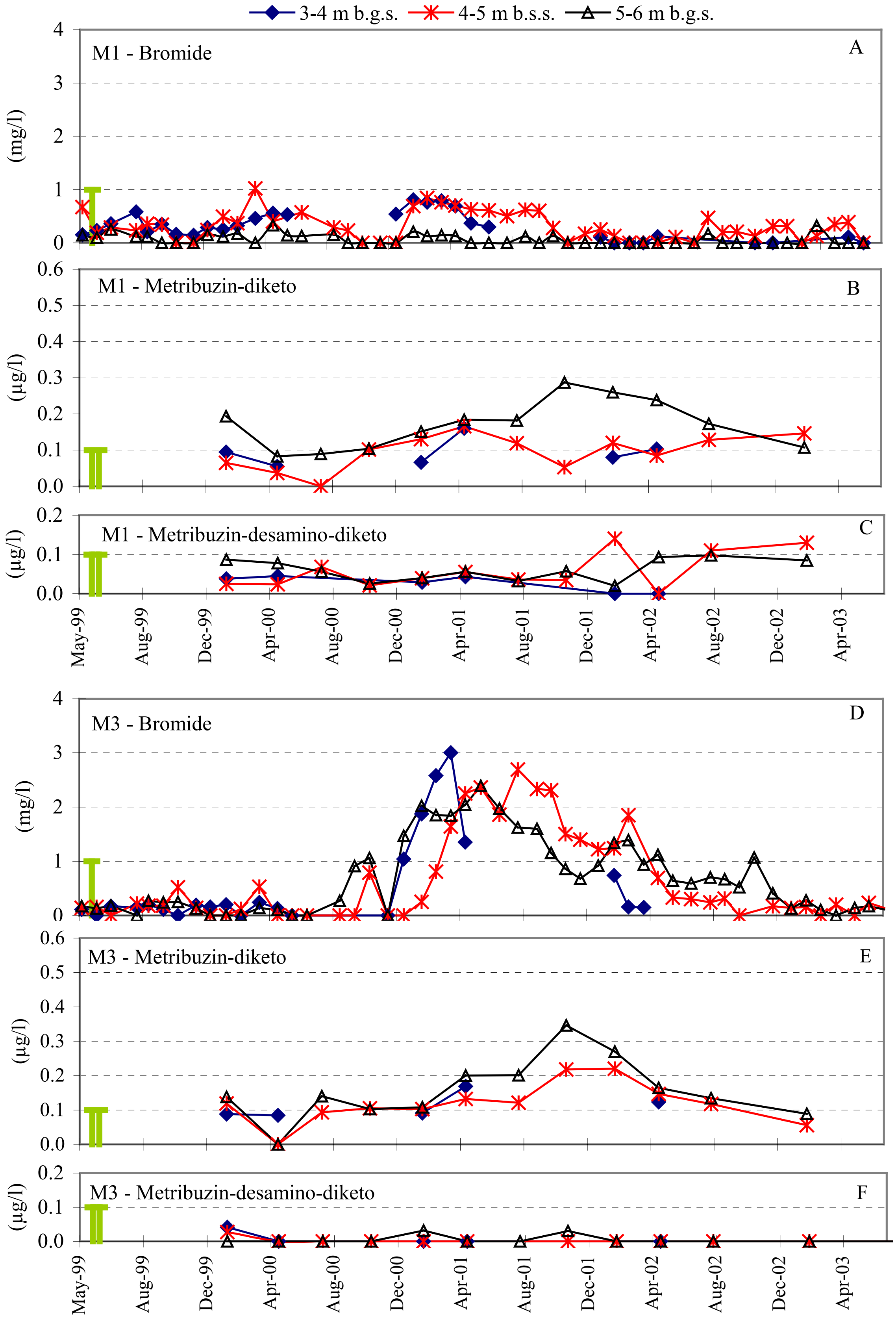

Figure 10. Bromide and pesticide concentrations in the groundwater at Tylstrup. The data derive from monitoring wells M1 (A,B,C) and M3 (D,E,F). Screen depth is indicated in m b.g.s. The green vertical lines indicate the dates of application.

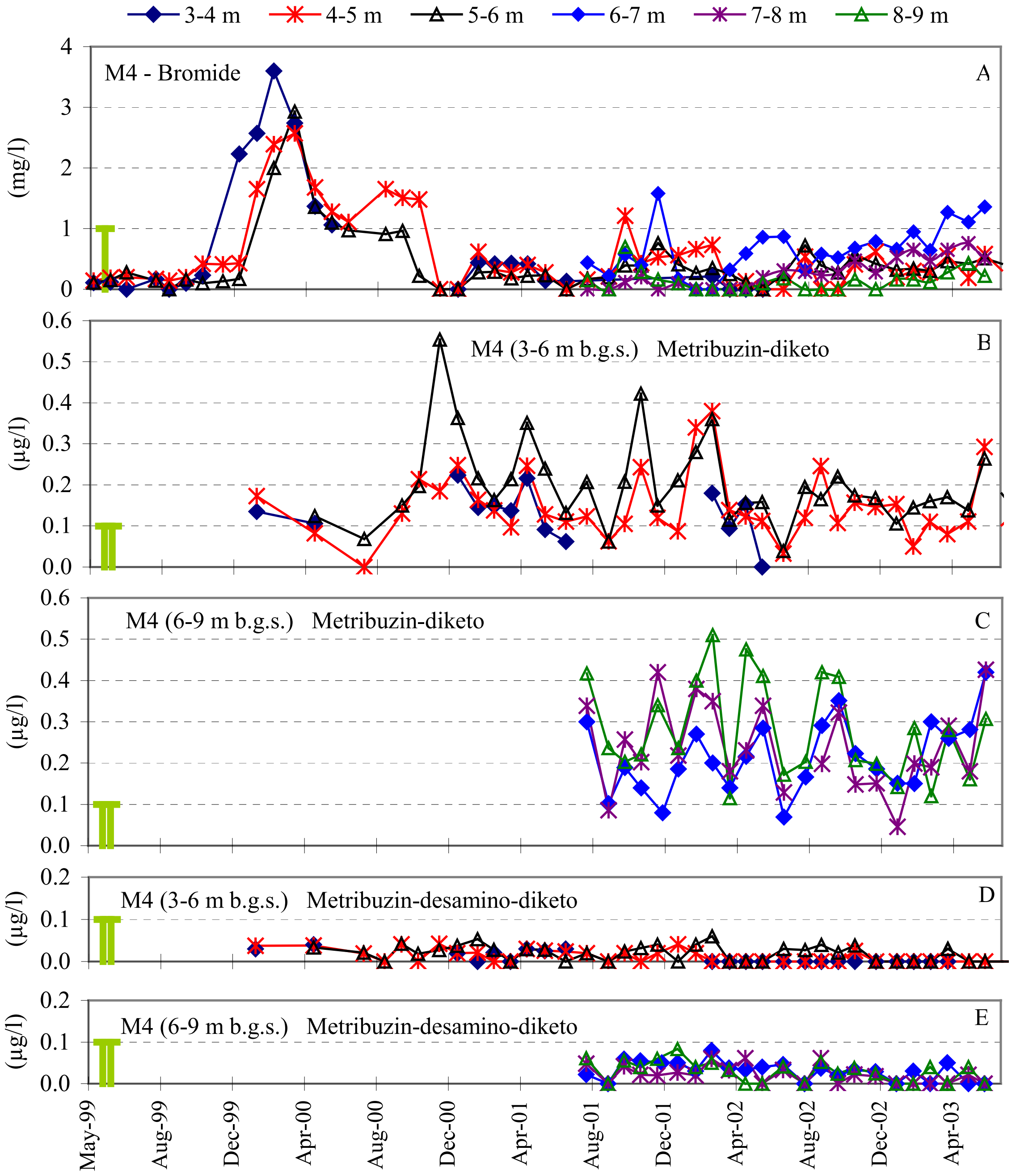

Figure 11. Bromide and pesticide concentrations in the groundwater at Tylstrup. The data derive from monitoring well M4. Screen depth is indicated in m b.g.s. The green vertical lines indicate the dates of application.

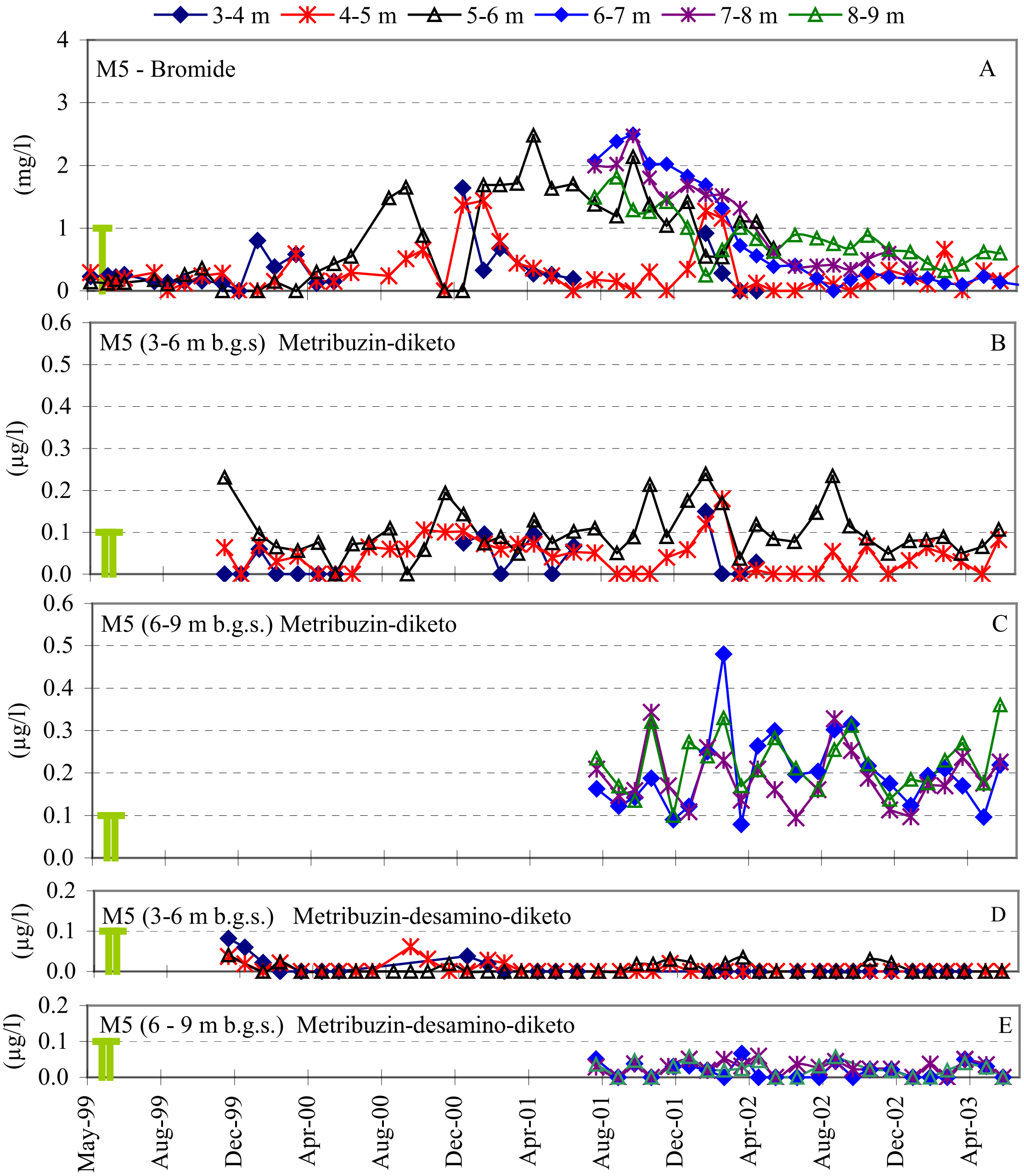

Figure 12. Bromide and pesticide concentrations in the groundwater at Tylstrup. The data derive from monitoring well M5. Screen depth is indicated in m b.g.s. The green vertical lines indicate the dates of application.

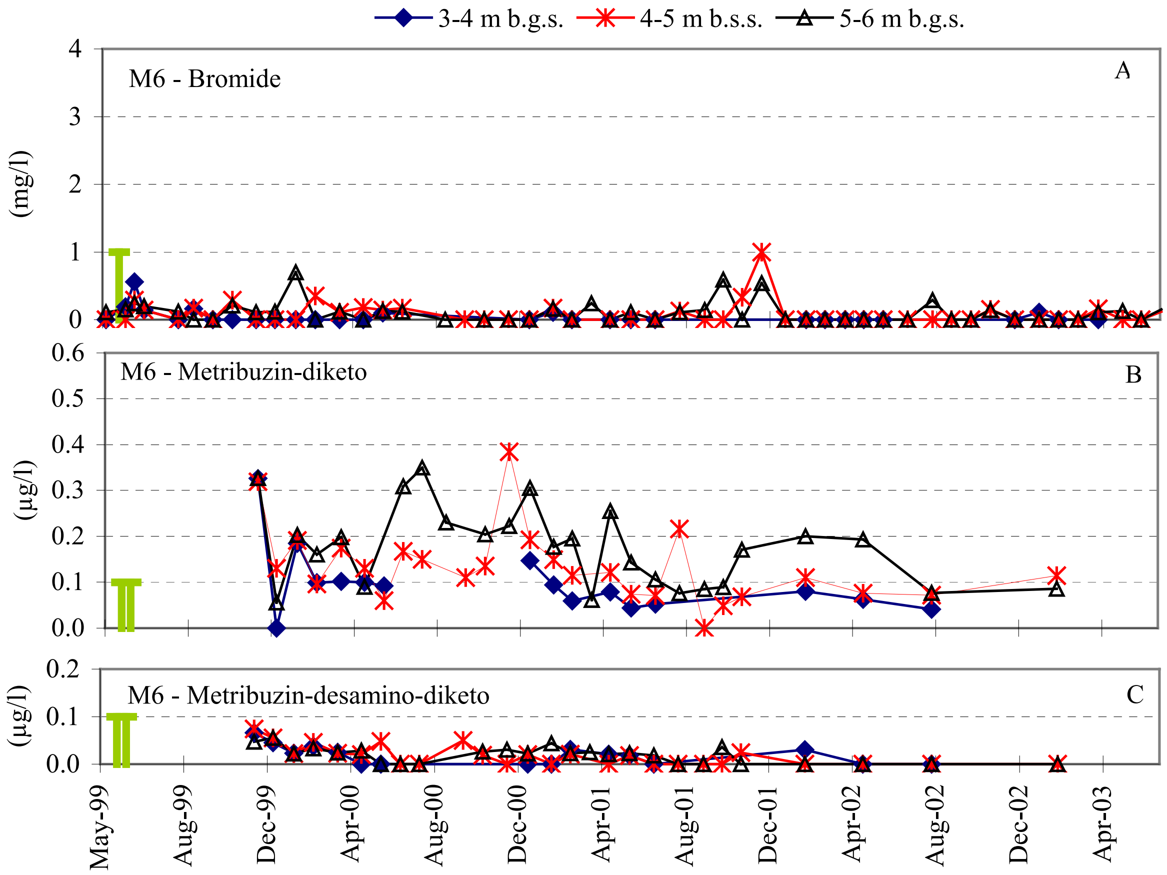

Figure 13. Bromide and pesticide concentrations in the groundwater at Tylstrup. The data derive from monitoring well M6. Screen depth is indicated in m b.g.s. The green vertical lines indicate the dates of application.

Figure 14 illustrates that the concentration of the two metabolites varies as a function of increasing depth. The median concentrations were estimated applying a concentration of half the detection limit for those samples in which the concentration was below the detection limit, as suggested by Standers (1994). When evaluating Figure 14 it should be kept in mind that data from 1 and 2 m b.g.s. refer to suction cups located in the unsaturated zone, whereas data from 3.5–9.5 refers to the monitoring screen located in the saturated zone. While the water sampled 1–2 m b.g.s. represents water infiltrated at the test site, the water sampled 3.5–9.5 m b.g.s. represents a mixture of water infiltrated at the actual test site and at the fields situated upstream of the test site. Water sampled in the deepest screens thus tends to represent water infiltrated at more distant areas. The marked contamination of metribuzin-diketo observed in these deepest screens is thus presumably due to previous application of metribuzin at more distant locations upstream of the test site.

With metribuzin-diketo, the concentration level in the unsaturated zone (1–2 m b.g.s.) was somewhat similar to that found in the uppermost groundwater (3–5 m b.g.s.). Thereafter the concentration level increased with increasing depth, and all samples from the deepest screen located 8–9 m b.g.s. contained more than 0.1 µg/l metribuzin-diketo. Metribuzin-desamino-diketo showed a reverse concentration pattern. In the root zone (1 m b.g.s.), leaching of

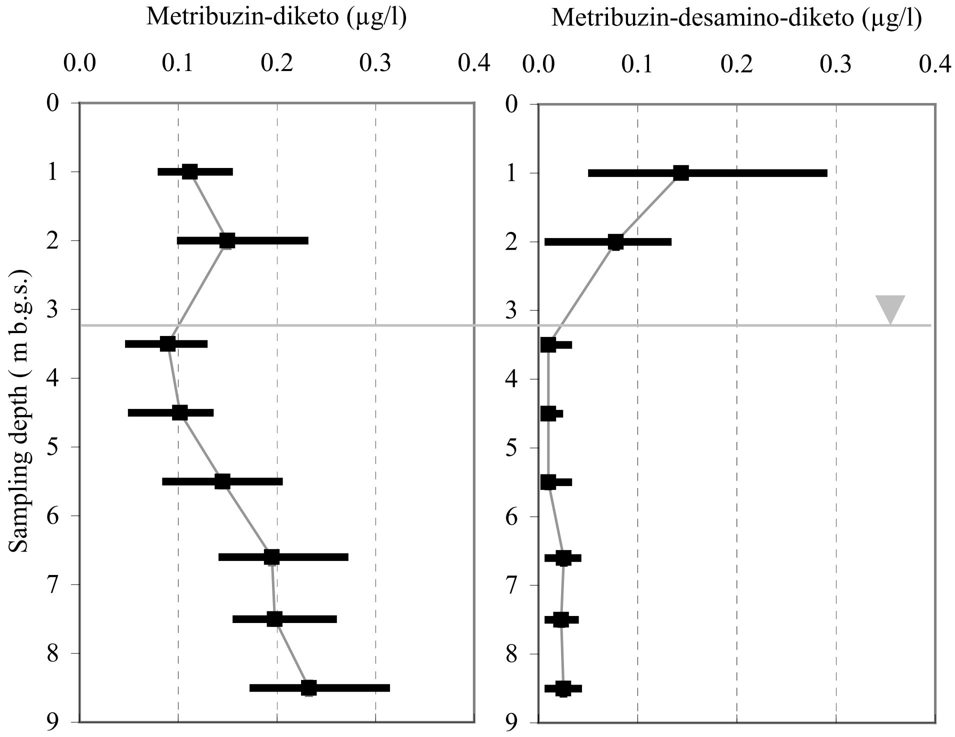

Figure 14. Median concentration of metribuzin-diketo and metribuzin-desamino-diketo as a function of sampling depth. 25% and 75% quartiles are indicated by error bars. The grey horizontal line indicates approximate position of the groundwater table. Data from 1 and 2 m b.g.s. refer to suction cups located in the unsaturated zone, whereas data from 3.5–9.5 m b.g.s. refer to the monitoring screens located in the saturated zone. The data cover the period 08.12.99–30.06.03 with the sampling frequency detailed in Appendix 2.

metribuzin-desamino-diketo was higher than that of metribuzin-diketo. Unlike with metribuzin-diketo, however, the concentration decreased down through the unsaturated zone with the concentration in the groundwater being markedly lower than in the unsaturated zone.

That root zone leaching (1 m b.g.s.) of metribuzin-desamino-diketo was higher than that of metribuzin-diketo is in accordance with Henriksen *et al.* (2004) who evaluated the sorption and degradation of metribuzin and its metabolites in Tylstrup soil by means of batch experiments. In the top soil, Henriksen *et al.* (2004) found that the leaching risk was higher with metribuzin-desamino-diketo than metribuzin-diketo because 1) The mobility of metribuzin-desamino-diketo was higher than that of metribuzin-diketo and 2) The amount of metribuzin-desamino-diketo produced during degradation of metribuzin was markedly higher than that of metribuzin-diketo as metribuzin-desamino-diketo is formed by both the metribuzin-diketo and the metribuzin-desamino degradation pathways (Figure 15). The supposition that metribuzin-desamino-diketo is more mobile than metribuzin-diketo is also supported by a lysimeter study of Bowman (1991) in a sandy soil.

That the concentration of metribuzin-desamino-diketo decreases down through the unsaturated zone while that of metribuzin-diketo remained more constant could be attributable to different sorption characteristics in the subsoil. Henriksen *et al.* (2004) thus found that

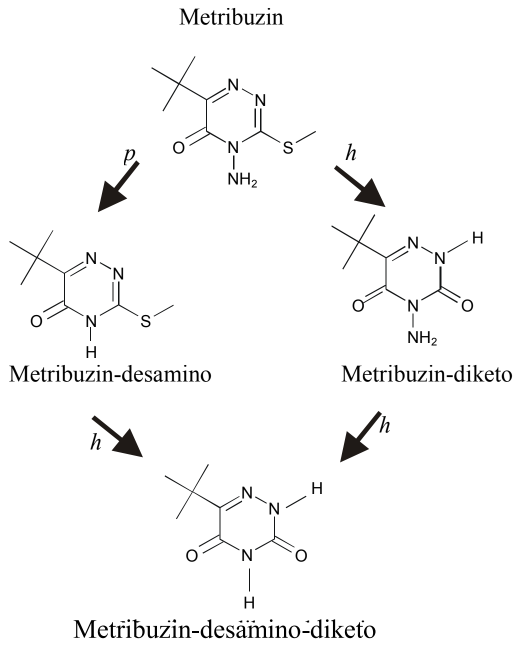

Figure 15. Metribuzin degradation pathways involving hydrolysis (h) and photodegradation (p).

sorption of metribuzin-desamino-diketo was minor in subsoil, while that of metribuzin-diketo was negligible. Moreover, neither of the two compounds was found to degrade in the subsoil. Thus once metribuzin-desamino-diketo and metribuzin-diketo have reached the subsoil, further degradation is unlikely. During movement through the subsoil metribuzin-desamino-diketo could therefore be retained longer, thus allowing metribuzin-diketo to reach the groundwater in a higher content and prior to metribuzin-desamino-diketo (Henriksen *et al.,* 2004).

Metribuzin-desamino was not detected in any of the water samples (Table 3). According to Henriksen *et al.* (2004), metribuzin-desamino is presumably retained in the topsoil, where sorption and degradation to metribuzin-desamino-diketo prevents it from leaching.

3 Pesticide leaching at Jyndevad

3.1 Materials and methods

3.1.1 Site description and monitoring design

Jyndevad is located in southern Jutland (Figure 1). The test site covers a cultivated area of 2.4 ha (135 x 184 m) and is practically flat. A windbreak borders the eastern side of the test site. The area has a shallow groundwater table ranging from 1 to 2 m b.g.s. The overall direction of groundwater flow is towards northwest (Figure 16). The soil can be classified as Arenic Eutrudept and Humic Psammentic Dystrudept (Soil Survey Staff, 1999) with coarse sand as the dominant texture class and topsoil containing 5% clay and 1.8% total organic carbon (Table 1). The geological description points to a rather homogeneous aquifer of meltwater sand, with local occurrence of thin clay and silt beds (Figure 17). A brief description of the sampling procedure is provided in Appendix 2. The monitoring design and test site are described in detail in Lindhardt *et al.* (2001) and the analysis methods in Kjær *et al.* (2002).

3.1.2 Agricultural management

Management practice during the two most recent growing seasons is briefly summarised below and detailed in Appendix 3 (Table A3.2). For information about management practice during the first two monitoring periods see Kjær *et al*. (2003).

The 2002 crop was potato (cv. Oleva) for starch production sown on 22 April. Before the potatoes emerged the field was treated with metribuzin to combat weeds on 13 May. Weeds were sprayed with rimsulfuron on 23 May, at which time the potatoes had just emerged. The field was irrigated with 20 mm/ha on 13 June and 25 mm on 12 August. Fungicide spraying was carried out 10 times between 18 June and 20 August, each time using fluazinam at a rate of 0.2 l Shirlan/ha. The potatoes were harvested on 24 September with a tuber yield of 515.8 hkg/ha, equivalent to 118.8 hkg/ha (100% dry matter) and slightly less than the average for that year. It should be noted that neither metribuzin nor fluazinam are included in the monitoring programme. Prior to the sowing of spring barley (cv. Otira) on 9 April 2003, potassium bromide tracer was applied on 12 March. The bromide application was the second since the monitoring program began. On 6 May, when 2 leaves had unfolded, the barley was sprayed with the herbicide metsulfuron-methyl. MCPA was applied on 3 June. Metsulfuron-methyl was not monitored, however. On 6 June , when the second joint was detectable, the fungicide propiconazole was used. The crop was irrigated once on 8 June using 26 mm/ha. On 25 June the fungicide propiconazole and the pesticide dimethoate were applied in combination. The barley was harvested on 4 August with a grain yield of 73.3 hkg/ha (85% dry matter), which was about the average for the year.

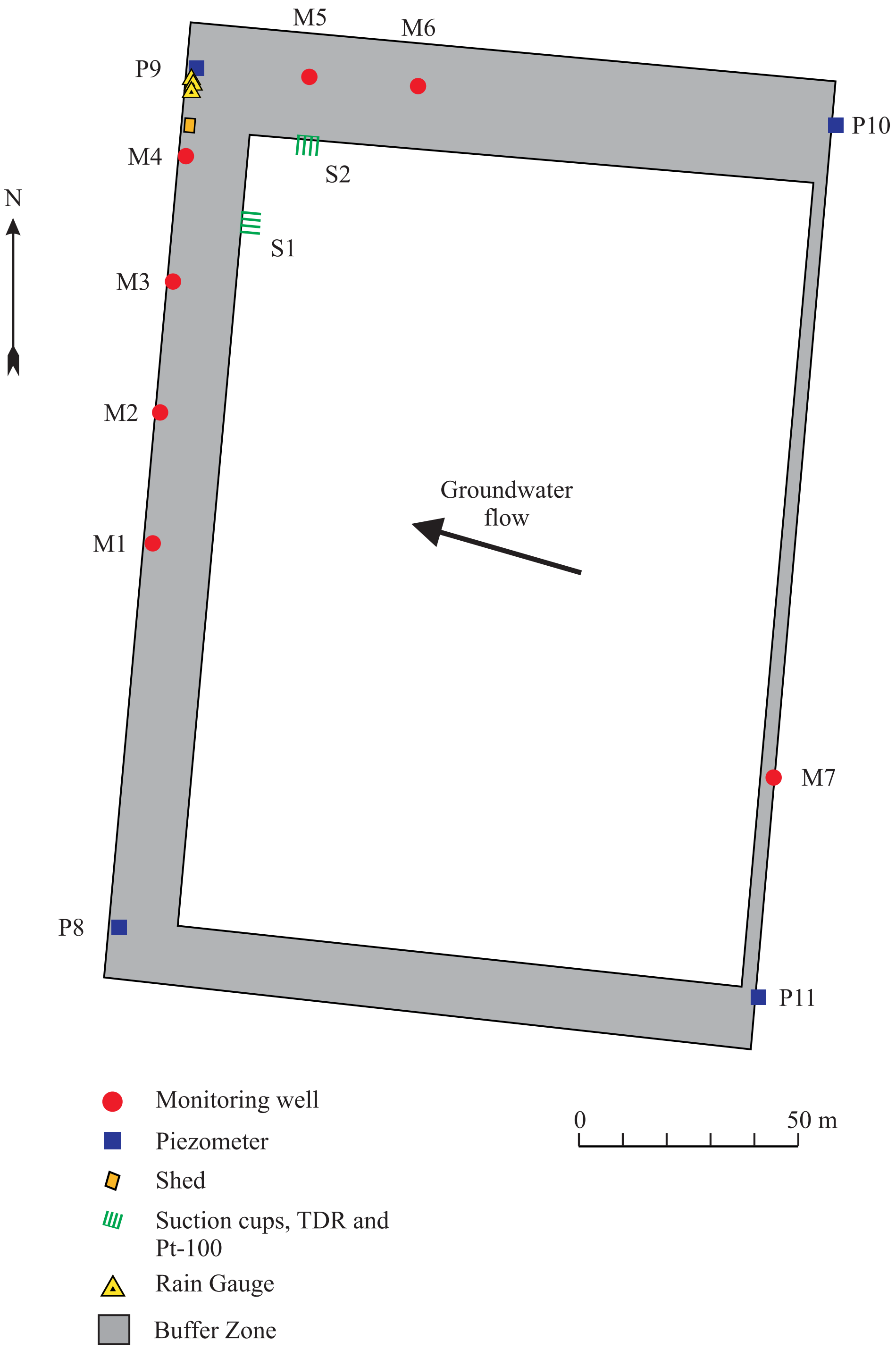

Figure 16. Overview of the Jyndevad test site. The innermost white area indicates the cultivated land, while the grey area indicates the surrounding buffer zone. The positions of the various installations are indicated, as is the direction of groundwater flow (by an arrow).

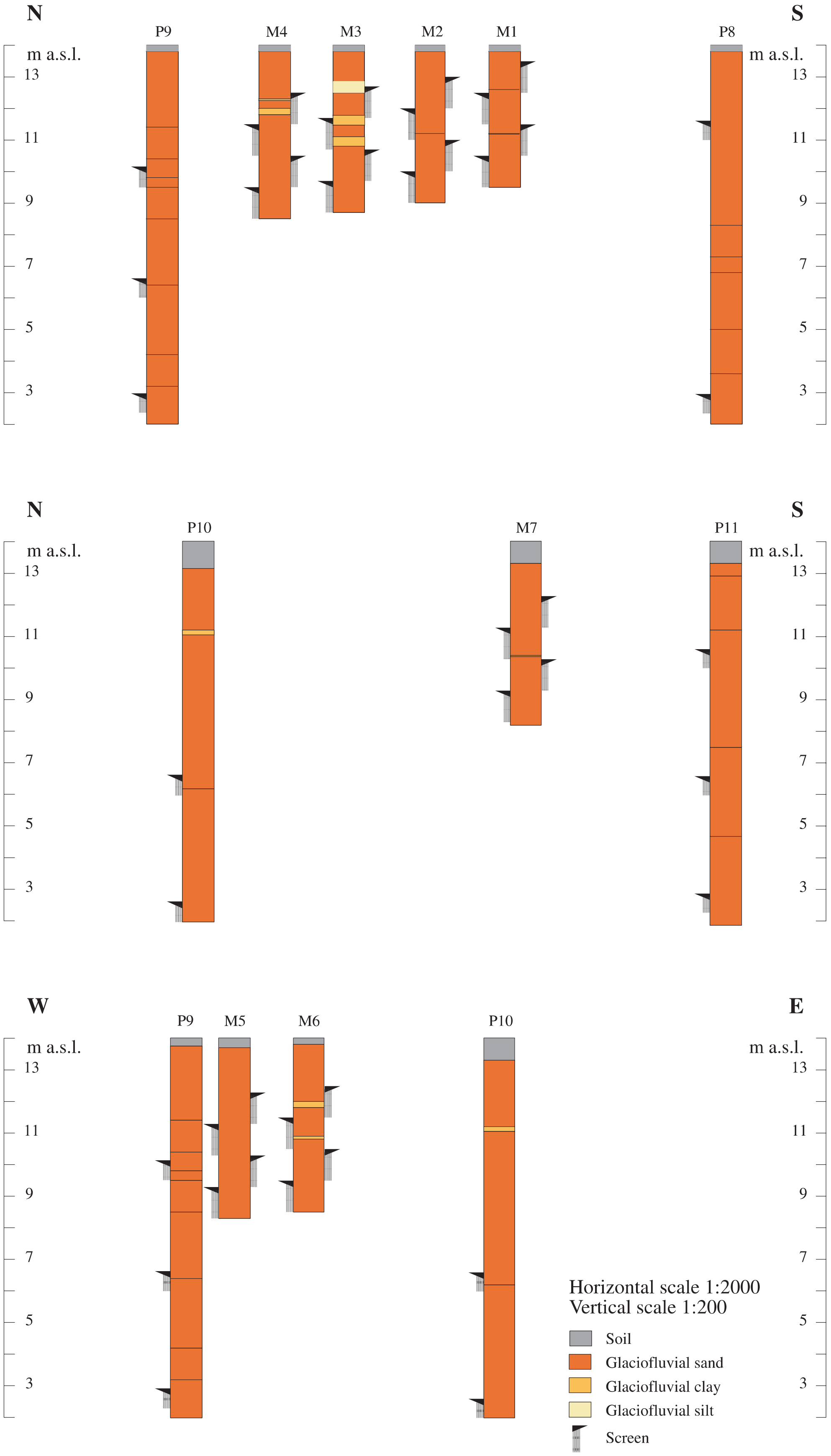

Figure 17. Geological description of the Jyndevad site (Lindhardt *et al*., 2001).Model set-up and calibration

3.1.3 Model set-up and calibration

The MACRO model was applied to the Jyndevad site covering the soil profile to a depth of 5 m b.g.s., always including the groundwater table. The model was used to simulate water flow and bromide transport in the unsaturated zone during the full monitoring period July 1999–June 2003 and to establish an annual water balance.

The model was calibrated to the observed groundwater table measured in the piezometers located in the buffer zone, as well as to measured time series of soil water content at three different depths (25, 60 and 110 cm b.g.s.) from the two profiles S1 and S2 (see Figure 16) and to the bromide concentration measured in the suction cups located 1 m b.g.s. The latest year of the monitoring period, July 2002–June 2003, is considered a validation period and no further model calibration has therefore been performed. The model set-up is thus identical to that reported in Kjær *et al.* (2003), although with the precipitation, evapotranspiration and plant data having been prolonged by one year. For a detailed description of data acquisition, model set-up and calibration procedures see Kjær *et al.* (2002) and Kjær *et al.* (2003).

3.2 Results and discussion

3.2.1 Soil water dynamics and water balances

The model validation shows that the latest model simulations, July 2002–June 2003, are generally consistent with the observed data, thus indicating a reasonable model description of the overall soil water dynamics in the unsaturated zone (Figure 18). The dynamics of the simulated groundwater table is well captured, as is the case for the previous years (Kjær *et al.*, 2003) (Figure 18B). However, the extreme precipitation in October (227 mm compared to a ”normal” of 111 mm) causes the simulated groundwater table to rise to a level about 40 cm higher than the measured level. This overestimation lasts from October to May. As noted earlier (Kjær *et al.*, 2003), the model has some difficulty in capturing the degree of soil water saturation 1.1 m b.g.s., which was also the case during the previous monitoring year (Figure 18E). Furthermore, the extreme precipitation in October is reflected by a greater increase in simulated water saturation 1.1 m b.g.s. than in measured water saturation.

The resulting water balance for Jyndevad for the four monitoring periods is shown in Tabel 5. The precipitation during the latest monitoring period (July 2002–June 2003) is very close to ”normal”, and is characterized by high precipitation in summer 2002, extremely high precipitation in October, and low precipitation in spring/early summer 2003 (Appendix 4). The high precipitation during summer 2002 resulted in continuous percolation throughout the summer months, starting as early as April 2002. High percolation rates are seen from the end of October until the beginning of November 2002 due to the high precipitation in October, whereas very low percolation is simulated in the less rainy spring/early summer 2003. For information about the water balance in previous monitoring periods see Kjær *et al.* (2003).

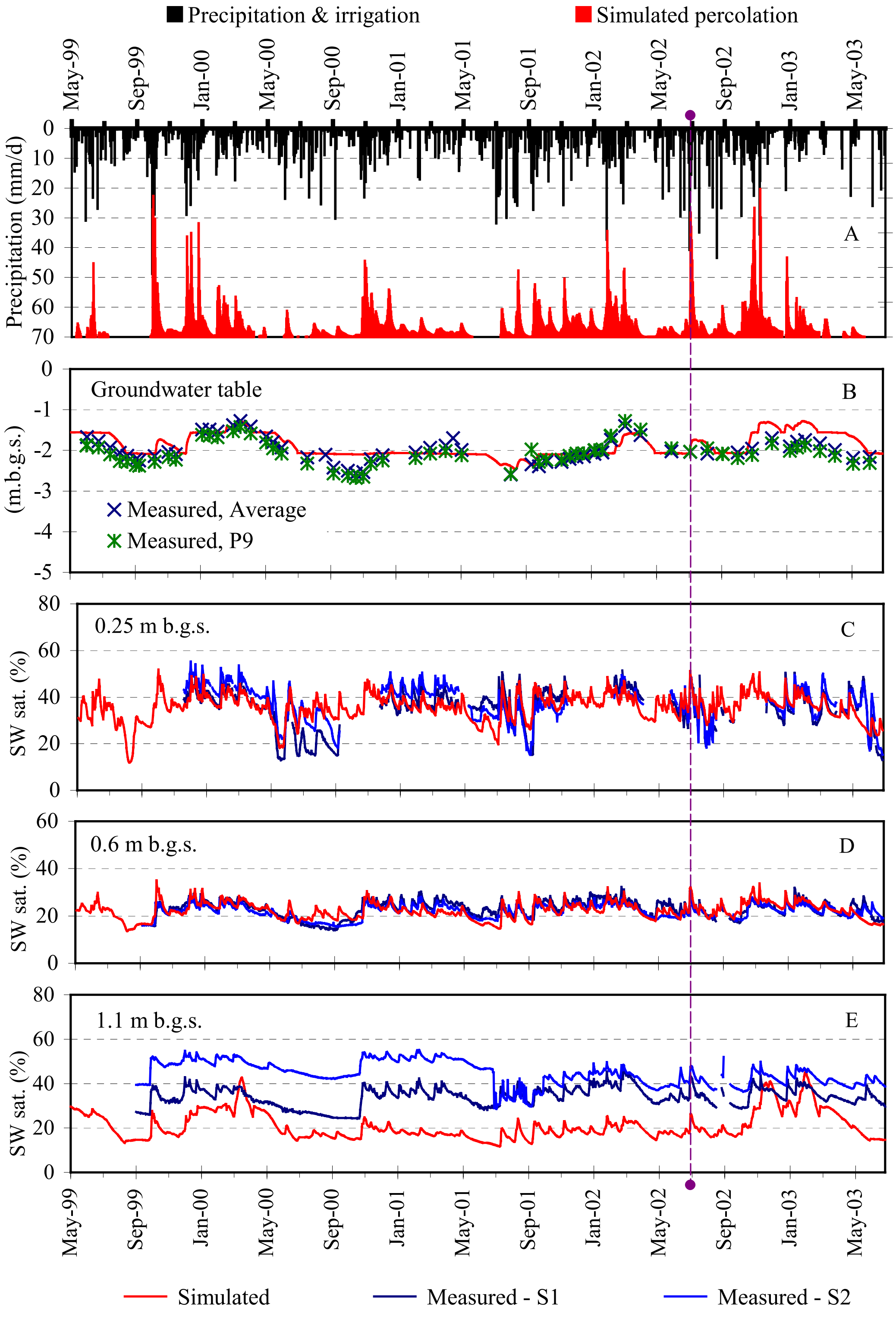

Figure 18. Soil water dynamics at Jyndevad: Measured precipitation, irrigation and simulated percolation 1 m b.g.s. (A), simulated and measured groundwater level (B), and simulated and measured soil water saturation (SW sat.) at three different soil depths (C, D and E). The measured data in B derive from piezometers located in the buffer zone. The measured data in C, D and E derive from TDR probes installed at S1 and S2 (see Figure 16). The broken vertical line indicates the beginning of the validation period (July 2002–June 2003).

Table 5. Annual water balance for Jyndevad (mm/yr). Precipitation is corrected to the soil surface according to the method of Allerup and Madsen (1979).

	Normal precipitation 1)	Precipitation	Irrigation	Actual evapotranspiration	Groundwater recharge 2)
1.7.99–30.6.00	995	1053	29	549	533
1.7.00–30.6.01	995	810	0	447	363
1.7.01–30.6.02	995	1204	81	511	774
1.7.02–30.6.03	995	991	51	488	554

1) Normal values based on time series for 1961–1990

2) Groundwater recharge is calculated as precipitation + irrigation - actual evapotranspiration

3.2.2 Bromide leaching

Bromide has now been applied twice at Jyndevad. The bromide concentrations shown in Figure 19 and Figure 20 relate to the bromide applied in autumn 1999, as described further in Kjær *et al.* (2003). Leaching of the bromide applied in March 2003 will be evaluated in due course as the results become available.

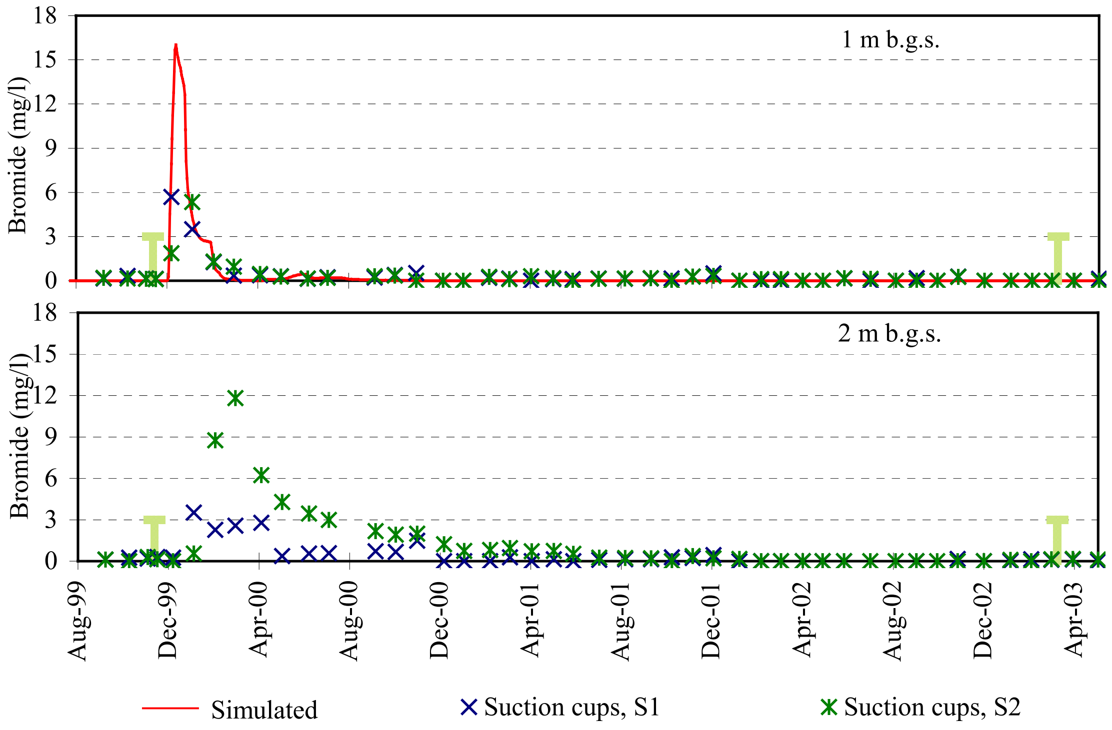

Figure 19. Simulated (solid line) and measured bromide concentration at Jyndevad. The data derive from suction cups installed 1 m b.g.s. and 2 m b.g.s. at locations S1 and S2 (see Figure 16). The green vertical lines indicate the dates of bromide application.

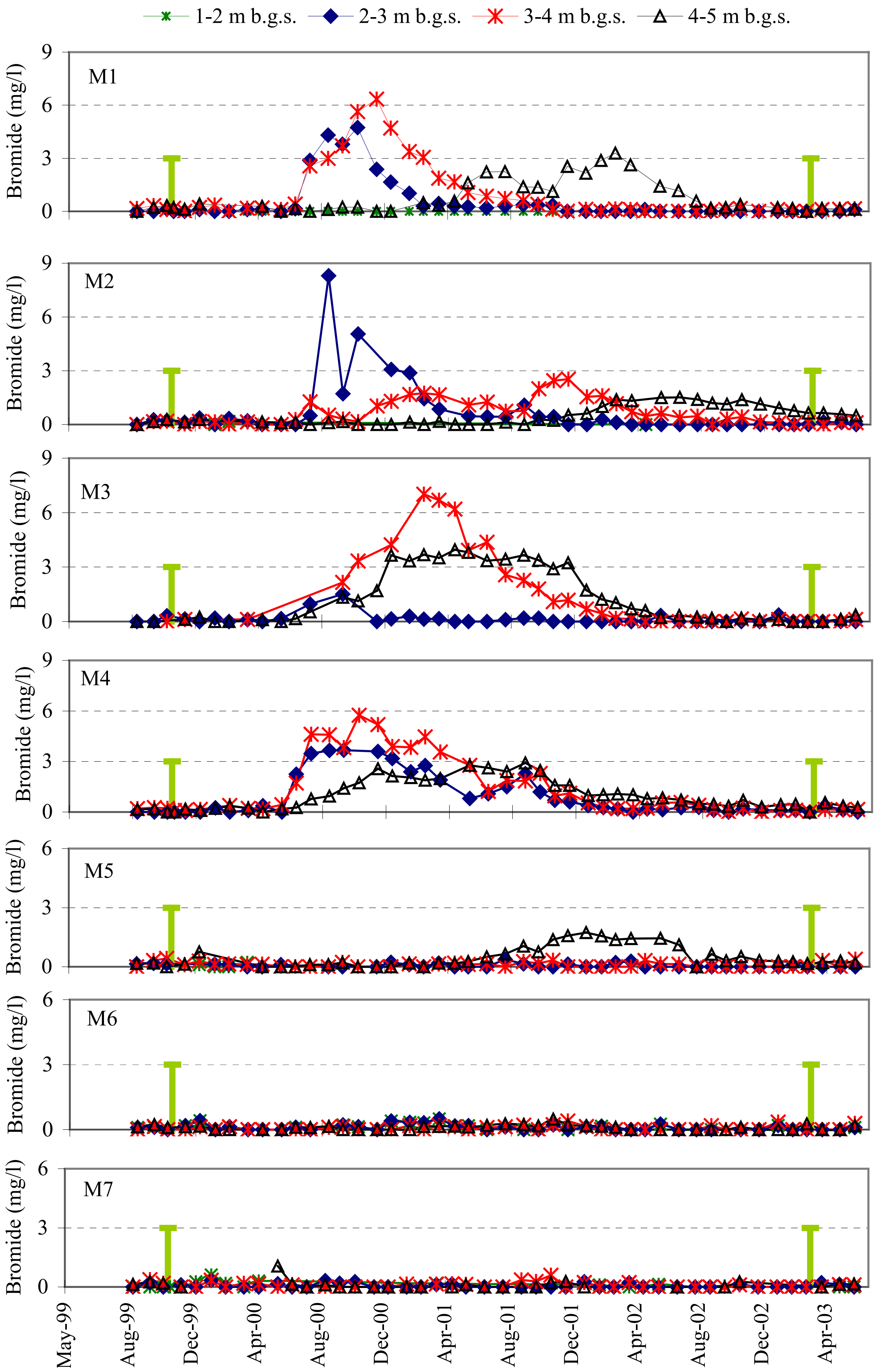

Figure 20. Bromide concentration in the groundwater at Jyndevad. The data derive from monitoring wells M1–M7. Screen depth is indicated in m b.g.s. The green vertical lines indicate the dates of bromide application.

3.2.3 Pesticide leaching

At Jyndevad, the monitoring encompassed 7 different pesticides and several degradation products applied during three growing seasons as indicated in Figure 21 and Table 6. It should be noted that precipitation in Table 6 is corrected to the soil surface according to Allerup and Madsen (1979), whereas percolation (1 m b.g.s.) refers to accumulated percolation as simulated with the MACRO model. It should also be noted that as tribenuron methyl (applied here as Express) and pyridate (applied here as Lido) degrade rapidly, the leaching risk is more associated with their respective degradation products, triazinamin-methyl and PHCP. For the same reasons it is the degradation products and not the parent compounds that are monitored in the PLAP (Table 6). Pesticides applied later than April 2003 are not evaluated in this report and hence are not included in Table 6.

Table 6. Pesticides analysed at Jyndevad with the product used shown in parentheses. Degradation products are in italics. Precipitation (prec.) and percolation (perc.) are accumulated from date of first application until end of monitoring. 1st month perc. refers to accumulated percolation within the first month after application. C_{mean} refers to average leachate concentration 1 m b.g.s the first year after application. The number of pesticide-positive samples is indicated in parentheses.

Crop and analysed pesticides	Application date	End of monitoring	Prec. (mm)	Perc. (mm)	1st month perc. (mm)	C_{mean} (µg/l)
Winter rye 2000						
Glyphosate (Roundup 2000)	Sep 99	Apr 02	2739	1603	149	<0.01 (0)
- *AMPA*						<0.01 (3)
Triazinamin-methyl 1) (Express)	Nov 99	Apr 02	2513	1436	95	<0.02 (0)
Propiconazole (Tilt Top)	Apr 00	Jul 02	2303	1094	0	<0.01 (0)
Fenpropimorph (Tilt Top)	Apr 00	Apr 02	1995	1034	0	<0.01 (2)
- *fenpropimorphic acid*						<0.01 (0)
Maize 2001						
Terbuthylazine (Lido)	May 01	Jul 03†	2383	1319	0	<0.01 (0)
- *desethylterbuthylazine*						<0.01-0.02 (28)
PHCP 2)(Lido)	May 01	Jul 03	2383	1319	0	<0.02 (0)
Potatoes 2002						
Rimsulfuron (Titus)	May 02	Jul 03†	1172	662	26	<0.02 (0)
- *PPU*						0.06–0.13 (23)
- *PPU-desamido*						0.01-0.03 (17)

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

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

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

†) *Monitoring will continue during the following year. The values for prec. and perc. are accumulated up to July 2003*

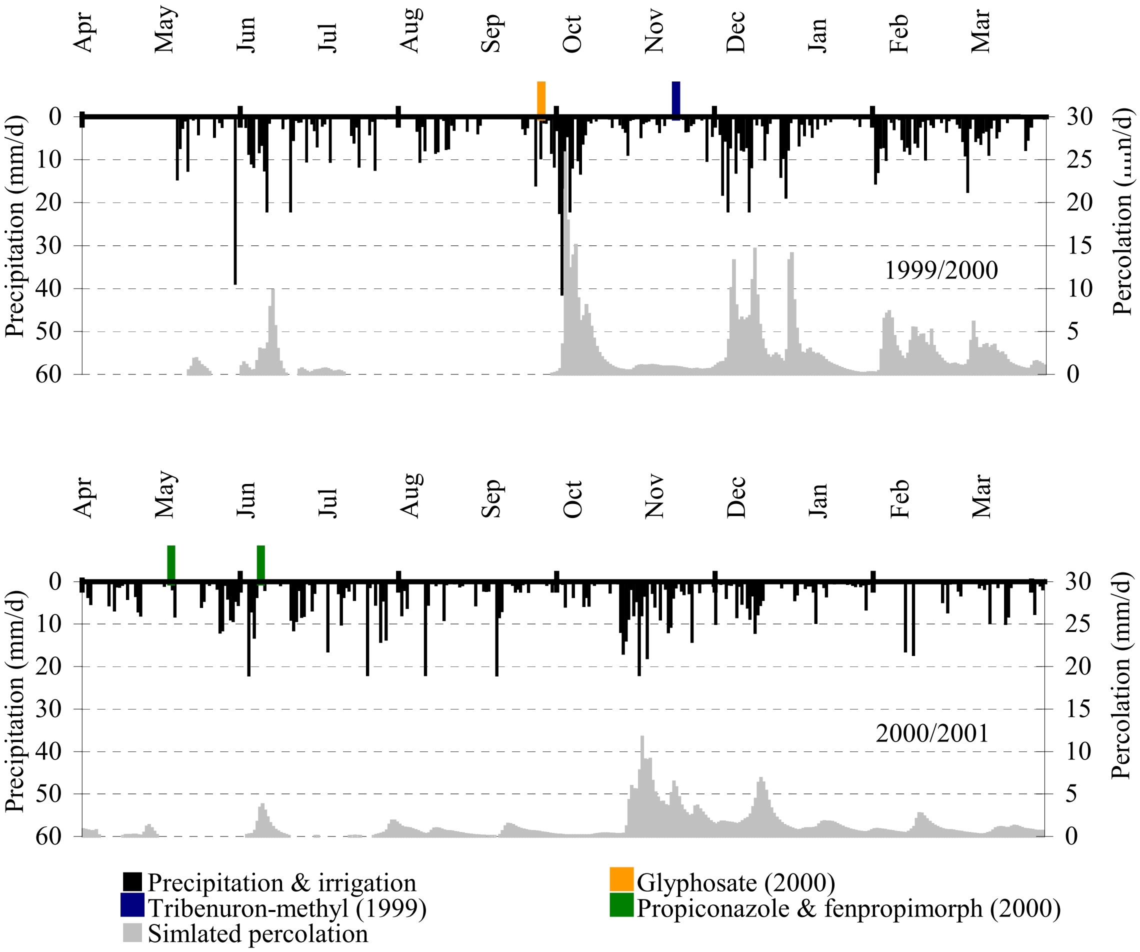

Figure 21. Pesticide application, precipitation and irrigation (primary axis) together with simulated percolation 1 m b.g.s. (secondary axis) at Jyndevad in 1999/2000 (upper) and 2000/2001 (lower). As tribenuron methyl degrades rapidly it is the degradation products triazinamin-methyl, that is monitored.

The leaching risk of pesticides applied in 1999/2000 (glyphosate, triazinamin-methyl, propiconazole and fenpropimorph) has already been evaluated in Kjær *et al.* (2003).

The leaching risk of the pesticides applied in 2001 can be summarized as follows:

Terbuthylazine has not been found to leach during the 2-year monitoring period. The degradation product ***desethylterbuthylazine*** did leach, however. In mid October 2001, about five months after application, desethylterbuthylazine was detected in the S1 suction cups located 1 m b.g.s. Up to May 2003, all but three of the monthly samples taken from S1 contained desethylterbuthylazine in the range 0.020–0.056 µg/l (Figure 23). Average concentration within the first and second year after application was both 0.02 µg/l. Desethylterbuthylazine has not been detected at S2, however. Apart from one sample (taken from M4 one year after application), desethylterbuthylazine has not been detected in the downstream monitoring wells. Desethylterbuthylazine has frequently been detected in the monitoring well M7 located upstream of the test site, however. During the 2-year period the M7 upstream well has been sampled 4 times, in all cases revealing low concentrations of desethylterbuthylazine (0.010–0.023 µg/l).

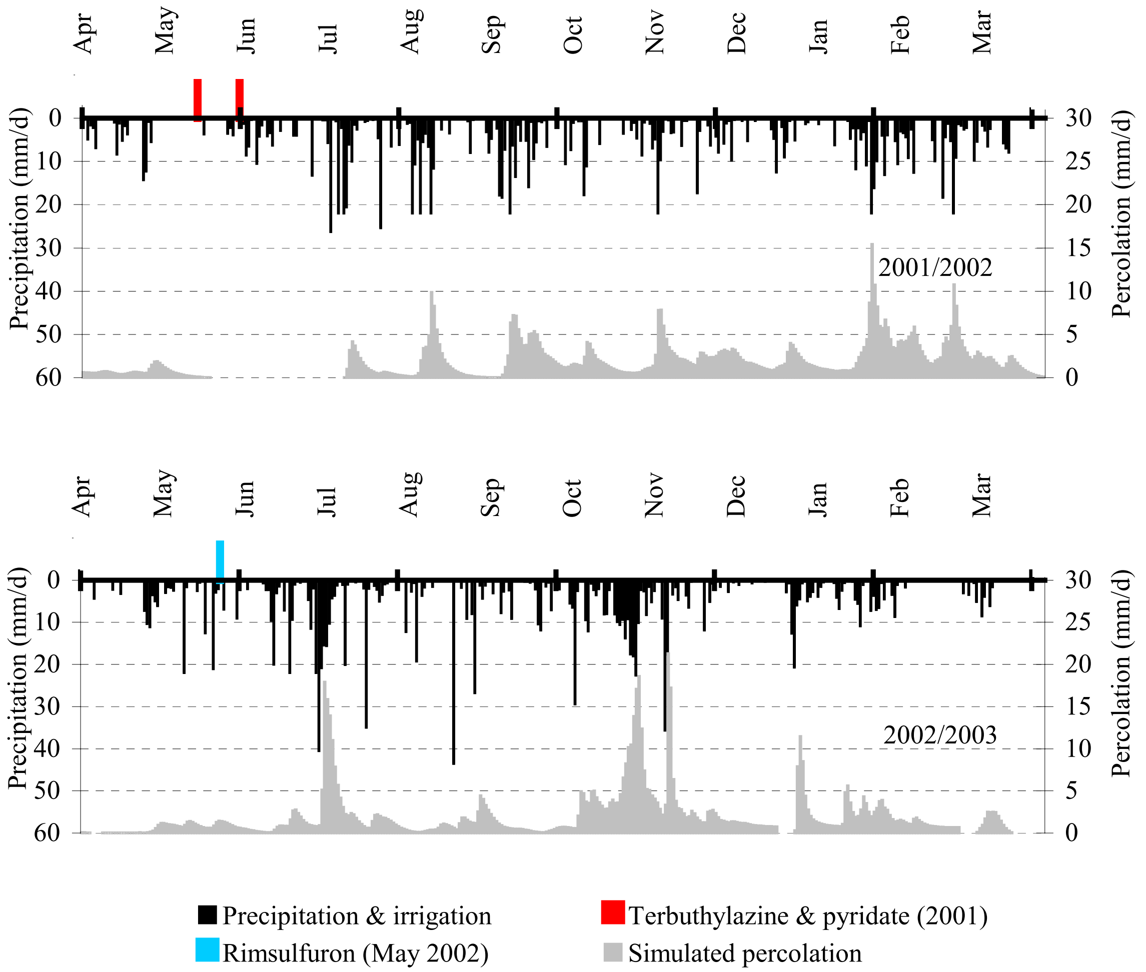

Figure 22. Pesticide application, precipitation and irrigation (primary axis) together with simulated percolation 1 m b.g.s. (secondary axis) at Jyndevad in 2001/2002 (upper) and 2002/2003 (lower). As pyridate degrade rapidly it is the degradation product PHCP, that is monitored.

This desethylterbuthylazine derives from prior application of terbuthylazine on the neighbouring field located upstream of the PLAP site and was detected in the initial screening analysis, thus indicating that desethylterbuthylazine was present in M7 before monitoring started in September 1999 (See Kjær *et al.,* 2001). The observed leaching should be viewed in relation to pesticide having been applied in the spring when hydrological conditions allow the applied compound a relatively long residence time in the root zone. Terbuthylazine was applied twice in May 2001, when precipitation input was close to normal and was counterbalanced by actual evapotranspiration (Appendix 4 and Figure 21). Hence, percolation did not occur until mid July, about 1.5 months after the last application (Figure 23). Desethylterbuthylazine was first detected after 190 mm of percolation, equivalent to 1.5 pore volumes.

Pyridate, which was applied at the same times as terbuthylazine, degrades rapidly such that the leaching risk is more associated with its degradation product **PHCP**. During the 2-year monitoring period leaching of PHCP has not been detected at Jyndevad.

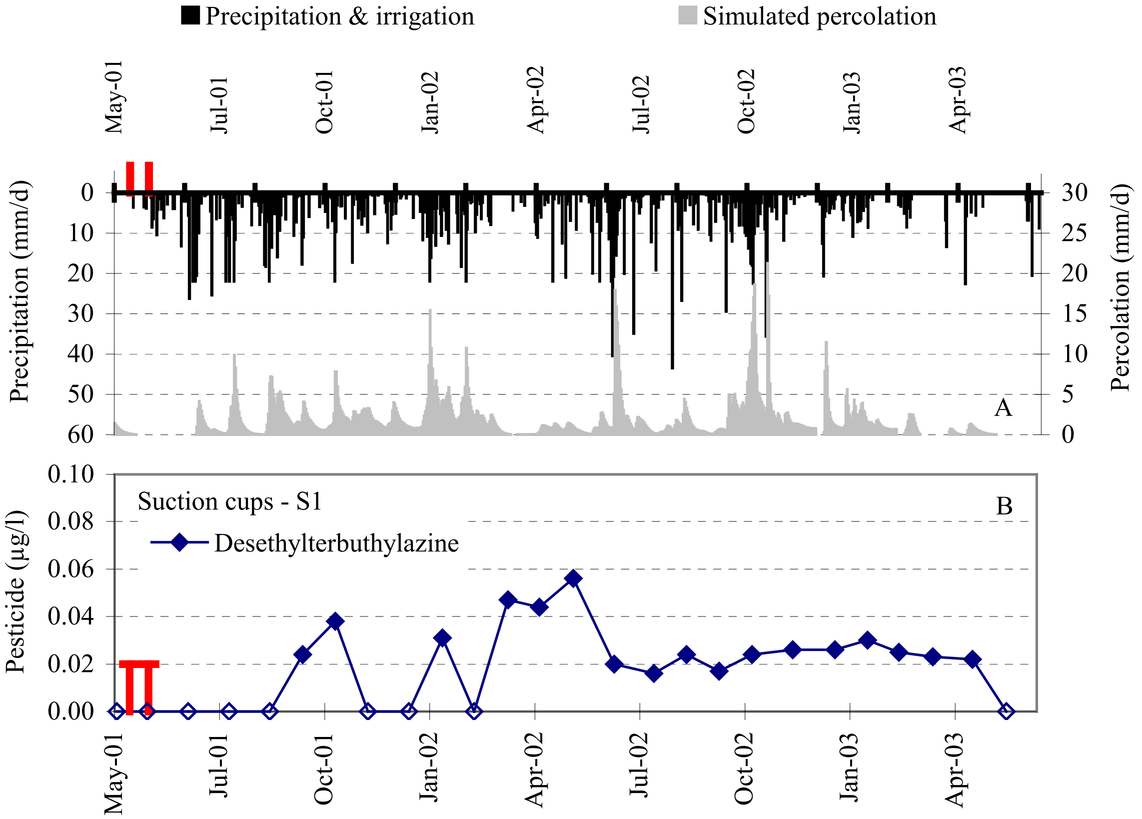

Figure 23. Precipitation, irrigation and simulated percolation 1 m b.g.s. (A) together with measured concentration of desethylterbuthylazine (B) at Jyndevad. The measured data derive from suction cups installed 1 m b.g.s. at location S1 (see Figure 16). The red vertical lines indicate the dates of pesticide application. Concentrations below the detection limit of 0.01 µg/l are indicated by open diamonds.

The leaching risk of ***rimsulfuron*** (applied May 2002) will not be evaluated until the 2004 monitoring results become available, i.e. when two years of monitoring data have been collated. So far, the substance has not been found in any of the water sampled, although its two degradation products PPU and PPU-desamido were detected at 1 m depth in the suction cups at S1 and S2 (Figure 24). PPU was detected for the first time on 3 June 2002 and PPU-desamido was detected the following month. In most cases the concentrations of PPU were higher than those of PPU-desamido. After their initial detection at S1, both metabolites were found in all subsequent water samples. At S2, PPU-desamido was not detected in the 5 following monthly samples unlike PPU, which was detected on one occasion. Elevated concentrations of PPU in particular were still seen towards the end of the current monitoring period, thus indicating that leaching of the compound from the uppermost metre of the soil has not yet ceased. Nevertheless, the average yearly concentration of PPU and PPU-desamido in the first monitoring year was 0.06–0.13 and 0.01–0.03 µg/l, respectively. The primary data and calculation methods are given in Appendix 6. Neither PPU nor PPU-desamido have yet reached the groundwater monitoring screens situated downstream of the test site.

When evaluating these result it should be noted that rimsulfuron was applied during spring/summer of 2003, when precipitation input and corresponding percolation were much higher than normal (Section 3.2.1, Appendix 4). Finally, it should be noted that PPU is un-

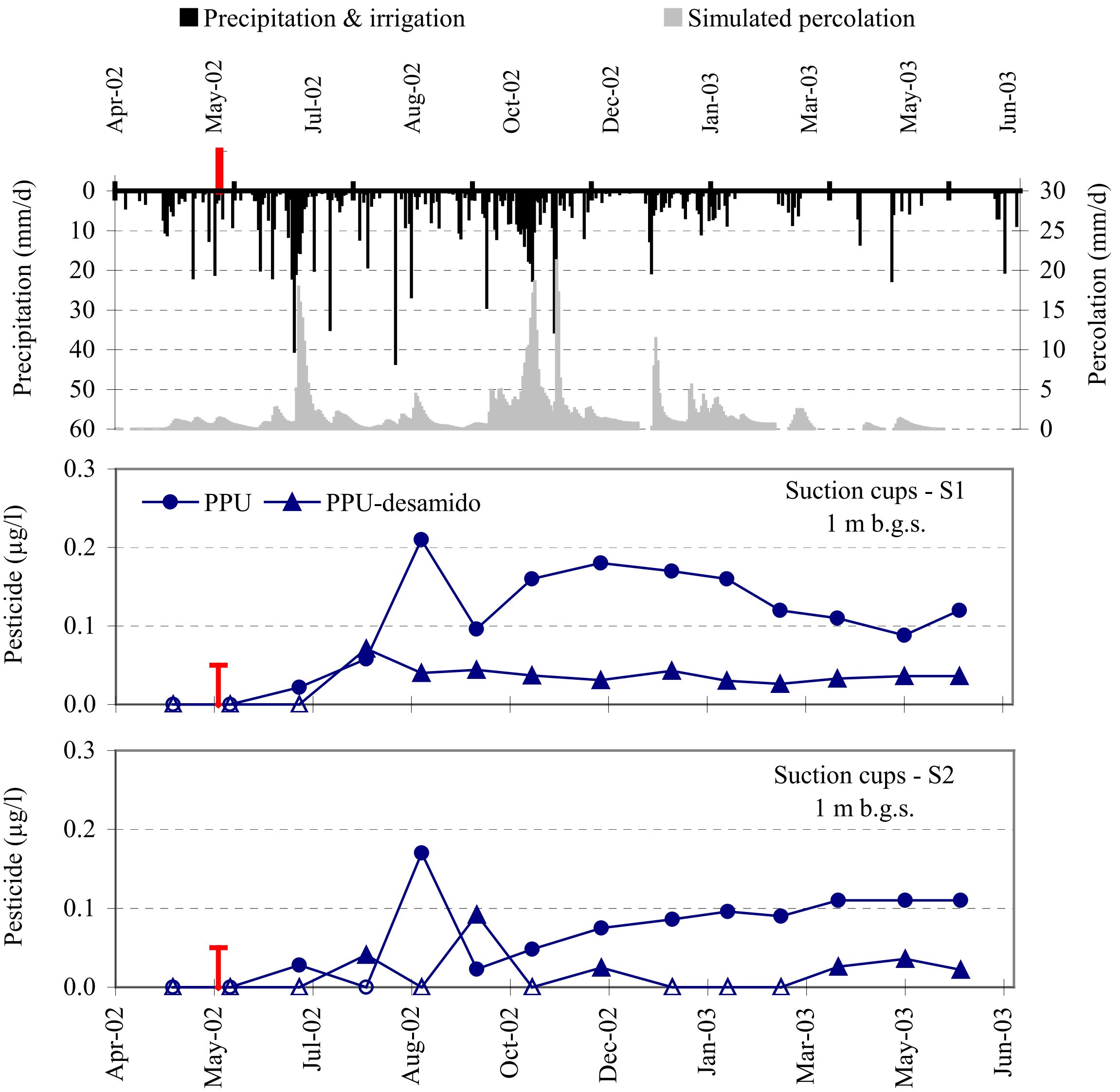

Figure 24. Precipitation, irrigation and simulated percolation 1 m b.g.s. (A) together with measured concentration of *PPU and PPU-desamido* (B) at Jyndevad. The measured data derive from suction cups installed 1 m b.g.s. at location S1 and S2 (see Figure 16). The red vertical line indicates the date of pesticide application. Concentrations below the detection limit of 0.01 µg/l are indicated by open circles and triangles.

stable. Results from the field-spiked samples thus indicate that PPU might have further degraded to PPU-desamido during the subsequent storage and transport (Section 8.2.2). The monitoring data thus does not allow any conclusion to be drawn as to whether the observed PPU-desamido derives from degradation in the soil or degradation in the sample during subsequent storage and transport. The concentration of PPU may be underestimated, while that of PPU-desamido overestimated.

4 Pesticide leaching at Silstrup

4.1 Materials and methods

4.1.1 Site description and monitoring design

The test field at Silstrup is located south of Thisted in northwestern Jutland (Figure 1). The cultivated area is 1.69 ha (91 x 185 m) and slopes gently 1–2° to the north (Figure 25). Based on two profiles excavated in the buffer zone bordering the field the soil was classified as Alfic Argiudoll and Typic Hapludoll (Soil Survey Staff, 1999). The topsoil content of clay in the two profiles was 18.3 and 26.6%, and the organic carbon content was 3.4 and 2.8% . The geological description showed a rather homogeneous clay till rich in chalk and chert, containing 20–35% clay, 20–40% silt and 20–40% sand (Figure 26). In some intervals the till was more sandy, containing only 12–14% clay. Moreover, thin lenses of silt and sand were found in some of the wells. The gravel content was approx. 5%, but could be as high as 20%. A brief description of the sampling procedure is provided in Appendix 2. The monitoring design and test site are described in detail in Lindhardt *et al.* (2001) and the analysis methods in Kjær *et al*. (2002).

4.1.2 Agricultural management

Management practice during the two most recent growing seasons is briefly summarised below and detailed in Appendix 3 (Table A3.3). For information about management practice during the first two monitoring periods see Kjær *et al*. (2003).

On 25 October 2001 the field was sprayed with glyphosate in the form of Roundup Bio (4.0 l/ha). The field was ploughed to a depth of 22 cm on 18 December. Maize (cv. Loft) was sown on 25 April 2002 after the field had been fertilized with cattle slurry (40.3 tonnes/ha) on 22 April. When two leaves had unfolded the maize was sprayed with pyridate + terbuthylazine to combat weeds. This was repeated on 3 June. On 19 June the maize was sprayed with clopyralid to combat weeds. The crop was harvested on 23 September yielding 134.3 hkg/ha (100% dry matter), somewhat less than other cultivars in the area that year.

Peas (cv. Attica) were sown on 14 April 2003. Only herbicides were applied to the crop. On 17 May, when four leaves had unfolded, bentazone and pendimethalin were applied. At the time, when nearly all the pea pods had attained their full size, rooks (Corvus frugilegus) invaded the field causing significant crop damage. As a consequence the yield was only 39.8 hkg/ha (86% dry matter), about 5-8 hkg/ha less than expected.

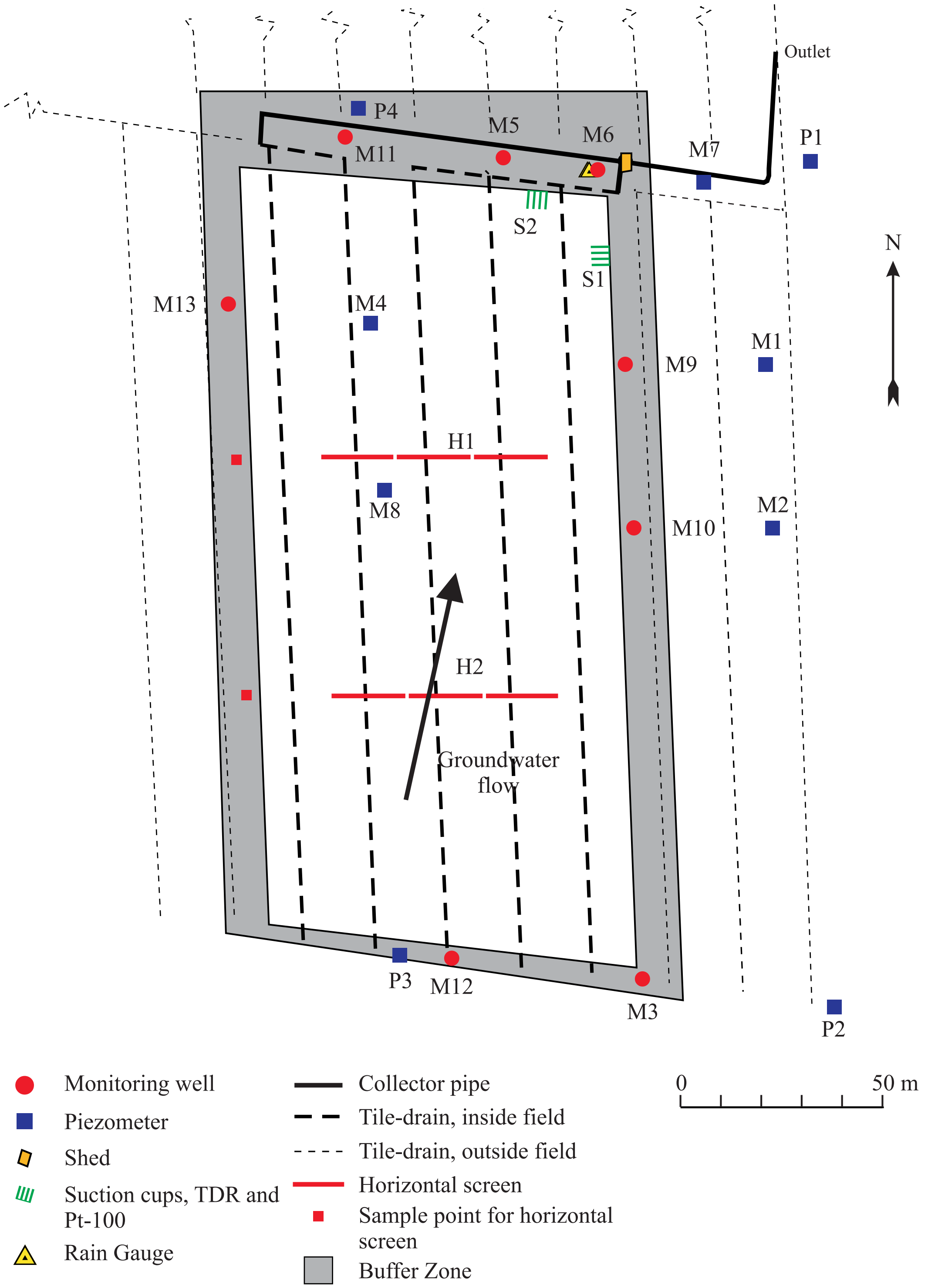

Figure 25. Overview of the Silstrup site. The innermost white area indicates the cultivated land, while the grey area indicates the surrounding buffer zone. The positions of the various installations are indicated, as is the direction of groundwater flow (by an arrow).

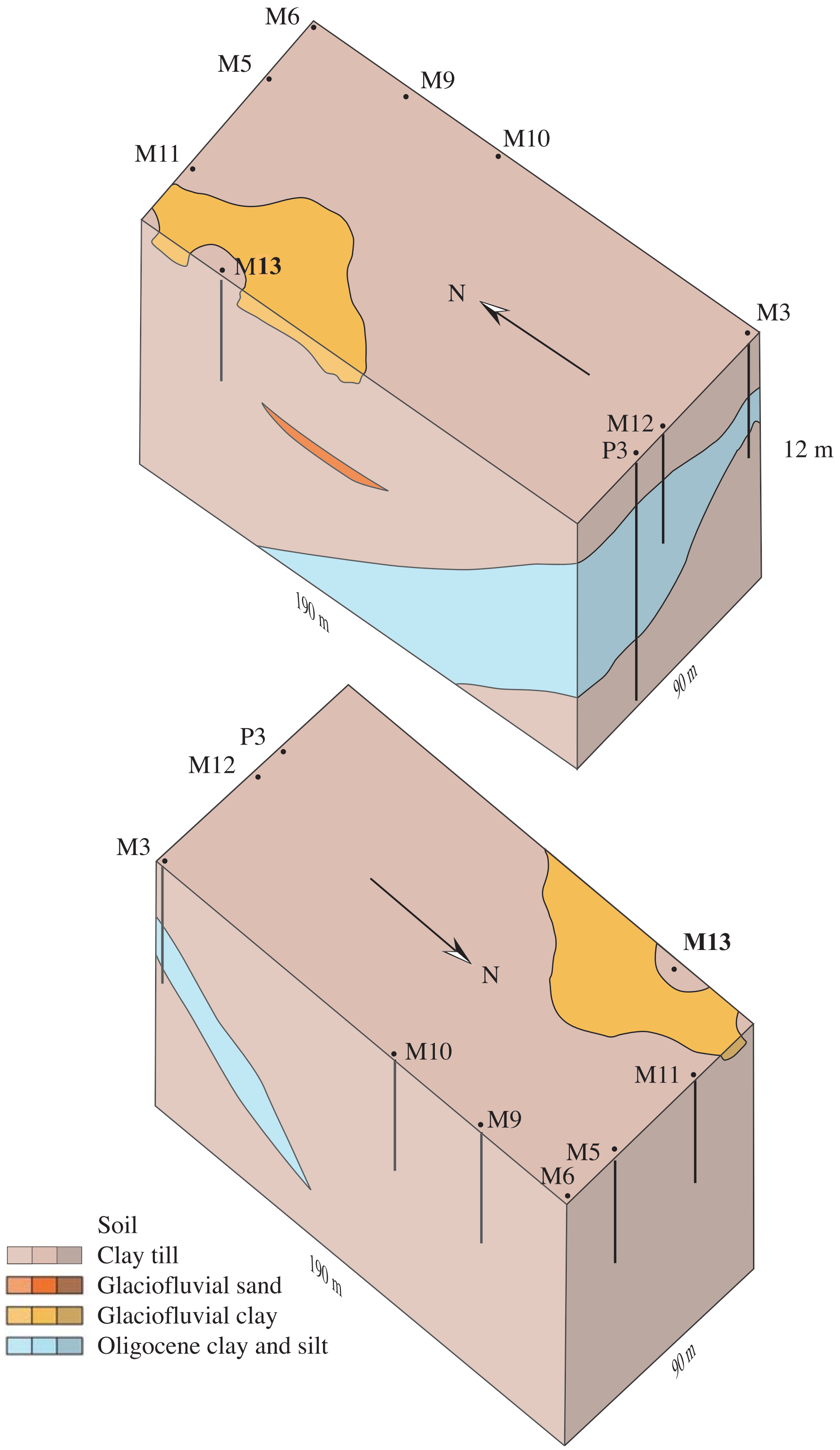

Figure 26. Geological description of the Silstrup site (Lindhardt *et al.,* 2001).

4.1.3 Model set-up and calibration

The MACRO model is applied to the Silstrup site covering the soil profile to a depth of 5 m b.g.s., always including the groundwater table. The model is used to simulate the water flow in the unsaturated zone during the full monitoring period April 2000–June 2003 and to establish an annual water balance.

The model was calibrated to the observed groundwater table measured in the piezometers located in the buffer zone, to time series of soil water content measured at three depths (25, 60 and 110 cm b.g.s.) from two profiles S1 and S2 (see Figure 27) as well as to the measured drainage flow. A simple calibration procedure was applied that only involved adjustment of the empirical BGRAD parameter regulating the boundary flow and the drain depth, which was determined by the groundwater level during drainage periods. All remaining parameters were based on measured data or literature/default values. For a detailed description of data acquisition, model set-up and calibration procedures see Kjær *et al.* (2002) and (2003).

The latest year of the monitoring period, July 2002–June 2003, is considered a validation period and no further model calibration has therefore been performed. The model set-up is thus identical to that reported in Kjær *et al.* (2003), although with the precipitation, evapotranspiration and plant data having been prolonged by one year.

4.2 Results and discussion

4.2.1 Soil water dynamics and water balances

Model validation shows that the latest model simulations, July 2002-June 2003, are largely consistent with the observed data, thus indicating a reasonable model description of the overall soil water dynamics in the unsaturated zone (Figure 27). As for previous years (Kjær *et al.*, 2003), the dynamics and level of the groundwater table are well captured by the model except for the initial rise in the autumn, when percolation and drainage flow is initiated. The delayed rise in the simulated groundwater table results in a delayed response in modelled drainage flow in the autumn (Figure 27C). The TDR probes at 0.25 and 0.6 m b.g.s. in S1 were unstable during most of the latest monitoring period and have been partly excluded from the analysis. Like the previous monitoring periods, the overall trends in soil water content could be modelled reasonably well in the latest monitoring period, especially in the A horizon (Figure 27D). As seen in the previous years, the model tends to describe the subsoil as being dryer during the summer period than measured by the deeper TDR probes (Figure 27E and F).

The resulting water balance for the four monitoring periods is shown in Table 7 (July to June). Precipitation and measured drainage flow were lowest in the latest monitoring period. Precipitation was particularly low in January to March (Appendix 4), causing the groundwater table to fall and resulting in low, measured drainage flow. Between mid February and mid May only one minor drainage event occurred (Figure 27C). The monitoring period July 2000–June 2001 and the latest monitoring period (July 2002–June 2003) are similar with respect to annual precipitation. Despite the lower drainage flow measured in

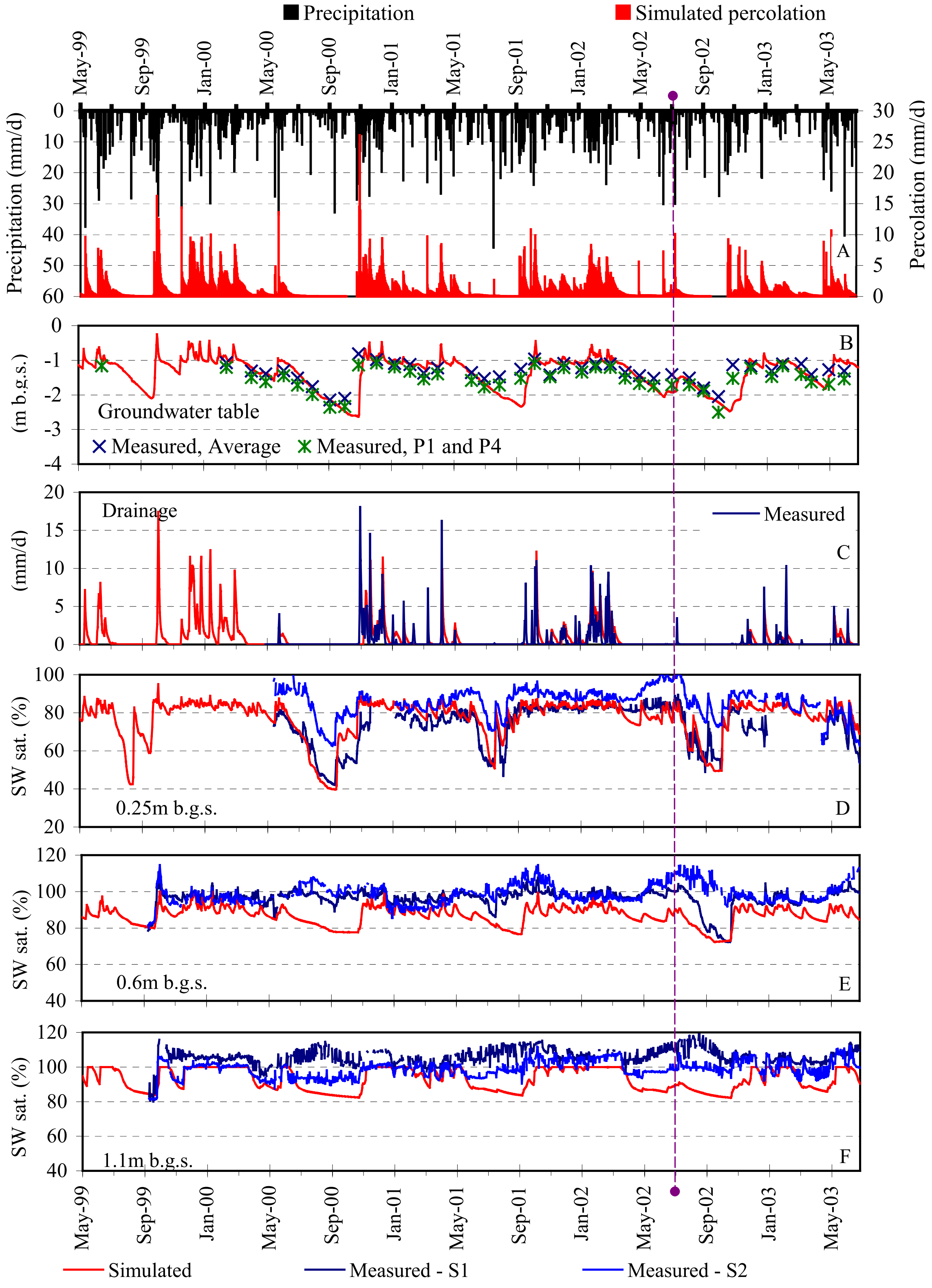

Figure 27. Soil water dynamics at Silstrup: Measured precipitation and simulated percolation 1 m b.g.s. (A), simulated and measured groundwater level (B), simulated and measured drainage flow (C), and simulated and measured soil water saturation (SW sat.) at three different soil depths (D, E and F). The measured data in B derive from piezometers located in the buffer zone. The measured data in D, E and F derive from TDR probes installed at S1 and S2 (see Figure 25). The broken vertical line indicates the beginning of the validation period (July 2002–June 2003)..

the latest monitoring period, groundwater recharge was similar due to the higher actual evapotranspiration during the latest period, which was mainly attributable to the crop (maize). As in previous monitoring periods, simulated percolation 1 m b.g.s. was continuous from October until late spring. Precipitation events exceeding approximately 15 mm/d are immediately reflected in the percolation (Figure 27A). The low precipitation in the months of January through March followed by high precipitation in April results in percolation being initially lower than normal for this time of the year and then higher than normal. For information about the water balance in previous monitoring periods see Kjær *et al.* (2003).

Table 7. Annual water balance for Silstrup (mm/year). Precipitation is corrected to the soil surface according to the method of Allerup and Madsen (1979).

	Normal precipitation [2)]	Precipitation	Actual evapotranspiration	Measured drainage	Simulated drainage	Groundwater recharge [3)]
1.7.99–30.6.00 [1)]	976	1175	439	–	479	257[4)]
1.7.00–30.6.01	976	909	392	217	256	300
1.7.01–30.6.02	976	1034	447	227	300	360
1.7.02–30.6.03	976	879	507	81	97	291

1) The monitoring was started in April 2000

2) Normal values based on time series for 1961–1990 corrected to soil surface

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

4) Where drainage flow measurements are lacking, simulated drainage flow was used to calculate groundwater recharge

4.2.2 Bromide leaching

Two large storm events occurred a few days prior to and after the application of the bromide tracer on 22 May 2000. The first event caused the onset of a minor flow of drainage water, while the second resulted in rapid percolation and breakthrough of bromide to the drainage system, with the concentration reaching 5.1 mg/l on 29 May (Figure 28C). At Silstrup the upper macropore zone extends down to 1.3 m b.g.s. (Lindhardt *et al*., 2001). The zone is heavily fractured and contains numerous biopores coated with clay and organic matter. When the bromide was applied, the groundwater table was located around 1.25 m b.g.s. (Figure 27B). The presence of macropores and the location of the groundwater at the time of bromide application were reflected in the almost instantaneous occurrence of bromide in the drainage water, suction cups S1 and S2 (Figure 28A, B and C) and in the uppermost filters of all but one of the downstream, vertical wells, M6 (Figure 29). Over the past 1½ years the bromide concentration has been elevated in the deepest filter of M6, however (Figure 29). This may be indicative of a bromide breakthrough. The orientation and magnitude of the fractures may also explain why bromide was detected in the lowermost screen of M12, which is located upstream of the test field.

The elevated bromide concentration detected in the suction cups and drainage water in 2003 indicates that there is a continuous leaching of bromide from the unsaturated zone as long as three years after tracer application. In conclusion, the overall distribution of bromide in the test field indicates that most of the bromide is retained in the upper part of the soil profile, probably in the soil matrix. Continuous, slow leaching of bromide can therefore be expected for a long period of time.

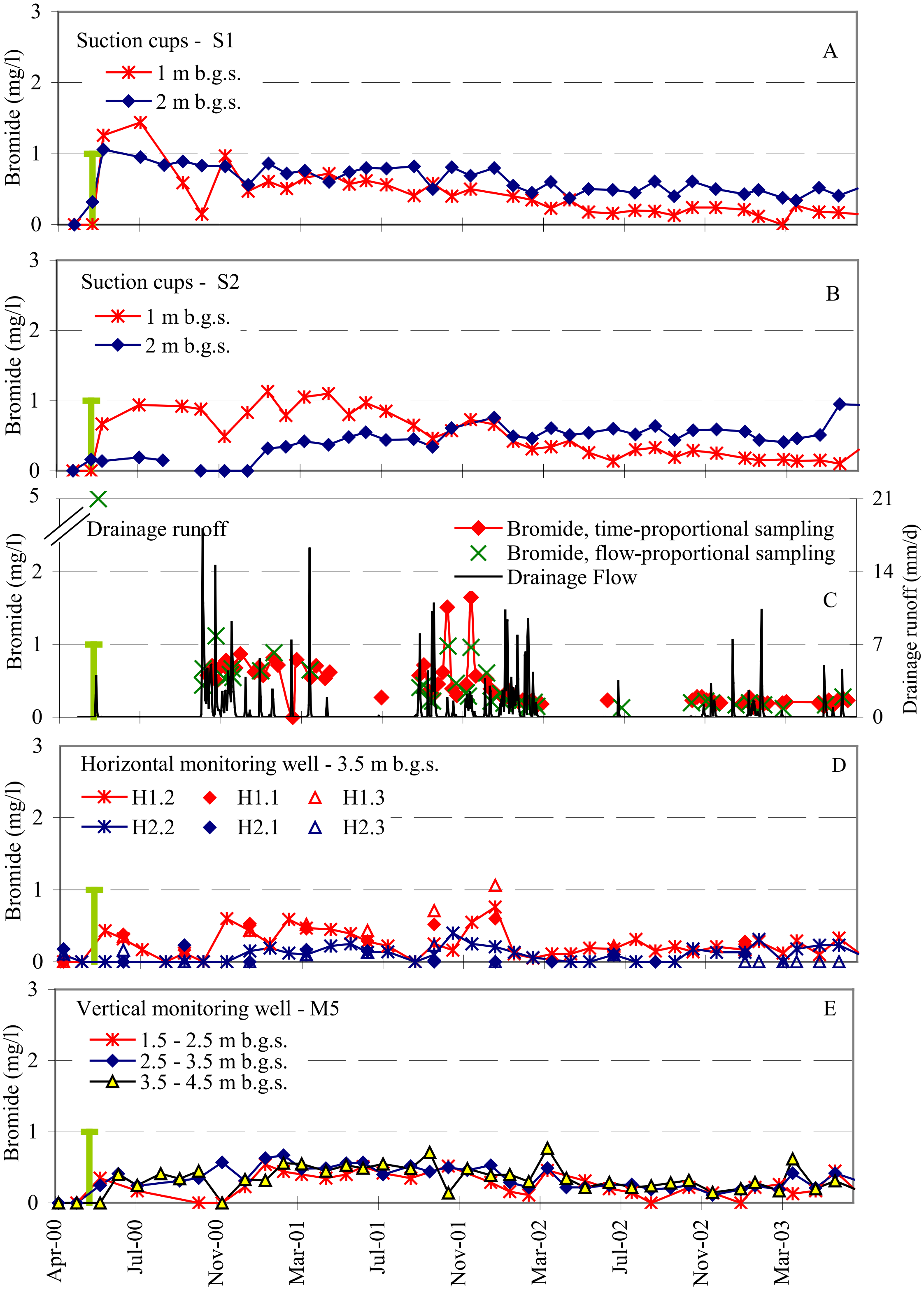

Figure 28. Bromide concentration at Silstrup. A and B refer to suction cups located at S1 and S2. The bromide concentration is also shown for drainage runoff (C), the horizontal monitoring wells H1 and H2 (D) and vertical monitoring well M5 (E). The green vertical line indicates the date of bromide application.

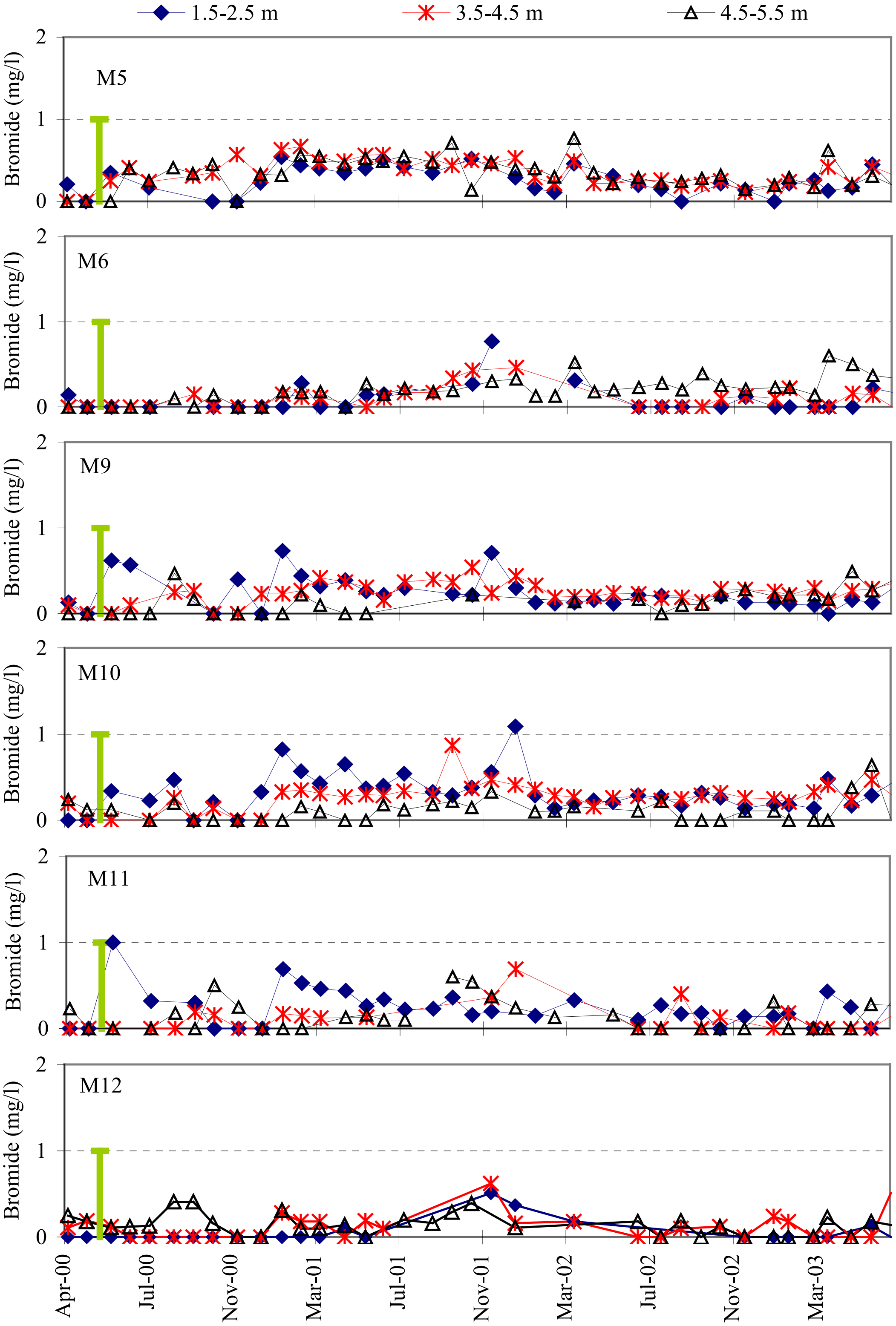

Figure 29. Bromide concentration at Silstrup. The data derive from the vertical monitoring wells (M5–M12). Screen depth is indicated in m b.g.s. The green vertical line indicates the date of bromide application.

4.2.3 Pesticide leaching

Monitoring began at Silstrup in April 2000 and as of April 2003 encompassed a total of 13 pesticides and several degradation products (Table 8 and Figure 30). It should be noted that precipitation in Table 8 is corrected to soil surface according to Allerup and Madsen (1979), whereas percolation (1 m b.g.s.) refers to accumulated percolation as simulated with the MACRO model

Table 8. Pesticides analysed at Silstrup with the product used shown in parentheses. Degradation products are in italics. Precipitation (prec.) and percolation (perc.) are accumulated from date of first application until end of monitoring. 1st month perc. refers to accumulated percolation within the first month after application. C_{mean} refers to average leachate concentration in the drainage water within the first drainage season after application (See Appendix 2 for calculation methods). The number of pesticide-positive samples is indicated in parentheses.

Crop and analysed pesticides	Application date	End of monitoring	Prec. (mm)	Perc. (mm)	1st month perc. (mm)	C_{mean} (µg/l)
Fodder beet 2000						
Metamitron (Goltix WG)	May 00	Apr 03	2634	1349	51	0.05 (69)
- *metamitron-desamino*						0.06 (61)
Ethofumesate (Betanal Optima)	May 00	Apr 03	2634	1349	51	0.03 (24)
Desmedipham (Betanal Optima)	May 00	Apr 03	2634	1349	51	<0.01 (1)
- *EHPC*						<0.02 (0)
Phenmedipham (Betanal Optima)	May 00	Apr 03	2634	1349	51	<0.01 (0)
- *MHPC*						<0.02 (0)
- *3-aminophenol*						<0.02 (0)
Fluazifop-P-butyl (Fusilade X-tra)	Jun 00	Jul 02	1953	1028	4	<0.01 (0)
- *fluazifop (free acid)*						<0.02 (1)
Pirimicarb (Pirimor)	Jul 00	Apr 03	2528	1295	3	0.01 (17)
- *pirimicarb-desmethyl*						<0.02 (1)
- *pirimicarb-desmethyl-formamido*						<0.02 (0)
Spring barley 2001						
Triazinamin-methyl 1) (Express)	May 01	Jul 03	1941	930	7	<0.02 (0)
Flamprop-M-isopropyl (Barnon Plus)	Jun 01	Jul 03†	1928	926	6	<0.01 (13)
- *flamprop (free acid)*						<0.01 (7)
Propiconazole (Tilt Top)	Jun 01	Jul 03†	1928	926	8	<0.01 (6)
Fenpropimorph (Tilt Top)	Jun 01	Jul 03	1928	926	8	<0.01 (0)
- *fenpropimorphic acid*						<0.01 (1)
Dimethoate (Perfection 500 S)	Jul 01	Jul 03	1882	921	6	0.02 (2)
Maize 2002						
Glyphosate (Roundup Bio)	Oct 01	Jul 03†	1487	779	44	0.13 (51)
-*AMPA*						0.06 (80)
PHCP 2) (Lido)	May 02	Jul 03†	1005	407	12	0.06 (18)
Terbuthylazine (Lido)	May 02	Jul 03†	1005	407	12	0.07 (70)
- *desethylterbuthylazine*						0.15 (85)
- *2-hydroxy terbuthylazine*						see text (12)
- *2-hydroxy-desethyl-terbuthylazine*						see text (16)
- *desisopropylatrazine*						see text (18)

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

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

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

†) *Monitoring will continue during the following year. The values for prec. and perc. are accumulated up to July 2003*

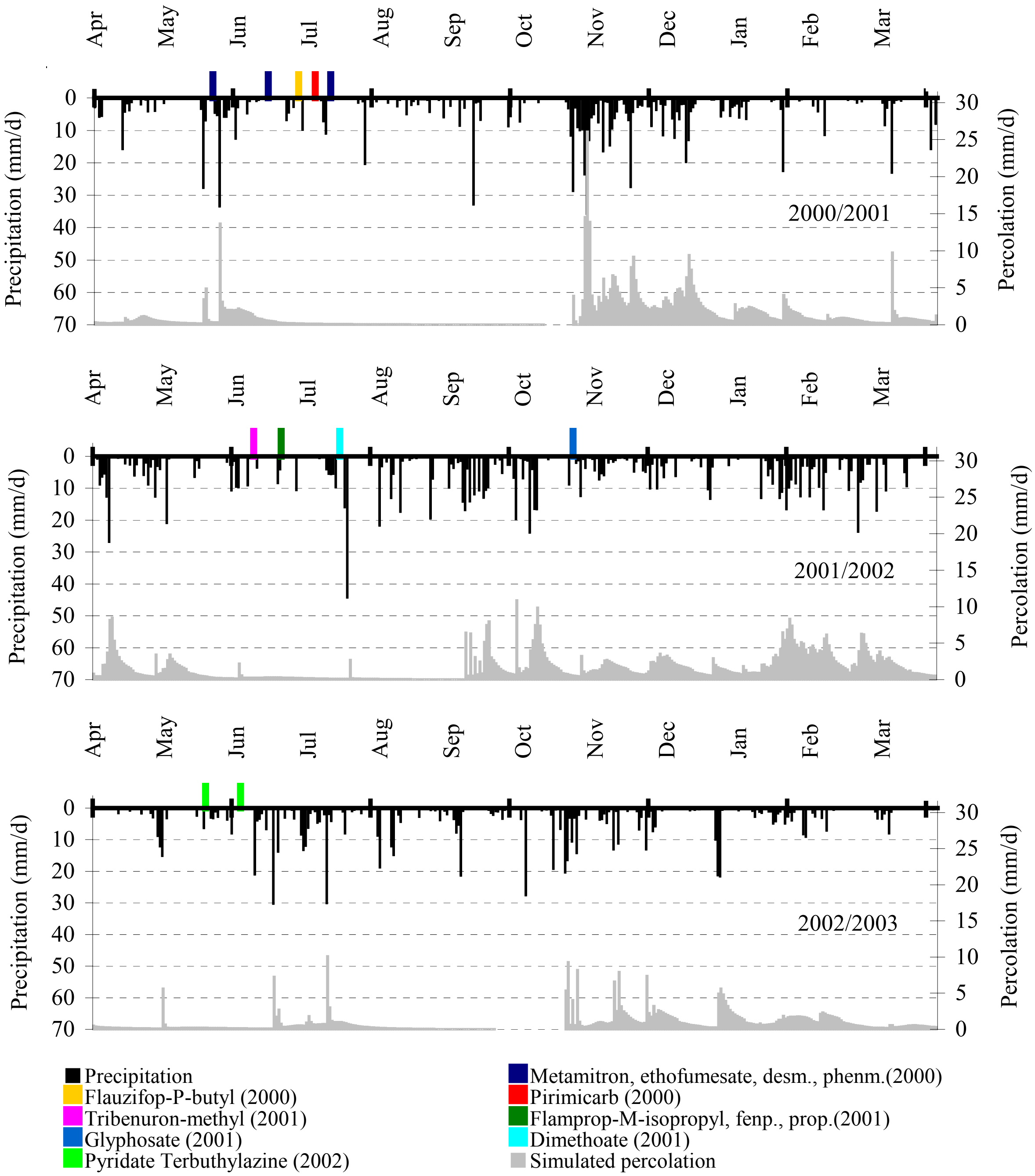

Figure 30. Pesticide application, precipitation and irrigation (primary axis) and simulated percolation 1 m b.g.s. (secondary axis) at Silstrup. Desm.: Desmedipham; Phenm.: Phenmedipham; Fenp.: Fenpropimorph; Prop.: Propiconazole. Pesticides applied later than April 2003 are not included. As pyridate and tribenuron methyl degrade rapidly it is their respective degradation products, PHCP and triazinamin-methyl, that are monitored.

It should also be noted that as tribenuron methyl (applied here as Express) and pyridate (applied here as Lido) degrade rapidly, the leaching risk is more associated with their respective degradation products, triazinamin-methyl and PHCP. For the same reasons it is the degradation products and not the parent compounds that are monitored in the PLAP (Table 8). Terbuthylazine has 4 relevant degradation products, of which only desethylterbuthylazine was included in the monitoring programme from the time terbuthylazine was applied. From February 2003 onwards the three remaining metabolites are also included, see Table 8. Pesticides applied later than April 2003 are not evaluated in this report and are hence are not included in Table 8.

The leaching risk of pesticides applied during 2000 has been evaluated in Kjær *et al.* (2003). The leaching risk of pesticides applied during 2001 and 2002 are summarised below.

No evidence was found to indicate leaching of ***fenpropimorph*** or of ***triazinamin-methyl.*** Apart from a single sample containing 0.019 µg/l fenpropimorphic acid, neither of the substances were detected.

Shortly after ***dimethoate*** had been applied in July 2001, a large precipitation event caused rapid leaching through the unsaturated zone (Figure 30). On 24 July, just eight days after application, dimethoate was detected at a concentration of 1.42 µg/l in the drainage water. This one sample is the reason why the average drainage water concentration of dimethoate is 0.02 µg/l (Table 8). In addition, dimethoate was detected in a concentration of 0.09 µg/l, in a sample from a horizontal screen approx. 3.5 m b.g.s.

Flamprop-M-isopropyl, flamprop (free acid), fenpropimorph (acid) and ***propiconazole*** leached in small amounts. All three substances were detected in several drain water samples. Apart from one sample containing 0.11 µg/l of flamprop-M-isopropyl, all concentrations were below 0.1 µg/l. See Kjær *et al.* (2003) for further details.

On 25 October 2001 the field was sprayed with ***glyphosate*** (1.44 kg/ha) in the form of Roundup Bio (4.0 l/ha). Prior to application there had been 4 major storm events yielding up to 11 mm/day of drainage runoff (Figure 31). The day before the field was sprayed there was 9 mm of precipitation. The preceding 13 days were practically precipitation-free, however. Five days after spraying, 12 mm of precipitation caused approximately 2 mm of runoff in which the flow-proportional concentration of glyphosate was 4.7 µg/l, and the time-proportional concentration was 1.9 µg/l. The corresponding AMPA concentrations were 0.06 and 0.14 µg/l, respectively (Figure 31B). The glyphosate concentration constantly decreased during the remainder of the leaching period 2001/2002. The AMPA concentration was lower, but more stable during the leaching period 2001/2002 (Figure 31C). Glyphosate and AMPA were detected in all drainage water samples except one. The weighted average concentration of glyphosate in the drainage water during 2001/2002 was 0.13 µg/l, while that of AMPA was 0.06 µg/l. Leaching might have been even greater had not November and December been so much dryer than usual (Appendix 4; Figure 31). It should be noted that drainage runoff commenced about one month prior to the application of glyphosate, and that the weighted average concentration in Table 8 refers to the period from the date of application until 1 July 2002. In the subsequent 2002/2003 leaching period both the number of pesticide-positive samples and the concentrations of glyphosate had decreased. The yearly average concentration in the drainage water amounted to 0.05 µg/l (Figure 31).

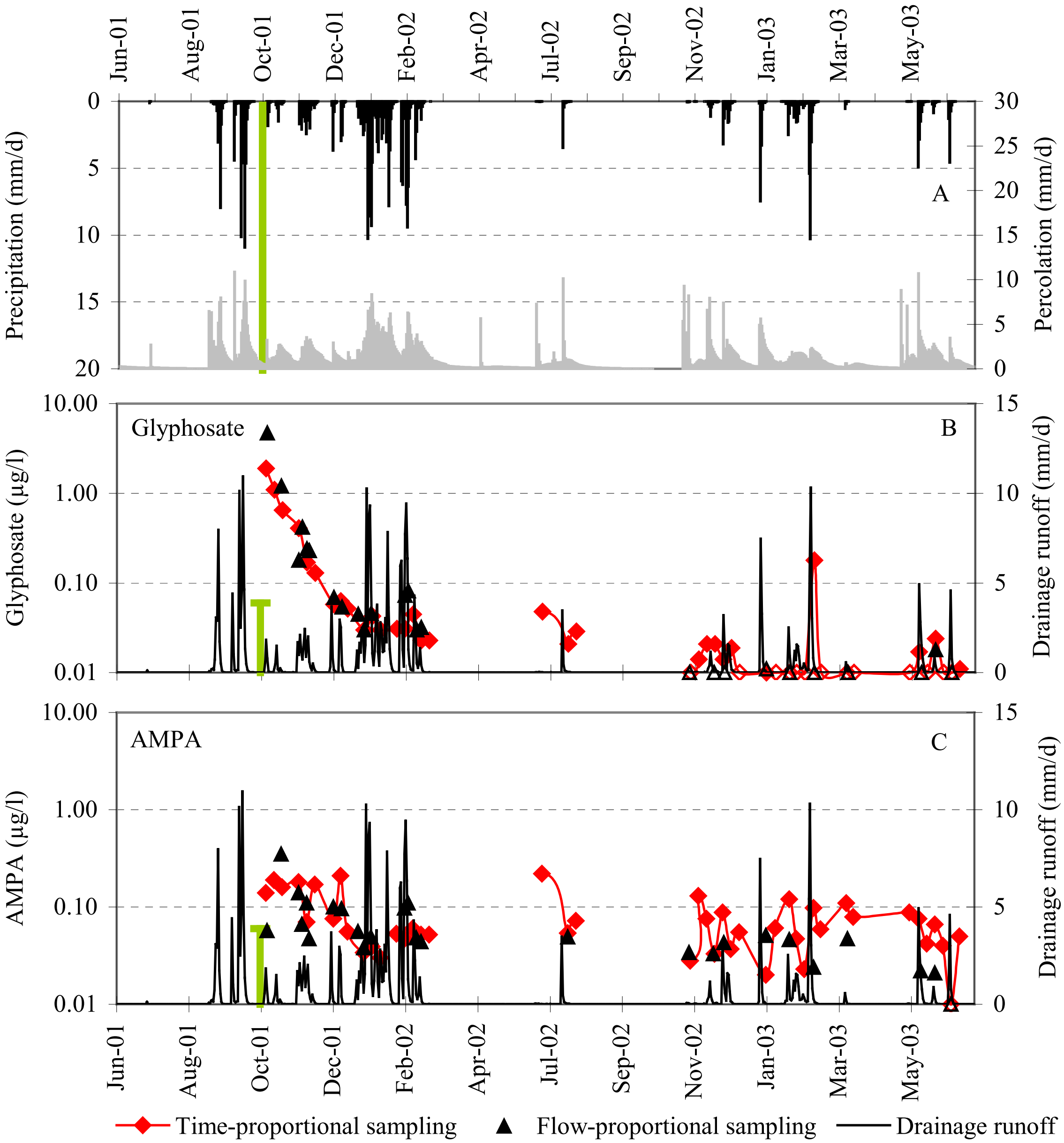

Figure 31. Precipitation and simulated percolation 1 m b.g.s. (A) together with concentration of glyphosate (B) and AMPA (C) in the drainage runoff at Silstrup. The green vertical line indicates the date of application.

Compared with glyphosate, the AMPA concentrations in 2002/2003 were markedly higher, as was the number of positive samples (Figure 31). AMPA-positive samples were numerous in both flow- and time-proportional drainage water samples. In fact, AMPA was present in all samples except one. Yearly average mean concentration of AMPA was 0.05 µg/l. In addition, glyphosate was detected in 4 samples from the groundwater monitoring screen and AMPA in 11, in each case at concentrations below 0.1 µg/l (Appendix 7).

In 2002 the field was sprayed with Lido, which contains pyridate and terbuthylazine. Pyridate is rapidly degraded and the leaching risk is therefore more associated with its degradation product PHCP. Besides terbuthylazine, at least four relevant degradation products are

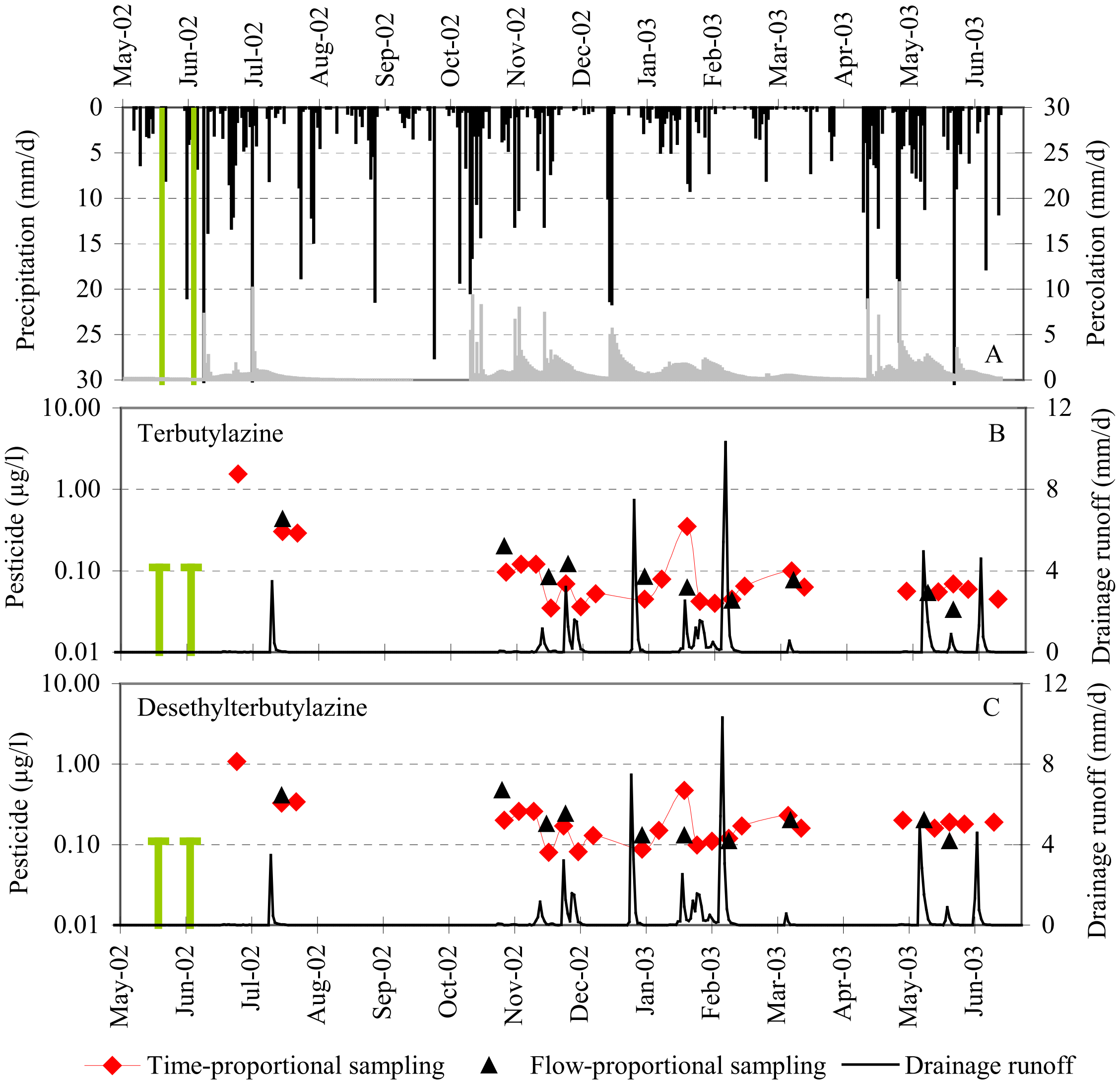

Figure 32. Precipitation and simulated percolation 1 m b.g.s (A) together with concentration of desethylterbuthylazine (B) and terbuthylazine (C) in the drainage runoff at Silstrup. The green vertical lines indicate the dates of application.

at risk of leaching. Unfortunately, however, only one of them, i.e. desethylterbuthylazine, was included from the start of the monitoring. Literature findings suggest that desethylterbuthylazine together with terbuthylazine pose the primary risk, whereas the remaining degradation products will mainly be mobilized later on in the degradation pathway (Guzella *et al.,* 2003). As at least two years of monitoring are needed before the leaching risk can be fully evaluated, the following results must be considered preliminary.

Terbuthylazine and its degradation product ***desethylterbuthylazine*** leached from the root zone to both the drainage system and several groundwater monitoring screens. Some 3 weeks after the second application of Lido, terbuthylazine and desethylterbuthylazine were thus found in a time proportional sample of drainage water in concentrations of 1.55 and 1.08 µg/l respectively (Figure 32). At the time of the first detection, drainage runoff was negligible, however. Total precipitation between the time of application and detection was

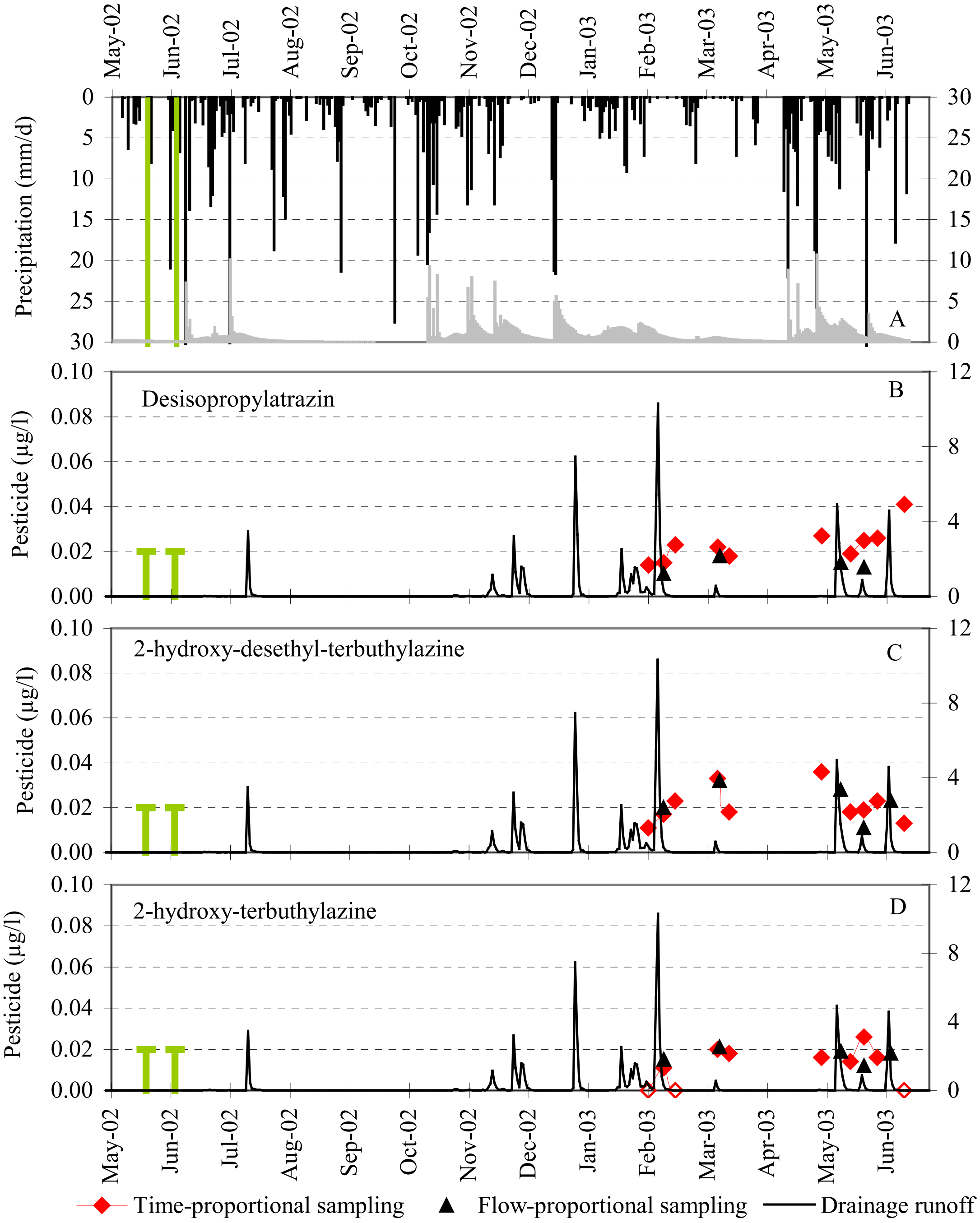

Figure 33. Precipitation and simulated percolation 1 m b.g.s. (A) together with concentration of desisopropylatrazine (B) and 2-hydroxy-desethyl-terbuthylazine (C) and 2-hydroxy-terbuthylazine (D) in the drainage runoff at Silstrup. The substances have been included in the monitoring programme since February 2003. The green vertical lines indicate the dates of terbuthyl application. Open diamonds indicate values below the detection limit of 0.01 µg/l.

85 mm, of which 65 mm fell on 3 separate days, the largest storm event amounting to 30 mm. Besides the sporadic detection of terbuthylazine and desethylterbuthylazine in June and July, both of the substances were found continuously from the onset of the main drainage period, which was at the end of October that year (Figure 32). Comparing on a day-by-day basis, the concentrations of desethylterbuthylazine in drainage water were higher than those of terbuthylazine. The weighted average concentration of terbuthylazine in drainage water this first year was 0.07 µg/l, whereas that of desethylterbuthylazine was 0.15 µg/l.

The concentrations of the remaining three metabolites are shown in Figure 33B C and D. These were much lower than those of terbuthylazine and desethylterbuthylazine. However, since they were not included from the beginning, it is difficult to determine whether the low concentrations are due to leaching prior to the start of the monitoring, or a time lag in their formation as compared to that of desethylterbuthylazine. Consequently their mean average concentrations have not been calculated. Re-evaluation of chromatograms revealed that desisopropylatrazine was not present at concentration exceeding 0.03 µg/l, however.

Terbuthylazine and desethylterbuthylazine have both been frequently detected in groundwater samples from both vertical and horizontal monitoring wells (Appendix 7). The concentrations of terbuthylazine and desethylterbuthylazine in monitoring well M5 are shown in Figure 34. On 18 June, the day before the second application, it rained 30 mm, yielding a modelled percolation of 7 mm. On the day of pesticide application itself it did not rain, but 14 mm fell the following day yielding 3 mm of percolation. From then on until sampling on 25 June the average, daily percolation was calculated to be less than 0.5 mm. In view of the time of the first detection – June – the likely explanation is preferential flow.

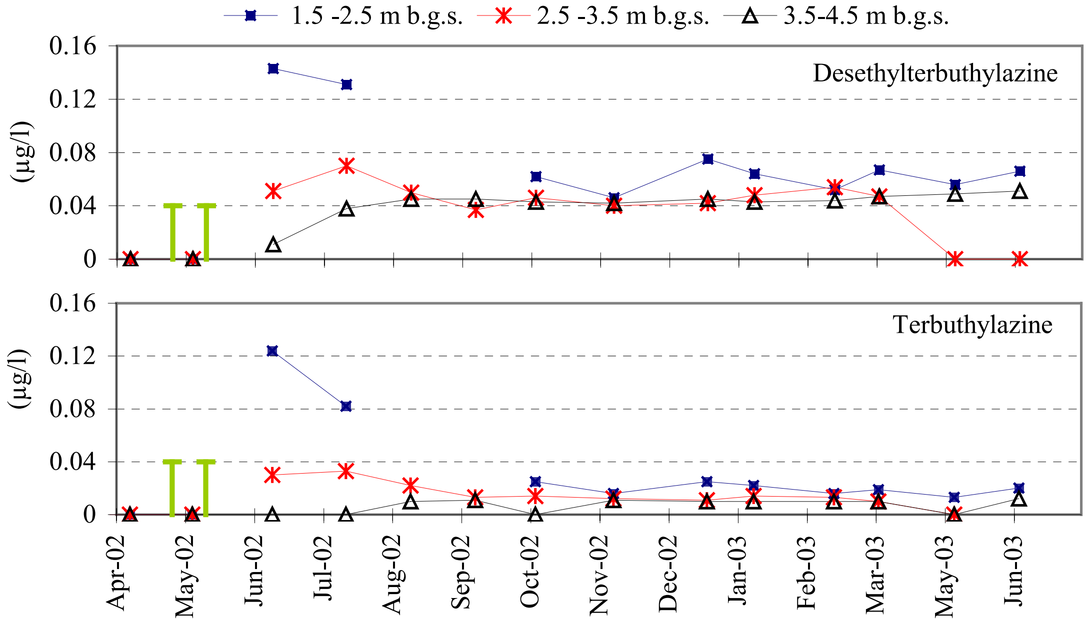

Figure 34. Concentration of desethylterbuthylazine and terbuthylazine in well M5. The green vertical lines indicate the dates of application.

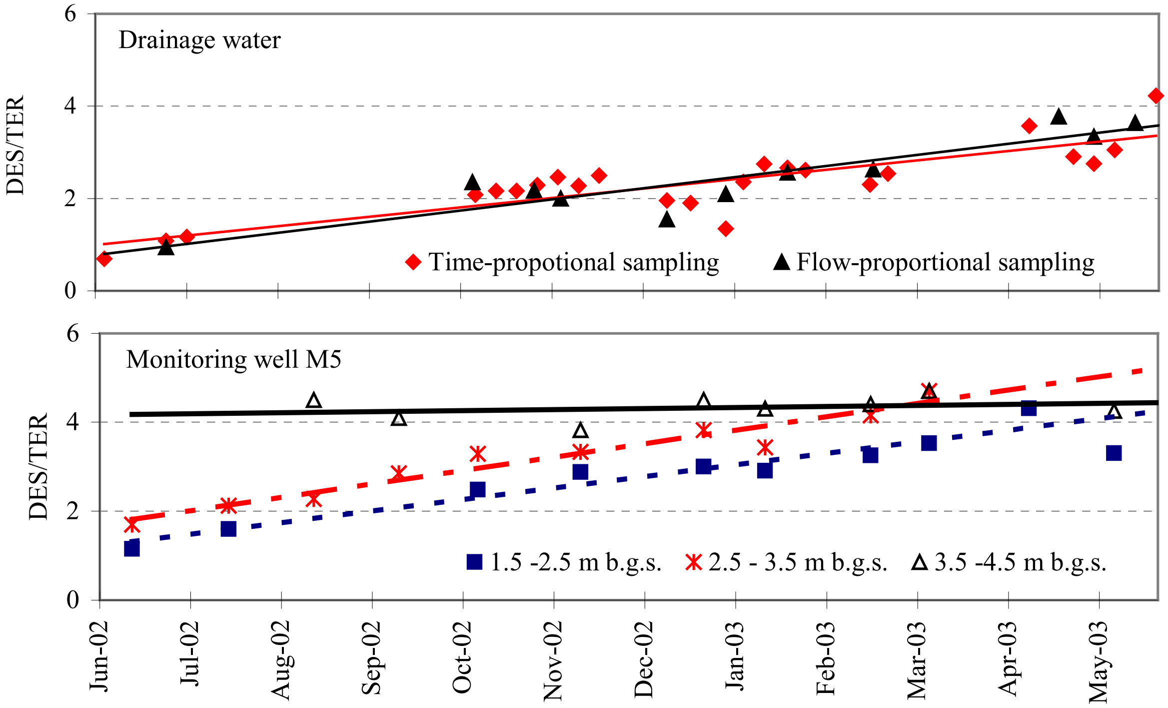

Figure 35. Ratio between measured concentration of terbuthylazine (TER) and desethylterbuthylazine (DES) in samples from both drainage water system (upper) and monitoring well M5 (lower). As the ratio could only be calculated when both substances were present in the samples, the five groundwater samples from M5 in which either TER or DES was absent (indicated in Figure 34) were excluded from the analysis.

The terbuthylazine:desethylterbuthylazine ratio has been calculated for samples collected from both the drainage water system and monitoring well M5 (Figure 35). The ratio increases with time in both drainage water and the two uppermost screens of M5, possibly due to an increasing concentration of desethylterbuthylazine as a consequence of terbuthylazine degradation or to a decrease in terbuthylazine due to adsorption. In the deepest filter of M5, desethylterbuthylazine was detected two months prior to terbuthylazine. Desethylterbuthylazine was always present in the highest concentrations. Throughout the monitoring period the terbuthylazine concentration was below or just slightly above the detection limit whereas desethylterbuthylazine was found in a significantly higher and almost constant concentration. The terbuthylazine:desethylterbuthylazine ratio in the water samples from the deepest screen seems to be constant over time. The terbuthylazine had already degraded to desethylterbuthylazine by the time the water entered the deep screen. This, so to say, indigenous content of terbuthylazine and desethylterbuthylazine was maintained throughout the monitoring period, probably due to the very low biological and chemical activity at this depth.

One of the three degradation products, i.e. 2-hydroxy-terbutylazine, has not been detected beneath the drains. The degradation product 2-hydroxy-desethyl-terbutylazine has been found just once in the M5.1, i.e. the uppermost filter, in a concentration of 0.016 µg/l. The last of the three degradation products, desisopropylatrazine, has been detected in M5 (1.5–2.5. m b.g.s.) in concentrations around 0.01 µg/l on three occasions – 4 February, 1 April and 1 July. In one instance, 3 June, desisopropylatrazine was detected in M5 (3.5–4.5 m

1 July. In one instance, 3 June, desisopropylatrazine was detected in M5 (3.5–4.5 m b.g.s.) at a concentration of 0.047 µg/l.

PHCP: As for terbuthylazine/desethylterbuthylazine, single precipitation events (occurring shortly after application) caused rapid leaching of PHCP, which reached both the drainage system and several groundwater monitoring screens (Appendix 7). On 3 July the PHCP concentration was 0.042 and 0.035µg/l in two of the horizontal screens of H1 located 3.5 m b.g.s. (Figure 25). In samples from the uppermost screens of the vertical monitoring wells M9 and M13 located alongside the test field (1.5 to 2.5 m b.g.s.) the PHCP concentration was 0.048 and 0.041 µg/l, respectively. In M5 located downstream of the test field, PHCP was present in the three upper screens (1.5 to 4.5 m b.g.s.) in concentrations decreasing with depth from 0.309 µg/l in the uppermost to 0.091µg/l in the lowermost. In M9 and M13, PHCP was detected just once. In the shallowest two screens of M5, PHCP was present in the following month. In the deeper screen it could be found 4 months after the initial detection in steadily decreasing concentrations (see Appendix 7). PHCP was first detected in drainage water on 25 June (2.64µg/l) in a time-proportional sample and subsequently on 16 July in time- and flow-proportional samples (1.107 and 0.207 µg/l, respectively). The following week it was detected in a concentration of 0.987 µg/l a time-proportional sample. No PHCP was detected in any of the subsequent drainage samples.

5 Pesticide leaching at Estrup

5.1 Material and methods

5.1.1 Site description and monitoring design

Estrup is located in central Jutland (Figure 1) west of the Main Stationary Line on a hill-island, i.e. a glacial moraine preserved from the Weischselian Glaciation. Estrup has thus been exposed to weathering, erosion, leaching and other geomorphologic processes for a much longer period than that of the other sites. The test field covers a cultivated area of 1.26 ha (105 x 120 m) and is virtually flat (Figure 36). The site is highly heterogeneous with considerable variation in both topsoil and aquifer characteristics (Table 1). Such heterogeneity is quite common for this geological formation, however. Based on three profiles excavated in the buffer zone bordering the field the soil was classified as Abruptic Argiudoll, Aquic Argiudoll and Fragiaquic Glossudalf (Soil Survey Staff, 1999). The topsoil is characterized as sandy loam with a clay content of 10–20% and an organic carbon content of 1.7–7.3%. The site is also characterized by a C horizon of low permeability. The saturated hydraulic conductivity in the C horizon is 10^{-8} m/s, which is about two orders of magnitude lower than at the other loamy sites (Table 1). The geological structure is complex comprising a clay till core with deposits of different age and composition (Figure 37). A brief description of the sampling procedure is provided in Appendix 2. The monitoring design and test site are described in detail in Lindhardt *et al.* (2001) and the analysis methods in Kjær *et al.* (2002). Please note that the geological conditions only allowed one of the planned horizontal wells to be installed as drilling in sand proved impossible.

5.1.2 Agricultural management

Management practice during the two most recent growing seasons is briefly summarised below and detailed in Appendix 3 (Table A3.4). For information about management practice during the first two monitoring periods see Kjær *et al*. (2003).

Winter wheat (cv. Ritmo) was sown on 19 October 2001, much later than usual due to the very wet weather in August and September. Due to the unusually high temperatures in October, however, the wheat emerged just 12 days later. Weeds were sprayed in autumn with ioxynil and bromoxynil on 20 November and again in spring using amidosulfuron on 25 April and MCPA on 13 May. Propiconazole was sprayed to combat fungi on 27 May and 17 June, while pirimicarb was sprayed to combat pests on 24 June. The winter wheat was harvested 9 August yielding 69.4 hkg/ha (85% dry matter). A higher yield could have been obtained had the crop been sown in due time. Ponding was observed at a small area of the southeastern part of the field near S2. In autumn 2002 this problem was solved by repairing a drainpipe inadvertently damaged, presumably during installation of the monitoring equipment in the buffer zone (Lindhardt *et al.,* 2001).

On 2 September 2002 the field was sprayed with glyphosate. On 14 April 2003 cattle slurry (60.8 tonnes/ha) was applied and the field ploughed the following day. On 16 April the field was sown with fodder beet (cv. Magnum). On the day of emergence, 8 May, the field was sprayed for the first of three times using the herbicides metamitron, phenmedipham, desmedipham and ethofumesate. Phenmedipham and desmedipham are not included in the monitoring programme, however. The second and third applications were on 22 May and 16 June. Wind drift of Amistar (azostrobin) and Stereo (cyprodinil and propiconazole) from the field to the west was observed on 13 June. This did not cause any visible damage to the crop, however. The pesticide pirimicarb was sprayed on 28 July to combat aphids. The crop was harvested on 20 October yielding 189.5 hkg/ha roots and 34.2 hkg/ha tops (both 100% dry matter).

5.1.3 Model set-up and calibration

The MACRO model is applied to the Estrup site covering the soil profile to a depth of 5 m b.g.s., always including the groundwater table. The model is used to simulate the water flow in the unsaturated zone during the monitoring period from July 2000–June 2003 and to establish an annual water balance.

The model was calibrated to the observed groundwater table measured in the piezometers located in the buffer zone as well as to measured drainage flow and measured time series of soil water content at one depth (25 cm b.g.s.) from a single soil profile S1 (Figure 36). The TDR probes installed at the other depths yielded unreliable data with saturations far exceeding 100% and dynamics with increasing soil water content during the drier summer periods. At present no explanation can be given for the unreliable data, and they have been excluded from the analysis. The data from the soil profile S2 have also been excluded due to a problem of water ponding above the TDR probes installed at S2, as mentioned in Kjær *et al.* (2003). Because of the erratic TDR data, calibration data is limited at this site. For a detailed description of data acquisition, model set-up and calibration procedures see Kjær *et al.* (2002) and (2003).

The latest year of the monitoring period, July 2002–June 2003, is considered a validation period and no further model calibration has therefore been performed. The model set-up is thus identical to that reported in Kjær *et al.* (2003), although with the precipitation, evapotranspiration and plant data having been prolonged by one year.

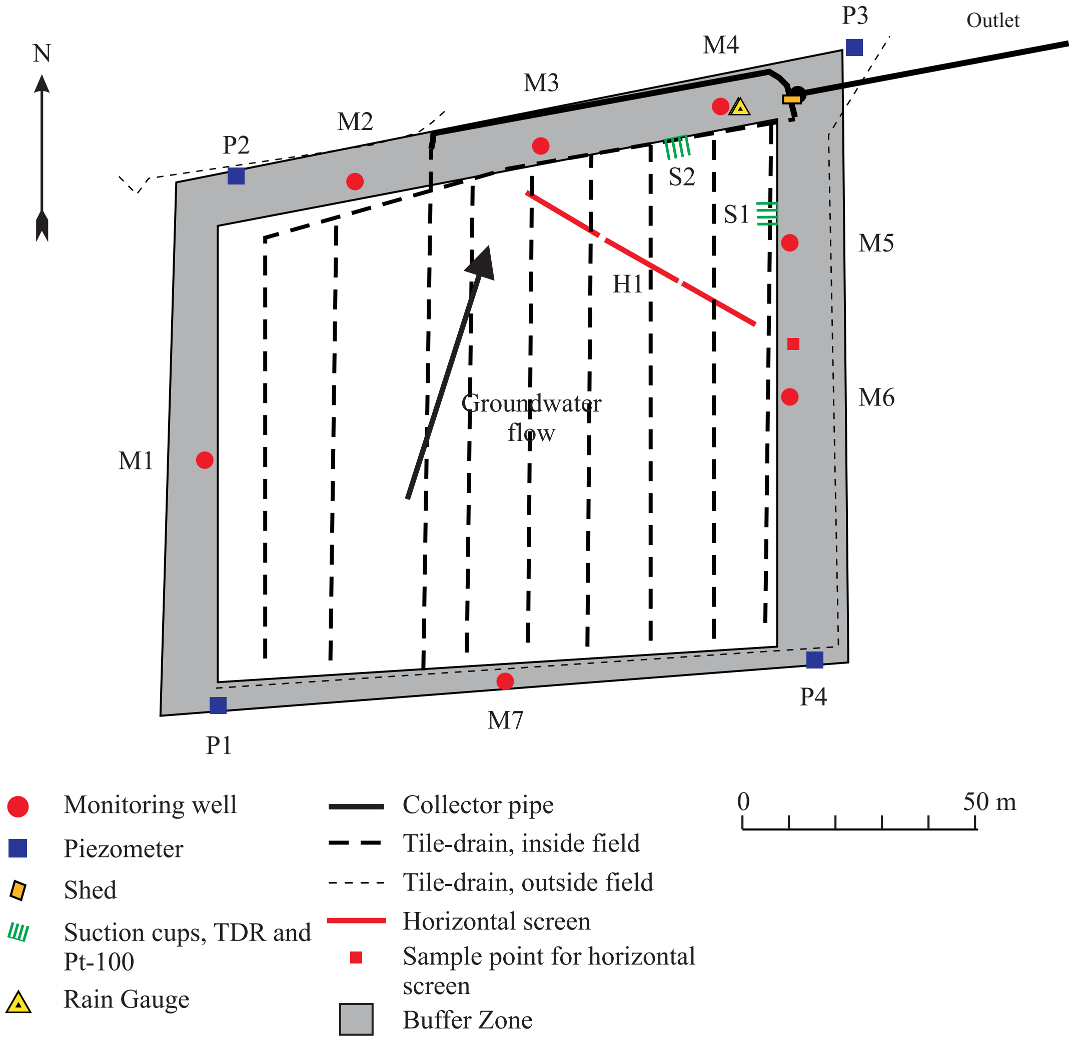

Figure 36. Overview of the Estrup site. The innermost white area indicates the cultivated land, while the grey area indicates the surrounding buffer zone. The positions of the various installations are indicated, as is the direction of groundwater flow (by an arrow).

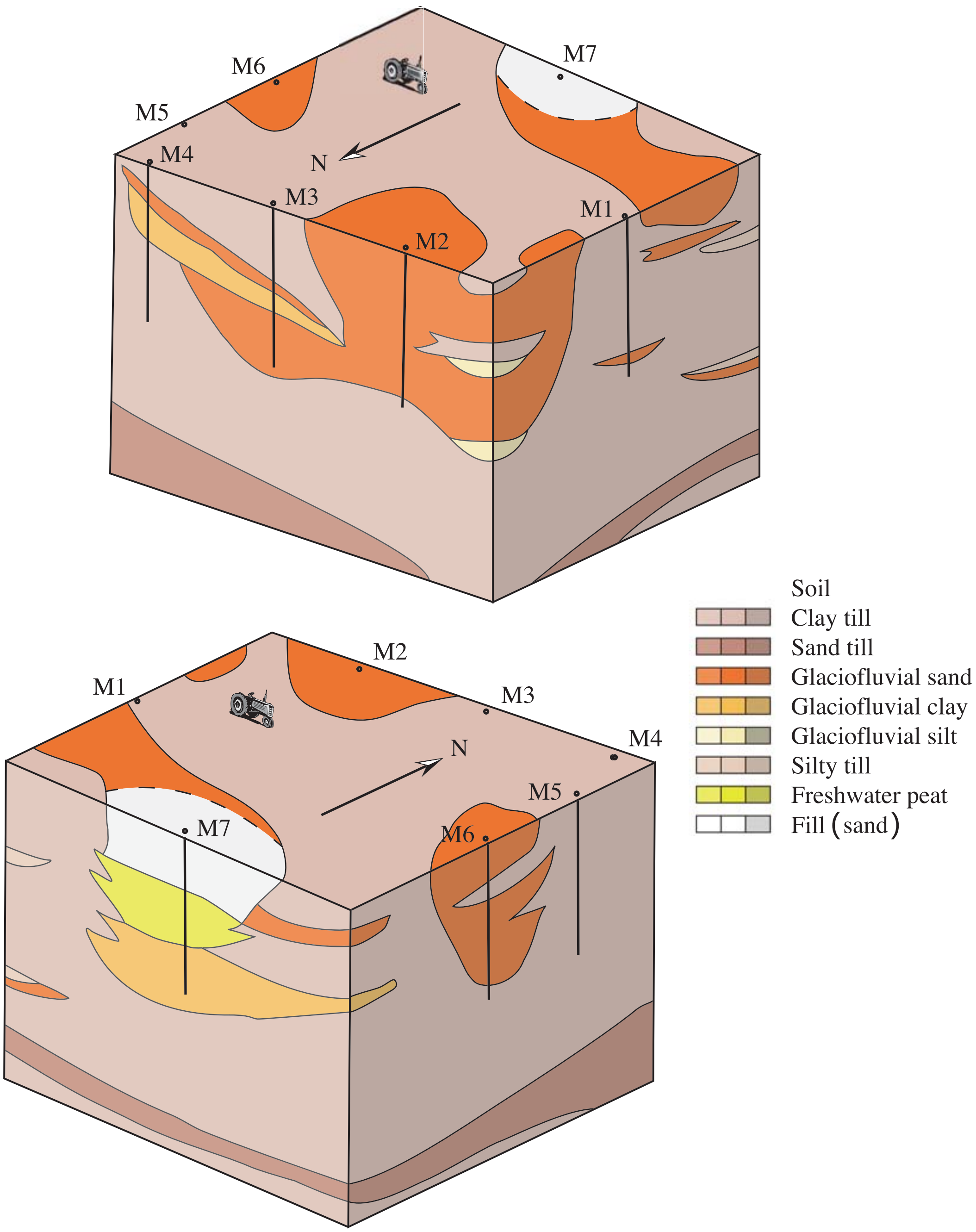

Figure 37. Geological description of the Estrup site (Lindhardt *et al.,* 2001).

5.2 Results and discussion

5.2.1 Soil water dynamics and water balances

Model validation shows that the latest model simulations, July 2002–June 2003, are generally consistent with the observed data (which is limited compared to other PLAP sites, as noted above), indicating a reasonable model description of the overall soil water dynamics in the unsaturated zone (Figure 38). The model provides an acceptable simulation of the overall level of the groundwater table, but the falling groundwater table during the dry periods of 2002/2003 is not well captured by the model (Figure 38B). Periods of low precipitation (Figure 38A) are seen to be followed by a drop in the level of measured groundwater table. The modelled groundwater table does not seem as sensitive to these periods of low precipitation, and the simulated groundwater table tends not to drop to the low measured values. This can be due to inaccurate model description of the macropore-matrix interaction causing drainage of macropores without the right exchange to the matrix is taking place, and will be studied later. As already mentioned, TDR data are limited in the subsoils, thus making a study of dynamics in these layers difficult. As in previous years (Kjær *et al.*, 2003) the simulated groundwater table often fluctuates slightly above the drain depth during periods of drainage flow.

The simulated drainage flow for the latest monitoring period (July 2002–June 2003) well matches the measured drainage flow, but not as well as for previous years (Figure 38C). The onset of the drainage flow is well captured, but the model does not replicate the two peaks in August. Moreover, from the end of January to the beginning of March the pattern is not fully consistent with the measurement data. The differences are most likely due to the above-mentioned inaccuracies in the simulated groundwater table. Drainage runoff last year is also high compared with that in the other three till sites investigated in the PLAP, this being due to the significantly lower permeability of the C horizon than that of the overlying A and B horizons (Kjær *et al.*, 2003).

Precipitation during the latest monitoring period (July 2002–June 2003) is characterised by high precipitation in the summer (July–August) and low precipitation during the winter (December–March) (Appendix 4). This is reflected in the drainage flow, which is higher during the summer and lower during the winter than in previous years (Figure 38C). Furthermore, the last drainage season is significantly different from past seasons. Drainage runoff is almost continuous throughout the latest monitoring period, with a brief respite in September (which receives little precipitation) and a longer respite in April (caused by low precipitation in the winter). In previous periods the drainage season was shorter, starting in September/October and continuing until April/June. During the last period, moreover, drainage runoff was higher in May/June due to several rain events. Peak flow was generally lower than in previous years.

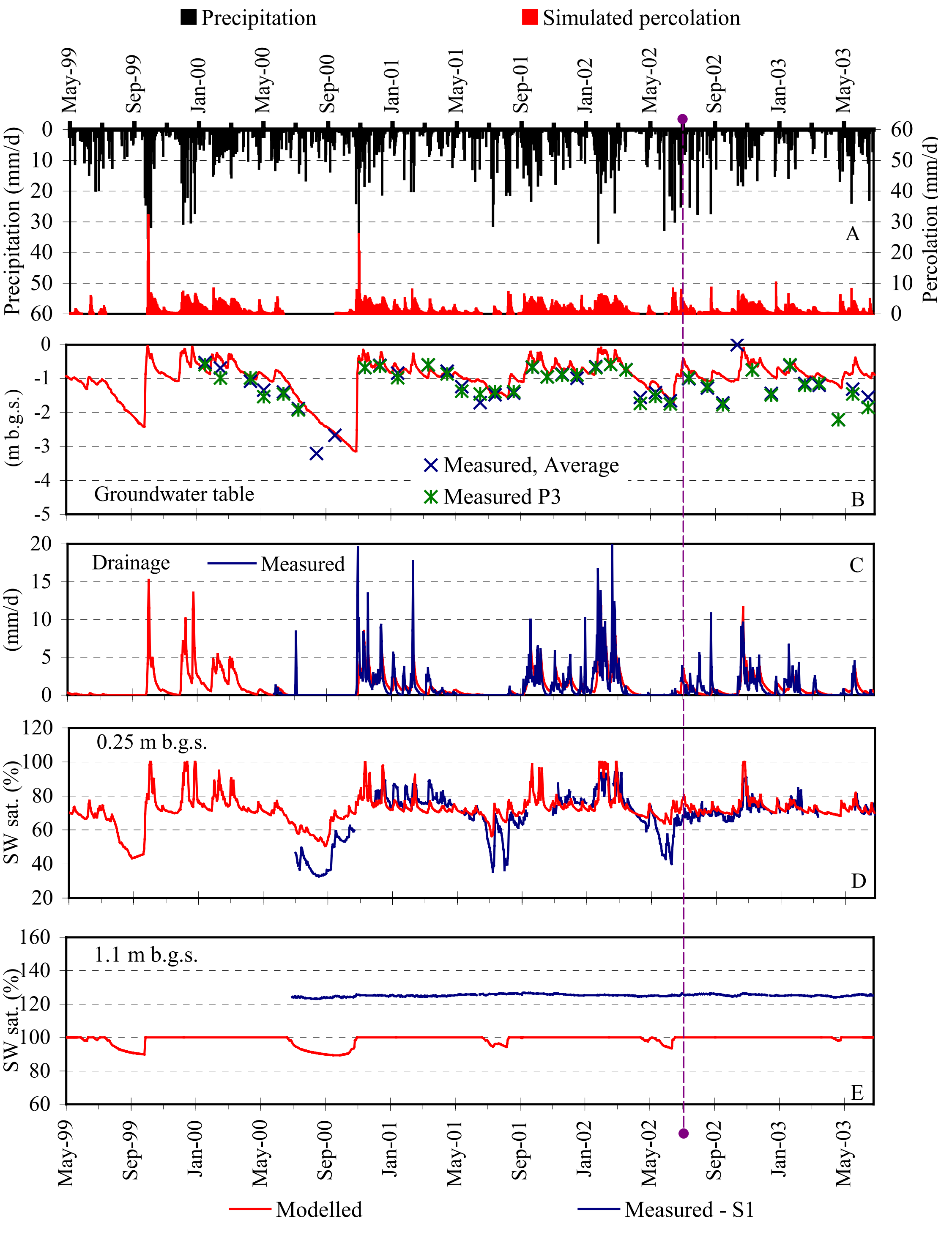

Figure 38. Soil water dynamics at Estrup: Measured precipitation and simulated percolation 0.6 m b.g.s. (A), simulated and measured groundwater level (B), simulated and measured drainage flow (C), and simulated and measured soil saturation (SW sat.) at two different soil depths (D and E). The measured data in B derive from piezometers located in the buffer zone. The measured data in D and E derive from TDR probes installed at S1 (see Figure 36). The broken vertical line indicates the beginning of the validation period (July 2002–June 2003).

Percolation at Estrup is shown at 0.6 m b.g.s. instead of at 1 m b.g.s. because the soil at 1 m b.g.s. is saturated for longer periods (Figure 38). In the latest monitoring period, percolation took place continuously from August to the end of the period. The earlier onset, as compared to previous years, is attributable to the rainy summer of 2002. From January to March, percolation in the latest monitoring period was lower than in previous periods due to the low precipitation in the winter. From April to May, percolation was greater because of a period with many rain events (Figure 38A).

The resultant annual water balance for Estrup is shown in Table 9 (July–June) for the four, modelled periods. Annual precipitation for the latest monitoring period is the closest to the "normal" value, but otherwise there is nothing particular to note about the water balance for the current period. For information about the water balance in previous monitoring periods see Kjær *et al.* (2003).

Table 9. Annual water balance for Estrup (mm/year). Precipitation is corrected to the soil surface according to the method of Allerup and Madsen (1979).

	Normal precipitation [2]	Precipitation	Actual evapotranspiration	Measured drainage	Simulated drainage	Groundwater recharge [3]
1.7.99–30.6.00 [1]	968	1174	440	–	518	216 [4]
1.7.00–30.6.01	968	887	386	356	307	145
1.7.01–30.6.02	968	1291	504	505	512	282
1.7.02–30.6.03	968	939	362	329	365	248

[1] *Monitoring started in April 2000*

[2] *Normal values based on time series for 1961–1990 corrected to the soil surface*

[3] *Groundwater recharge is calculated as precipitation - actual evapotranspiration - measured drainage*

[4] *Where drainage flow measurements are lacking, simulated drainage flow was used to calculate groundwater recharge*

5.2.2 Bromide leaching

At Estrup, total recovery of bromide in the drainage water during the three-year monitoring period amounted to 5.2 kg/ha, indicating that 27% of the applied tracer had leached into the drains. The concentration level decreased over the monitoring period and during the last year was very close to the detection limit of 0.1 mg/l in suction cups situated 1 m b.g.s. as well as in the drainage water (Figure 39A and B). In conclusion, the major part of the bromide is still retained within the root zone (1 m b.g.s.), probably in the matrix. Although the retained bromide can be expected to leach continuously for a long period of time, the data indicates decreased leaching over time. During the latest monitoring period (1.7.02–30.6.03) the leaching of bromide into the drainage system amounted to just 0.4 kg/ha.

The bulk of the leached bromide probably left the system through drainage runoff as the modelled water balance suggested that 53–77% of the percolating water left through the drainage system. However, the results did show subsequent leaching of small amounts of bromide to the suction cups and monitoring screen situated beneath the drainage system (Figure 39B and D). Slightly elevated concentrations were detected in suction cups located 2 m b.g.s as well as in the horizontal well situated 3.5 m b.g.s. Although the concentrations and frequencies of detection were very low, slightly elevated concentrations were also seen in the downstream monitoring wells, especially in wells M3 and M4 (Figure 40).

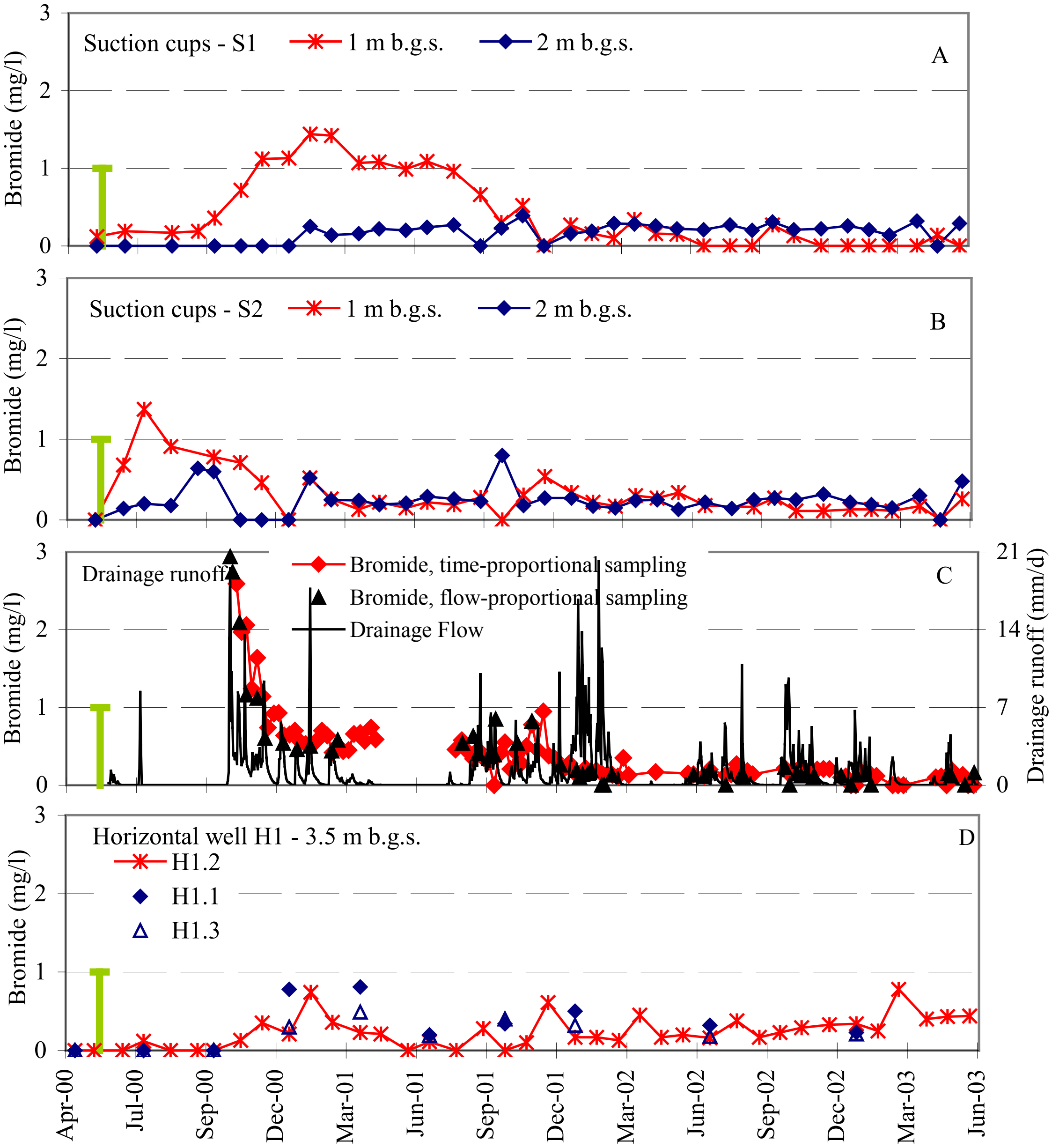

Figure 39. Bromide concentration at Estrup. A and B refer to suction cups located at S1 and S2. The bromide concentration is also shown for drainage runoff (C) and the horizontal monitoring well H1 (D). The green vertical line indicates the date of bromide application.

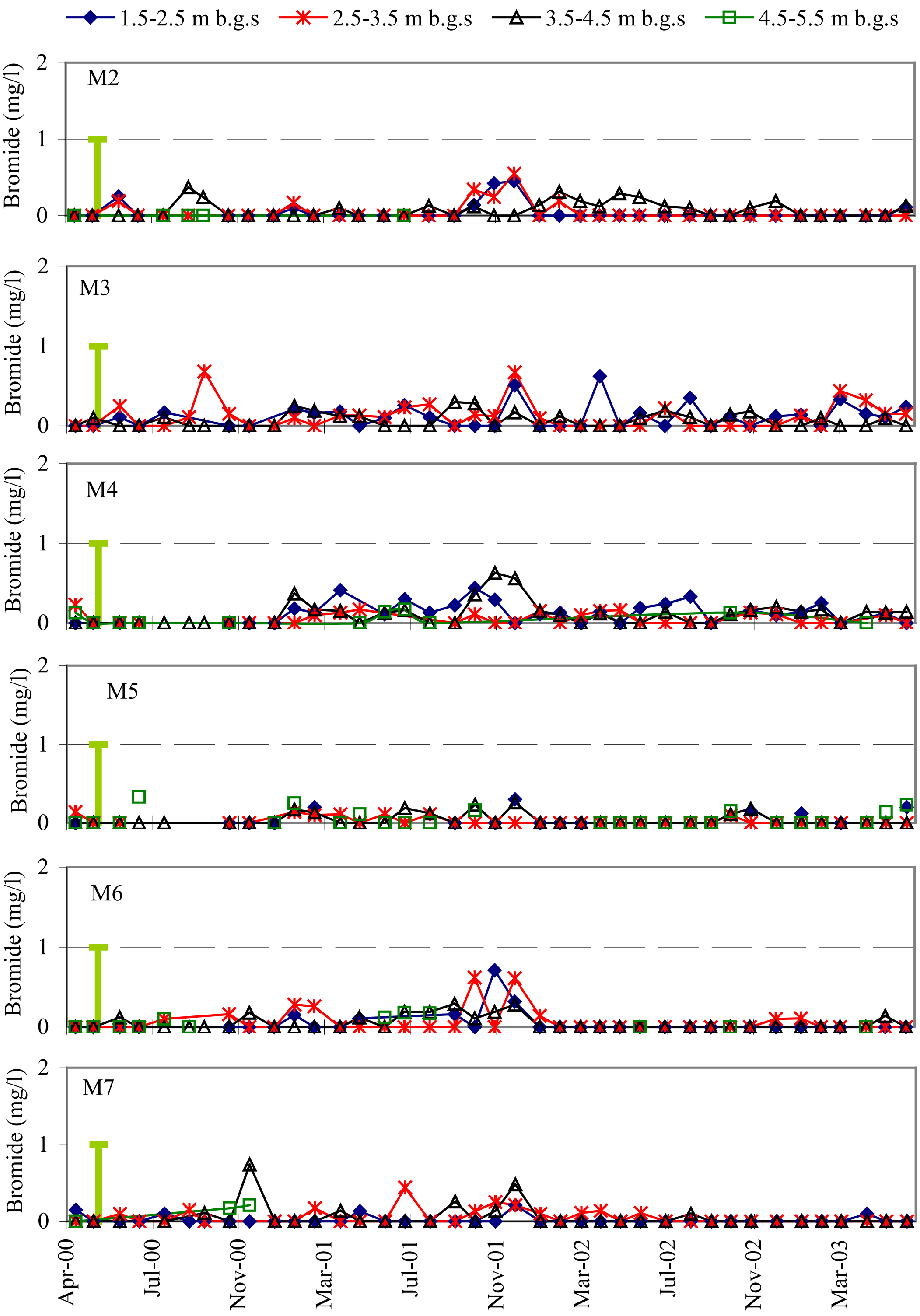

Figure 40. Bromide concentration at Estrup. The data derive from the vertical monitoring wells (M2–M7). Screen depth is indicated in m b.g.s. The green vertical line indicates the date of bromide application.

5.2.3 Pesticide leaching

Monitoring began at Estrup in April 2000 and presently encompasses 13 pesticides and several degradation products as indicated in Table 10 and Figure 41. It should be noted that precipitation in Table 10 is corrected to the soil surface according to Allerup and Madsen (1979), whereas percolation (0.6 m b.g.s.) refers to accumulated percolation as simulated with the MACRO model (Section 5.2.1). Moreover, pesticides applied later that April 2003 are not evaluated in this report and hence are not included in Table 10.

Table 10. Pesticides analysed at Estrup with the product used shown in parentheses. Degradation products are in italics. Precipitation (prec.) and percolation (perc.) are accumulated from the date of first application until the end of monitoring. 1st month perc. refers to accumulated percolation within the first month after application. C_{mean} refers to average leachate concentration in the drainage water within the first drainage season after application (See Appendix 2 for calculation methods). The number of pesticide-positive samples is indicated in parentheses.

Crop and analysed pesticides	Application date	End of monitoring	Prec. (mm)	Perc. (mm)	1st month perc. (mm)	C_{mean} (µg/l)
Spring barley 2000						
Metsulfuron-methyl (Ally)	May 00	Apr 03	2990	1637	33	<0.01(1)
- *triazinamin*						<0.02(1)
Flamprop-M-isopropyl (Barnon Plus)	May 00	Apr 03	2914	1614	5	0.02(20)
- *flamprop (free acid)*						0.01(13)
Propiconazole (Tilt Top)	Jun 00	Jul 03	3150	1718	0	0.01(26[*])
Fenpropimorph (Tilt Top)	Jun 00	Jul 02	2211	1158	0	<0.01(1)
- *fenpropimorphic acid*						<0.02(0)
Dimethoate (Perfection 500 S)	Jun 00	Jul 02	2211	1158	0	<0.01(0)
Pea 2001						
Glyphosate (Roundup Bio)	Oct 00	Jul 03[†]	2899	1725	135	0.54(121[*])
- *AMPA*						0.17(136[*])
Bentazone (Basagran 480)	May 01	Jul 03	2302	1246	15	0.03(52)
- *2-amino-N-isopropyl-benzamid*						<0.02(1)
Pendimethalin (Stomp)	May 01	Jul 03	2302	1246	15	<0.01(4)
Pirimicarb (Pirimor)	Jun 01	Jul 03	2235	1231	9	0.01(28[*])
- *pirimicarb-desmethyl*						<0.02(0)
- *pirimicarb-desmethyl-formamido*						<0.02(6[*])
Winter wheat 2002						
Ioxynil (Oxitril CM)	Nov 01	Jul 03[†]	1674	957	56	0.03(20)
Bromoxynil (Oxitril CM)	Nov 01	Jul 03[†]	1674	957	56	0.01(3)
Amidosulfuron (Gratil 75 WG)	Apr 02	Jul 03[†]	1220	612	12	<0.01 (0)
MCPA (Metaxon)	May 02	Jul 03[†]	1163	599	0	<0.01(12)
- *4-chlor,2-methylphenol*						<0.01(1)
Propiconazole (Tilt 250 EC)	May 02	Jul 03[†]	1132	601	38	0.02 (26[*])
Pirimicarb (Pirimor)	Jun 02	Jul 03[†]	959	561	63	0.01(28[*])
- *pirimicarb-desmethyl*						<0.02(0)
- *pirimicarb-desmethyl-formamido*						<0.02(6[*])
Fodder beet 2003						
Glyphosate (Roundup Bio)	Sep 02	Jul 03[†]	704	467	15	0.43(121[*])
- *AMPA*						0.19(136[*])

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

*) *Pesticide have been applied twice and the findings are not necessarily related to one specific application*

†) *Monitoring will continue during the following year. The values for prec. and perc. are accumulated up to July 2003*

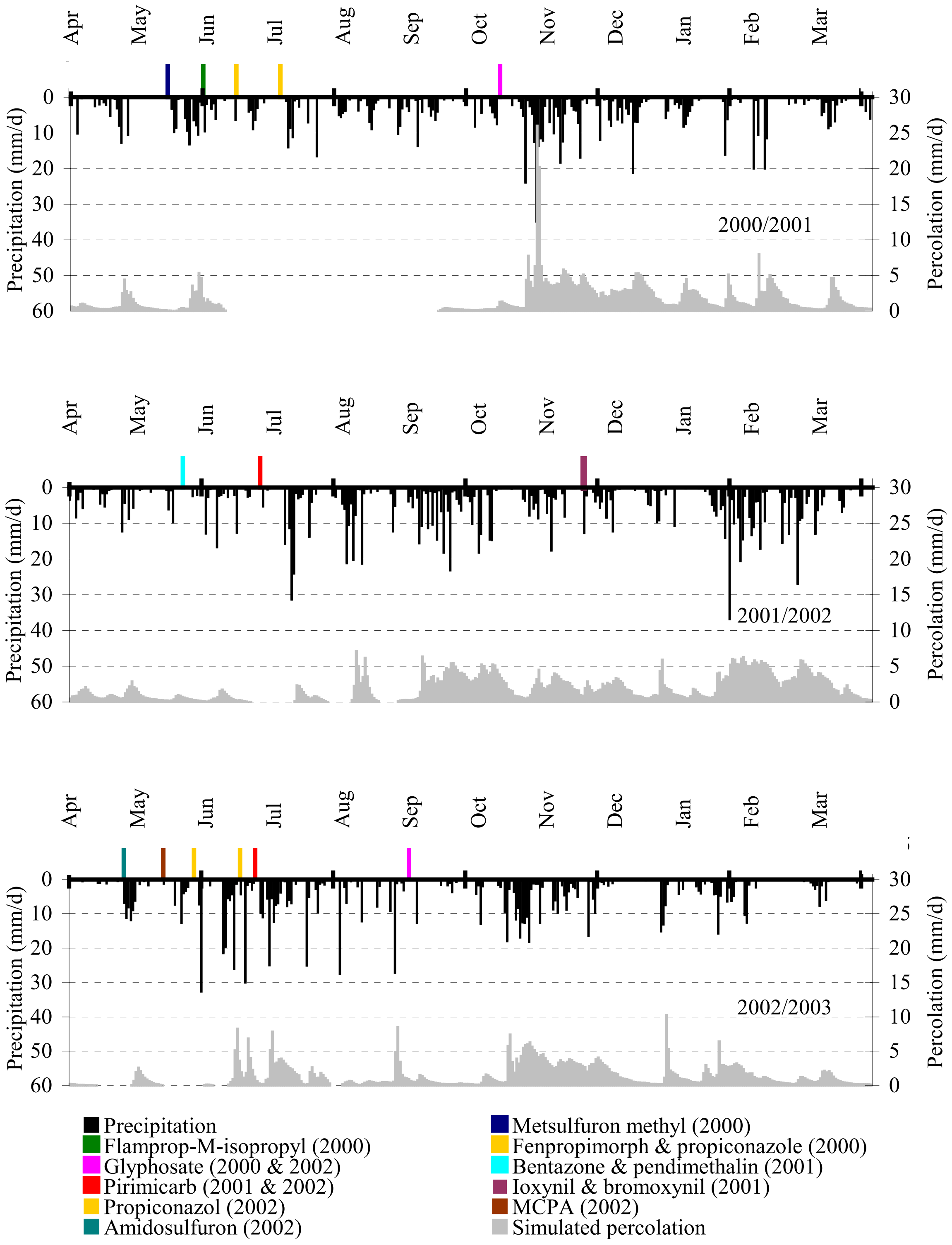

Figure 41. Pesticide application and precipitation (primary axis) together with simulated percolation 0.6 m b.g.s. (secondary axis) at Estrup. Pesticides applied later than April 2003 are not included.

The leaching risk of pesticides applied during 2000 has been evaluated in Kjær *et al.* (2003).

The pesticides applied during 2001 did leach from the root zone, but not at unacceptable levels. The findings are briefly summarized below. For a detailed description of the leaching pattern, see Kjær *et al*. (2003).

Pendimethalin and ***bromoxynil*** were both detected in the drainage water, but only in very few samples (Table 10). Leaching of pendimethalin was confined to a five-month period ending in October 2001, with concentrations in the range 0.01–0.04 µg/l. Leaching of bromoxynil was confined to a one-month period ending in December 2002, with concentrations in the range 0.07–0.6 µg/l.

Slight leaching of ***ioxynil***, ***pirimicarb***, and ***bentazone*** was observed. All three substances were detected in several drainage water samples during the 2001/2002 leaching period. In some cases the concentration exceeded 0.1 µg/l, but the average concentrations were relatively low, in the range 0.01–0.03 µg/l (Table 10). The most frequently detected substance was bentazone, which, was present in 81% of the analysed drainage water samples during the 2001/2002 leaching period (Kjær *et al.,* 2003). In the 2002/2003 leaching period, bentazone was only found in four drainage water samples and in very low concentrations (<0.02 µg/l). Leaching of ioxynil was confined to a four-month period ending in March 2002. It should be noted that drainage runoff commenced about two and a half months prior to the application of ioxynil and bromoxynil. The weighted concentrations of ioxynil and bromoxynil in Table 10 refer to the period from the date of application until 1 July 2002.

The leaching risk of bromoxynil and ioxynil should be viewed in relation to its late autumn application, with percolation reaching 56 mm within the first month after application (Table 10). In contrast, pendimethalin/bentazone and pirimicarb were applied during spring/summer 2000, when precipitation input was nearly normal (Appendix 4). During this period, precipitation input was almost counterbalanced by actual evapotranspiration such that only 15 and 9 mm percolated during the first month after application of bentazone/pendimethalin and pirimicarb, respectively (Table 10 and Figure 41).

The leaching risk of pesticides applied in 2002 will not be fully evaluated until the 2004 monitoring results are available, i.e. when two years of monitoring data have been collated. The preliminary findings are summarised below.

Amidosulfuron did not leach. It should be noted that the leaching risk of amidosulfuron is also associated with its two degradation products. Unfortunately, methods for analysing these substances are not yet available.

Minor leaching was observed with ***pirimicarb***, ***propiconazole*** and ***MCPA.*** All three substances were detected in several drainage water samples. Apart from a few samples taken shortly after application (containing 0.34 and 0.86 µg/l propiconazole, 0.15 and 3.9 µg/l MCPA), all concentrations were below 0.1 µg/l (Figure 42). When evaluating these results it should be noted that these pesticides were applied during spring/summer 2002, when precipitation input and corresponding percolation were much higher than normal (Table 10 and Section 5.2.1).

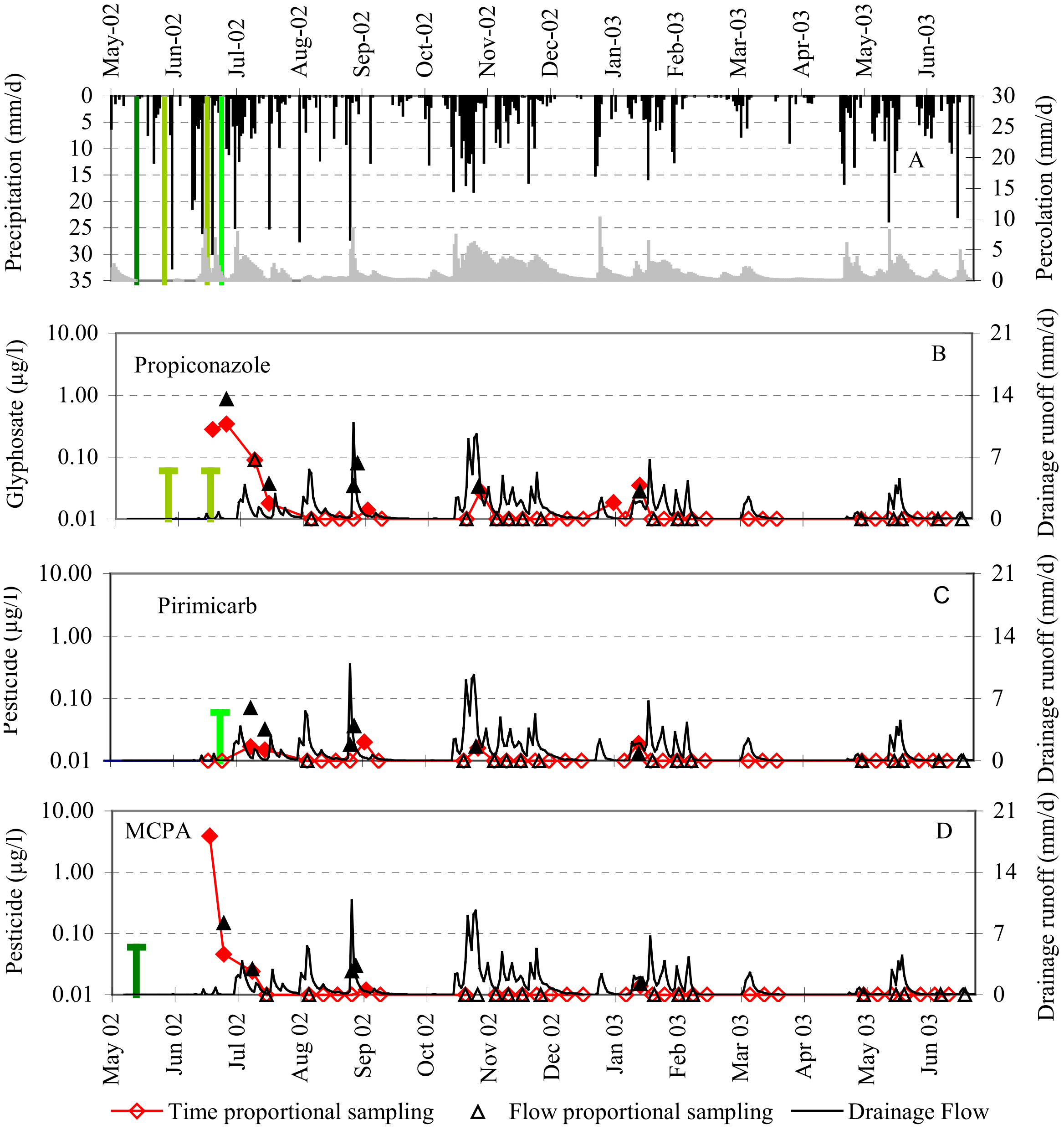

Figure 42. Precipitation and simulated percolation (A) together with concentration of propiconazole (B) and pirimicarb (C) and MCPA (D) in the drainage runoff at Estrup in 2002/2003. The green vertical lines indicate the dates of application. Open diamonds and triangles indicate values below the detection limit of 0.01 µg/l.

Glyphosate and its degradation product ***AMPA*** leached from the root zone in average concentrations considerably exceeding 0.1 µg/l, especially in the case of glyphosate. Thus the average concentration in the drainage water during the 2002/2003 leaching period was 0.43 µg/l, while that of AMPA was 0.19 µg/l (Table 10 and Figure 43.). Four days after the pesticide had been applied on 2 September 2002, 13mm of precipitation caused leaching of both glyphosate and AMPA in concentrations reaching 1.1 µg/l and 0.058 µg/l, respectively. The following period was remarkably dry (Figure 43A). Marked precipitation was only seen in mid October (one and a half months after application), when as much as 131 mm fell within a two-week period. The drainage runoff responded rapidly to these heavy storm events, inducing marked, rapid leaching of both glyphosate and AMPA (Figure 43B,

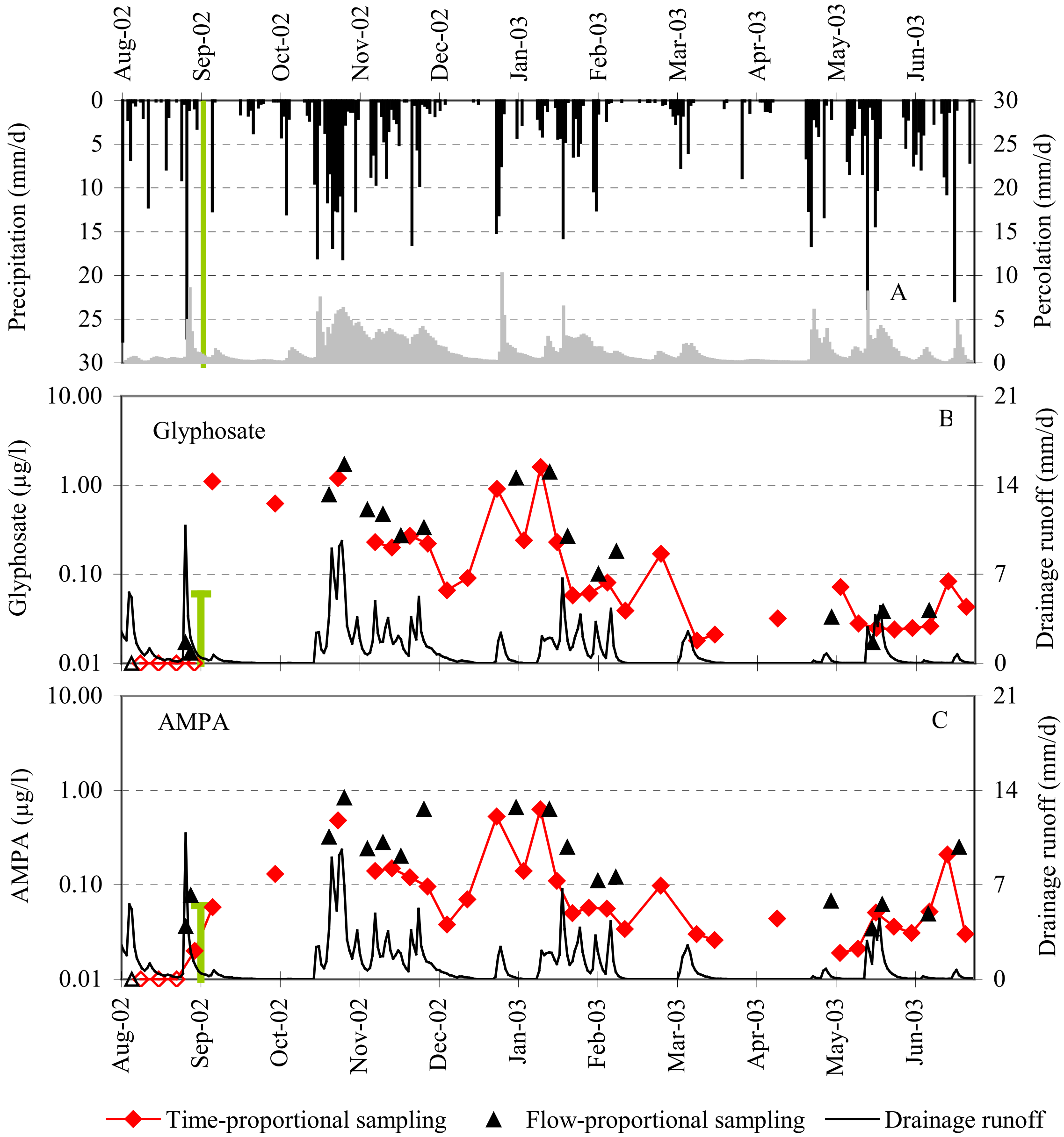

Figure 43. Precipitation and simulated percolation (A) together with concentration of glyphosate (B) and AMPA (C) in the drainage runoff at Estrup in 2002/2003. The green vertical lines indicate the date of application. Open diamonds and triangles indicate values below the detection limit of 0.01 µg/l.

C). Both substances leached continuously during the whole 2002/2003 drainage runoff period (Appendix 8, Figure 43B, C). These results should be viewed in relation to a monitoring period characterised by a rather irregular precipitation pattern yielding very little precipitation and drainage runoff during autumn/winter 2002/2003. September was particularly dry with only 22 mm precipitation, 77% less than normal. The present result are consistence with previous data that also indicate marked root zone leaching of glyphosate and AMPA at Estrup (Kjær *et al.,* 2003). When glyphosate was applied at Estrup in autumn 2000, it was followed by marked precipitation and percolation reaching as much as 135 mm within the first month (Table 10), very unlike the situation following the recent application in 2002.

Despite the very different hydrological conditions following the two applications, the leaching pattern was somewhat similar. Both were characterised by continuous leaching over a relatively long time period and by weighted average concentrations exceeding 0.1 µg/l (Figure 44).

Pesticide leaching at Estrup has hitherto mainly been confined to the depth of the drainage system. Apart from seven samples containing 0.01–0.04 µg/l glyphosate, pesticides have only sporadically been detected in groundwater monitoring screens below the depth of the drainage system (Appendix 9). The bulk of pesticide leaching at Estrup occurred with drainage runoff. The water balance suggests that 53–77% of the percolation ran off through the drainage system (Section 5.2.1). Due to decreased hydraulic conductivity, water and solute transport at Estrup were much slower beneath the drainage system than above it (Lindhardt *et al.*, 2001). Slow transport may allow for dispersion, dilution, sorption and degradation, thereby further reducing the deep transport.

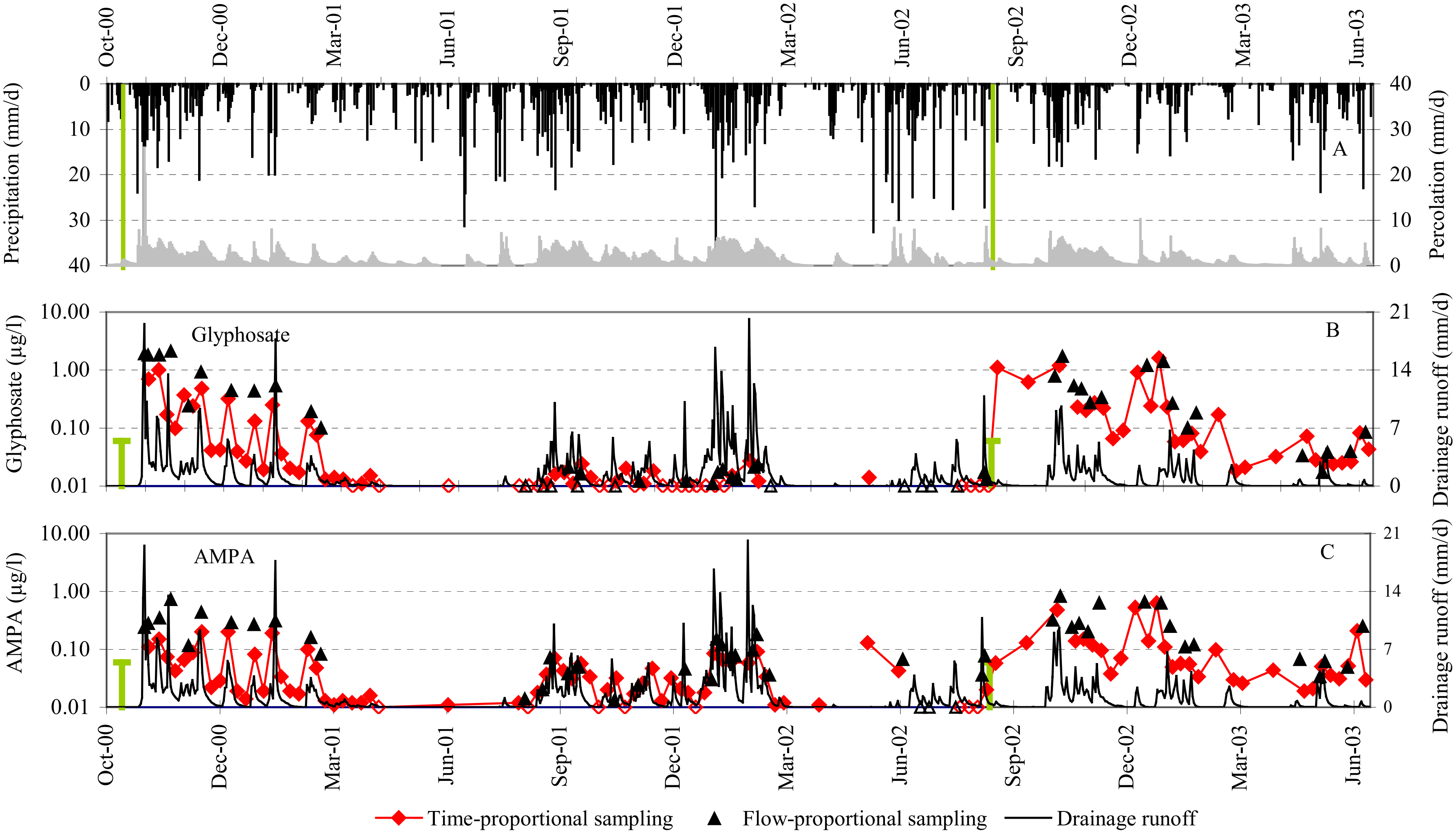

Figure 44. Precipitation and simulated percolation (A) together with concentration of glyphosate (B) and AMPA (C) in the drainage runoff at Estrup. Data represent a three-year period including two applications of glyphosate as indicated by the green vertical lines. Open diamonds and triangles indicate values below the detection limit of 0.01 µg/l.

6 Pesticide leaching at Faardrup

6.1 Materials and methods

6.1.1 Site description and monitoring design

Faardrup is located in southern Zealand (Figure 1). The test field covers a cultivated area of 2.3 ha (150 x 160 m). The terrain slopes gently to the west by 1–3° (Figure 45). Based on three profiles in the buffer zone bordering the field, the soil was classified as Haplic Vermudoll, Oxyaquic Hapludoll and Oxyaquic Argiudoll (Soil Survey Staff, 1999). The topsoil is characterized as sandy loam with 14–15% clay and 1.4% organic carbon (Table 1). 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 (Figure 46). The calcareous matrix and the reduced matrix begin at 1.5 m and 4.2 m b.g.s., respectively (Table 1). The dominant direction of groundwater flow is towards the west in the upper part of the aquifer (Figure 46 Figure 45). During the monitoring period the groundwater table was located 1–2 and 2–3 m b.g.s. in the lower and upper parts of the area, respectively. During fieldwork within the 5 m deep test pit it was observed that most of the water entering the pit came from an intensely horizontally fractured zone in the till at a depth of 1.8–2.5 m. The intensely fractured zone could very well be hydraulically connected to the sand fill in the deep channel, which might drain part of the percolation. The bromide tracer study showed that virtually none of the applied bromide reached the vertical monitoring well (M6) located in the sand-filled basin (Section 6.2.2), however, thus indicating that hydraulic contact with the surface in the "basin" does not differ from that in other parts of the test field and that the basin is a small pond filled with sediments from local sources. A brief description of the sampling procedure is provided in Appendix 2. The monitoring design and test site are described in detail in Lindhardt *et al.* (2001) and the analysis methods in Kjær *et al*. (2002).

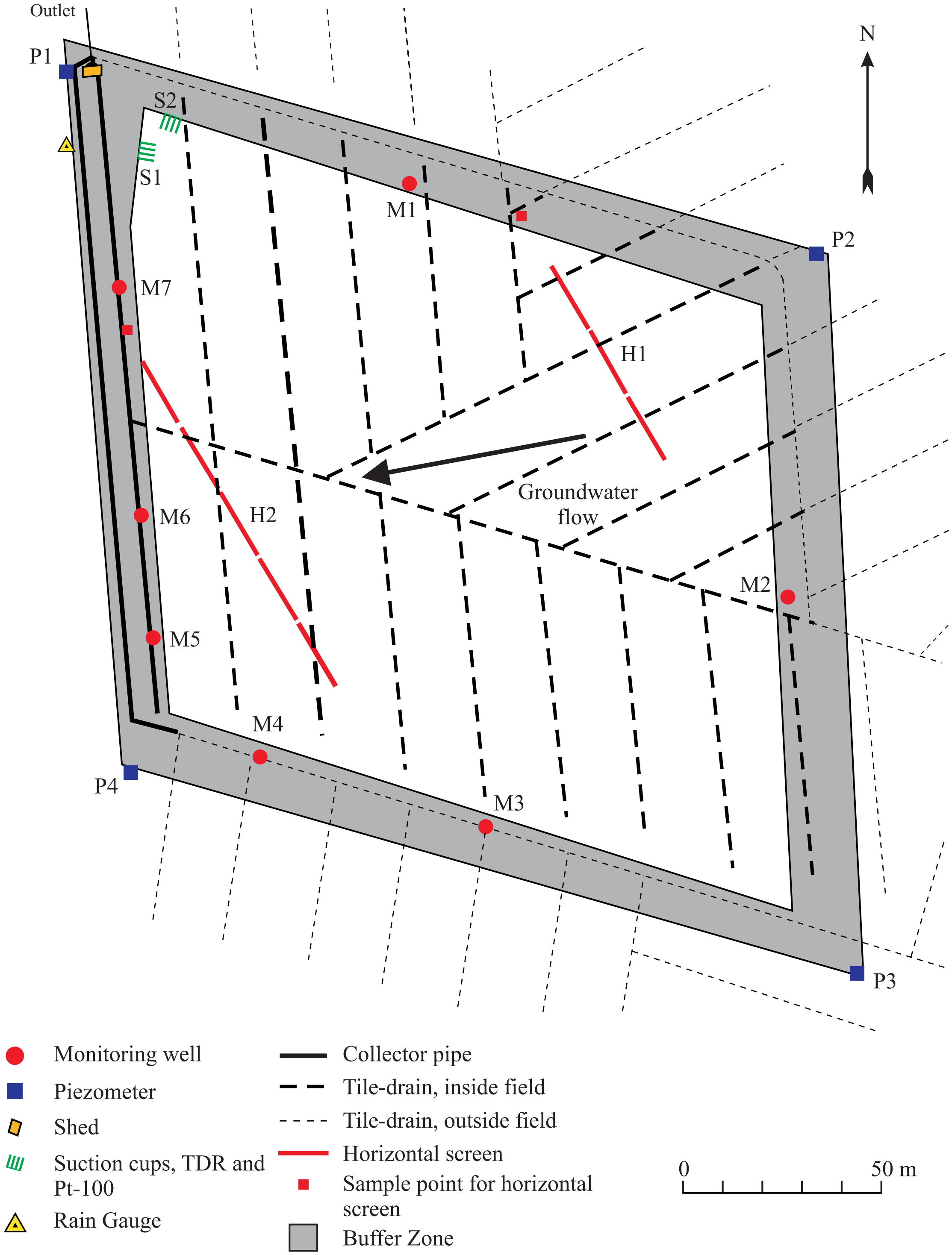

Figure 45. Overview of the Faardrup site. The innermost white area indicates the cultivated land, while the grey area indicates the surrounding buffer zone. The positions of the various installations are indicated, as is the direction of groundwater flow (by an arrow).

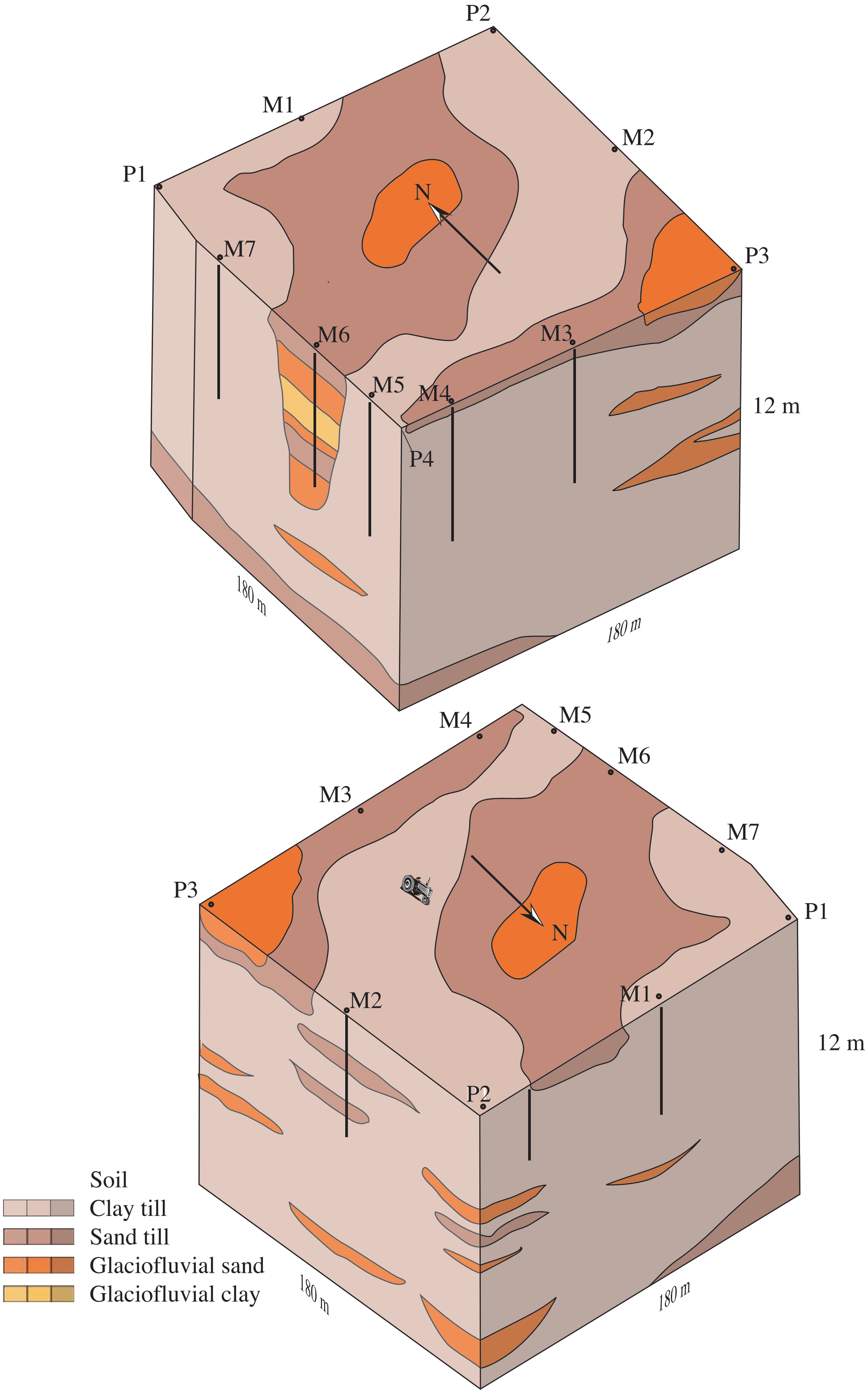

Figure 46. Geological description of the Faardrup site (Lindhardt *et al.*, 2001).

6.1.2 Agricultural management

Management practice during the two most recent growing seasons is briefly summarised below and detailed in Appendix 3 (Table A3.5). For information about management practice during the first two monitoring periods see Kjær *et al*. (2003).

The field was ploughed on 30 October 2001. Due to the good weather conditions, spring barley (cv. Barke) was sown earlier than usual on 28 March 2002. When the barley had 2 leaves, weeds were sprayed with tribenuron methyl on the 7 May. Herbicide spraying was also carried out on 22 May using MCPA and on 25 May using flamprop-M-isopropyl. The barley was sprayed with the fungicide propiconazole and the and a pesticide dimethoate on 4 June. The crop was harvested on 9 August yielding 65.6 hkg/ha of grain (85% dry matter), which was a high yield for that particular cultivar that year. Ten days later the field was ploughed. Management practice at the site is detailed in Appendix 3 (Table A3.5).

After a fertilization with 30 kg N/ha the field was sown with winter rape (cv. Canberra) on 22 August 2002. The next day the herbicide clomazone was applied. On 25 September, when the rape had 5 leaves unfolded, the herbicide clopyralid was applied. Clopyralid was not included in the monitoring, however. An additional 145 kg N was applied on the 24 March. The crop was treated with the pesticide alpha-cypermethin on 24 April, but this is not included in the monitoring program. The rape was windrowed on 17 July and threshed on 28 July. Rapeseed yield was just 28.7 hkg/ha (91% dry matter), a low yield when compared to trials by the Danish Farmers Association. There may be several reasons for the low yield. Thus the crop suffered from frost die back during the winter time and the plots to be used for the yield measurements were not laid out at the sowing time, which may have caused spillage of seeds both when windrowing and in the long interval between windrowing and harvest due to rainy conditions.

6.1.3 Model set-up and calibration

The MACRO model is applied to the Faardrup site covering the soil profile to a depth of 5 m b.g.s., always including the groundwater table. The model is used to simulate the water flow in the unsaturated zone during the full monitoring period September 1999–June 2003 and to establish an annual water balance.

The model was calibrated to the observed groundwater table measured in the piezometers located in the buffer zone and to time series of soil water content measured at three depths (25, 60 and 110 cm b.g.s.) from the two profiles S1 and S2 (Figure 45). A simple calibration procedure was applied that only necessitated adjustment of the empirical BGRAD parameter regulating the boundary flow and the drain depth, which was determined by the groundwater level during drainage periods. All remaining parameters were based on measured data or literature/default values. For a detailed description of data acquisition, model set-up and calibration procedures see Kjær *et al.* (2002) and (2003).

The latest year of the monitoring period, July 2002–June 2003, is considered a validation period and no further model calibration has therefore been performed. The model set-up is thus identical to that reported in Kjær *et al.* (2003), although with the precipitation, evapotranspiration and plant data having been prolonged by one year. Due to an electronic noise problem, precipitation measured at Flakkebjerg 3 km east of Faardrup is used for the previ ous monitoring periods (July 1999–June 2002) (see Kjær *et al.,* 2003). The problem has now been solved and precipitation measured at Faardrup is thus used for the latest monitoring period (July 2002–June 2003).

6.2 Result and discussion

6.2.1 Soil water dynamics and water balances

Model validation show that latest model simulations, July 2002–June 2003, are generally consistent with the observed data, thus indicating a good model description of the overall soil water dynamics in the unsaturated zone (Figure 47). As for previous years (Kjær *et al.*, 2003), the dynamics and level of the measured groundwater table are well captured by the model, as is the dynamics of the soil water content in all three horizons (Figure 47D, E and F).

The drainage pattern for the latest monitoring period seems to be better described by the model than that in previous years. The duration and timing of the drainage period 2002/2003 is well captured and there is no under- or overestimation of the drainage flow (in previous years flow was underestimated). As for the two previous periods (July 2000–June 2001 and July 2001–June 2002), the simulated peak at the onset of the drainage flow is higher than measured. The better consistency with measured data for the latest monitoring period is most likely due to the use of precipitation measured at Faardrup for this period. In the previous monitoring periods (July 1999–June 2002) it was necessary to use precipitation measured at nearby Flakkebjerg because of uncertainty in Faardrup data, see Kjær *et al.* (2003). Comparison of annual precipitation measured at Flakkebjerg and Faardrup during the latest monitoring period (July 2002–June 2003) reveals that precipitation is approximately 90 mm lower at Flakkebjerg. If this finding is also applicable for the previous years it can explain the modelled underestimation of drainage flow for previous monitoring periods.

Table 11. Annual water balance for Faardrup (mm/year). Precipitation is corrected to the soil surface according to the method of Allerup and Madsen (1979).

	Normal precipitation [1]	Precipitation [2]	Actual evapotranspiration	Measured drainage	Simulated drainage	Groundwater recharge [3]
1.7.99–30.6.00	626	715	533	192	129	-10
1.7.00–30.6.01	626	639	318	50	37	271
1.7.01–30.6.02	626	810	492	197	174	121
1.7.02–30.6.03	626	633	405	49	52	179

[1] *Normal values based on time series for 1961–1990*

[2] *For 1.7.99–30.6.02, measured at the DIAS Flakkebjerg meteorological station located 3 km from the test site (see text)*

[3] *Groundwater recharge is calculated as precipitation - actual evapotranspiration - measured drainage*

The resultant annual water balance for Faardrup is shown for each monitoring period (July–June) in Table 11. Annual precipitation in the latest monitoring period (July 2002–June 2003) is the closest to “normal” for the monitored periods and is characterized by high precipitation during the autumn (October-November) as well as low precipitation in the winter/spring (December-March) (Appendix 4). The monitoring period July 2000–June 2001

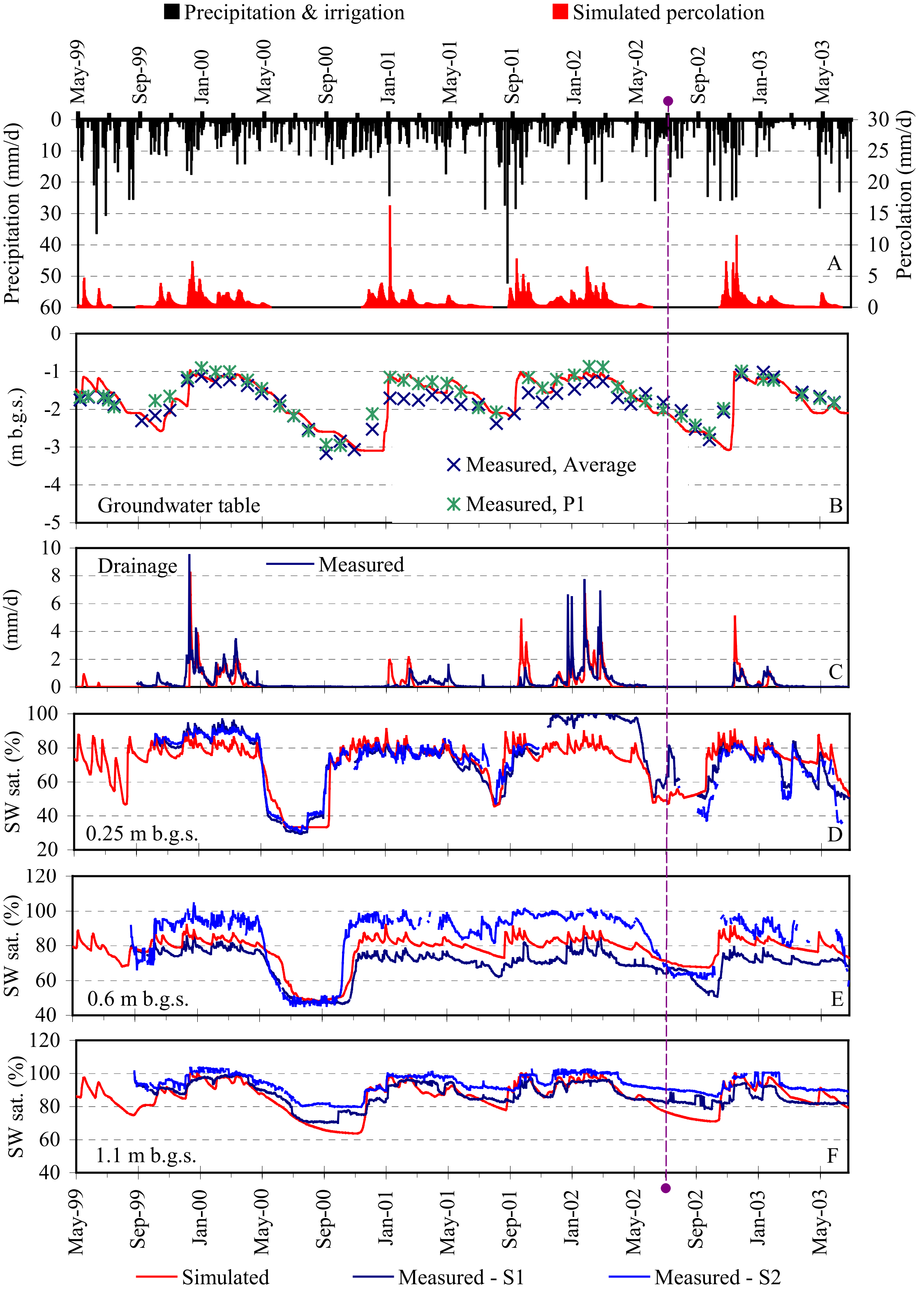

Figure 47. Soil water dynamics at Faardrup: Measured precipitation and simulated percolation 1 m b.g.s. at Faardrup (A), simulated and measured groundwater level (B), simulated and measured drainage flow (C) and simulated and measured soil water saturation (SW sat.) at three different soil depths (D, E, and F). The measured data in B derive from piezometers located in the buffer zone. The measured data in D, E and F derive from TDR probes installed at S1 and S2 (see Figure 45). The broken vertical line through the figure indicates the beginning of the validation period (July 2002–June 2003).

and the latest monitoring period are similar with respect to annual precipitation, dynamics and level of the measured groundwater table and amount of drainage flow. Differences are that the low precipitation in the winter/spring of the latest monitoring period causes the groundwater table to fall after a shorter time (2 instead of 4 months), resulting in a short drainage season (mid November to the beginning of March) and to percolation below 0.1 mm/d from mid March to the end of April. Due to the rainy autumn, moreover, percolation starts earlier in the latest monitoring period than in the period July 2000–June 2001 and approx. 70% of the total percolation at 1 m b.g.s. occurs from mid October to the end of December. Despite annual precipitation and measured drainage flow in the latest monitoring period being similar to that in the monitoring period July 2000–June 2001, the simulated groundwater recharge is significantly lower. This is due to the higher actual evapotranspiration in the latest monitoring period, which is mainly caused by winter crop (rape). For information about the water balance in previous monitoring periods see Kjær *et al.* (2003).

6.2.2 Bromide leaching

At Faardrup, total recovery during the 4-year monitoring period amounted to 4.2 kg/ha, indicating that only 21% of the applied tracer had leached into the drains. Concentration levels decreased in suction cups situated 1 m b.g.s. during 2002/2003, whereas elevated bromide concentrations were still detected in both suction cups 2 m b.g.s. and in drainage water sampled in 2002/2003. The results are thus consistent with those for Silstrup and Estrup and indicate that part of the bromide is retained in the upper part of the soil profile, probably in the matrix. Although the retained bromide can be expected to leach continuously for a long period of time, the data indicate that leaching is gradually decreasing.

The results also showed subsequent minor transport of bromide to a depth of 2 and 3.5 m b.g.s. (Figure 48A, B and D). Slightly elevated bromide concentrations were detected 2 m b.g.s in the suction cups as well as in a horizontal well 3.5 m b.g.s. A small part of the applied bromide also reached the downstream monitoring wells. Elevated bromide concentrations were thus detected in M4 from autumn 2001 onwards. During autumn 2001, slightly elevated concentrations were also detected in M5 and to a minor extent in M6 (Figure 49). For further details of bromide transport at Faardrup see Kjær *et al.* (2003).

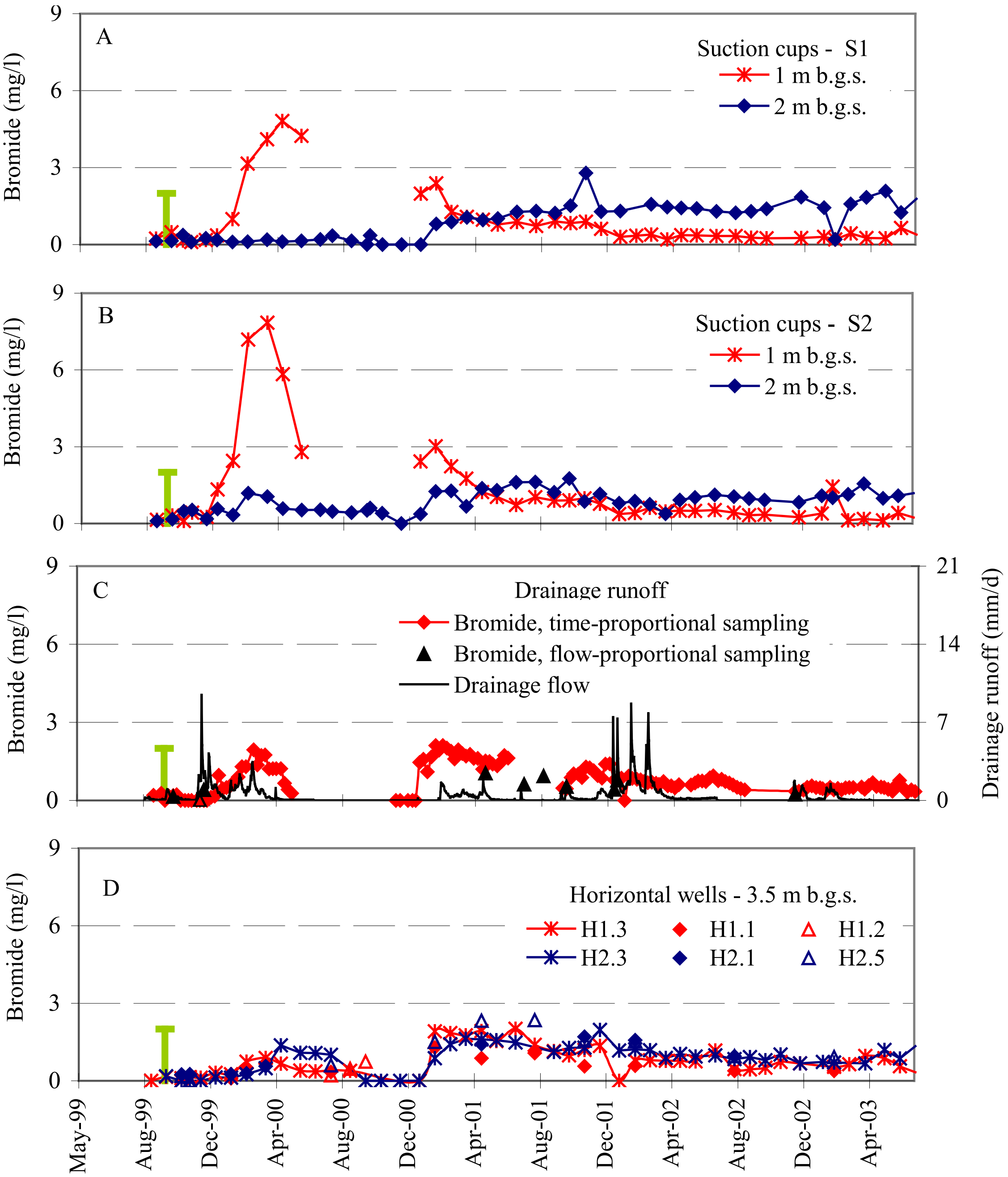

Figure 48. Bromide concentration at Faardrup. A and B refer to suction cups located at S1 and S2. The bromide concentration is also shown for drainage runoff (C) and the horizontal monitoring wells (D). The green vertical line indicates the date of bromide application.

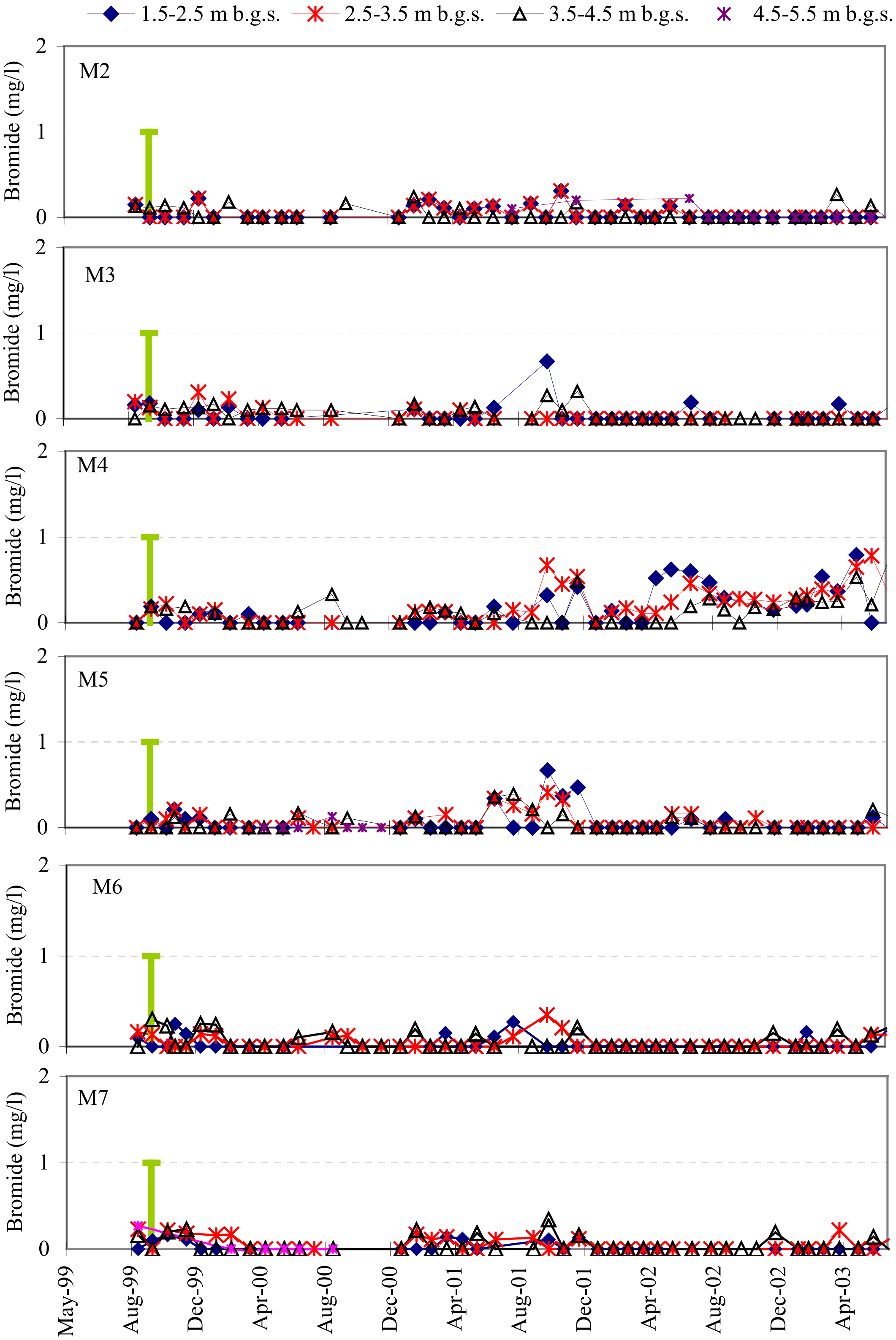

Figure 49. Bromide concentration at Faardrup. The data derive from the vertical monitoring wells (M2–M7). Screen depth is indicated in m b.g.s. The green vertical line indicates the date of bromide application.

6.2.3 Pesticide leaching

Monitoring began at Faardrup in September 2000 and presently encompasses 17 pesticides and several degradation products. Pesticide application is shown together with precipitation and simulated percolation in Figure 50 and Figure 51, and is summarized in Table 12.

Table 12. 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 (app. date) until the end of monitoring. 1st month perc. refers to accumulated percolation within the first month after application. C_{mean} refers to average leachate concentration in the drainage water the first drainage season after application (See Appendix 2 for calculation methods). The number of pesticide-positive samples is indicated in parentheses.

Crop and analysed pesticides	Application date	End of monitoring	Prec. (mm)	Perc. (mm)	1st month perc. (mm)	C_{mean} (µg/l)
Winter wheat 1999						
Glyphosate (Roundup 1999)	Aug 99	Apr 03	2526	1078	1	<0.01(8*)
- *AMPA*						<0.01(17*)
Bromoxynil (Briotril)	Oct 99	Apr 02	1738	841	36	<0.01(0)
Ioxynil (Briotril)	Oct 99	Apr 02	1738	841	36	<0.01(2)
Fluroxypyr (Starane 180)	Apr 00	Apr 02	1408	580	13	<0.01(1)
Propiconazole (Tilt Top)	May 00	Jul 03	2151	782	1	<0.01(1*)
Fenpropimorph (Tilt Top)	May 00	Jul 02	1518	578	1	<0.01(1)
- *fenpropimorphic acid*						<0.01(0)
Pirimicarb (Pirimor G)	Jun 00	Jul 03	2066	785	0	<0.01(9*)
- *pirimicarb-desmethyl*						<0.01(9*)
- *pirimicarb-desmethyl-formamido*						<0.02(5*)
Sugar beet 2001						
Glyphosate (Roundup 2000)	Oct 00	Jul 03	1747	791	0	<0.01(8*)
- *AMPA*						0.01(17*)
Metamitron (Goltix WG)	May 01	Jul 03	1512	565	8	0.01(35)
- *metamitron-desamino*						0.01(63)
Ethofumesate (Betanal Optima)	May 01	Jul 03	1512	565	8	0.06(45)
Desmedipham (Betanal Optima)	May 01	Jul 03	1512	565	8	<0.01(0)
- *EHPC*						<0.02(0)
Phenmedipham (Betanal Optima)	May 01	Jul 03	1512	565	8	<0.01(2)
- *MHPC*						<0.02(3)
Fluazifop-P-butyl (Fusilade X-tra)	Jun 01	Jul 03	1460	556	3	<0.01(0)
- *fluazifop (free acid)*						0.02(17)
Pirimicarb (Pirimor G)	Jul 01	Jul 03	1460	556	3	<0.01(9*)
- *pirimicarb-desmethyl*						<0.01(9*)
- *pirimicarb-desmethyl-formamido*						<0.02(5*)
Spring barley 2002						
Flamprop-M-isopropyl (Barnon Plus)	May 02	Jul 03†	726	204	0	<0.01(1)
- *Flamprop-M (free acid)*						<0.01(1)
MCPA (Metaxon)	May 02	Jul 03†	743	204	0	<0.01(0)
- *4-chlor,2-methylphenol*						<0.02(0)
- *Triazinamin-methyl* $^{1)}$ (Express)	May 02	Jul 03†	747	210	6	<0.02(0)
Dimethoate (Perfection 500 S)	Jun 02	Jul 03†	716	203	0	<0.01(0)
Propiconazole (Tilt 250 EC)	Jun 02	Jul 03†	716	203	0	<0.01(1*)
Winter rape 2003						
Clomazone (Command CS)	Aug 02	Jul 03†	521	207	7	<0.02(0)
-propanamide-clomazone						<0.02(0)

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

$^{1)}$ *Degradation product of tribenuron methyl. The parent compound degrades too rapidly to be detected by monitoring*

$^{*)}$ *Pesticide have been applied twice and the findings are not necessarily related to one specific application*

†) *Monitoring will continue during the following year. The values for prec. and perc. are accumulated up to July 2003*

It should be noted that precipitation is corrected to the soil surface according to Allerup and Madsen (1979), whereas percolation (1 m b.g.s.) refers to accumulated values as simulated with the MACRO model. It should also be noted that as tribenuron methyl (applied here as Express) degrades rapidly, the leaching risk is more associated with its degradation product, triazinamin-methyl. For the same reason it is the degradation product and not the parent compound that is monitored in the PLAP (Table 12).

The leaching risk of pesticides applied during 2000 has been evaluated in Kjær *et al.* (2003). The findings regarding the pesticides applied during 2001 are briefly summarized below. For a detailed description of the leaching pattern, see Kjær *et al*. (2003).

- ***Phenmedipham*** was detected in 2 samples collected from monitoring well M5 on 8 August 2001 (0.01 and 0.025 µg/l). Its degradation product ***MHPC*** (0.03–0.19 µg/l) was detected in samples of drainage water collected in summer 2001 and in a sample collected from monitoring well M5 on 4 February 2003.
- Neither ***desmedipham*** nor its degradation product ***EHPC*** were detected in any of the analysed samples.
- ***Pirimicarb*** and its degradation products were detected in several drainage water samples as well as in groundwater samples. In all cases the concentrations measured were below 0.1 µg/l. As Pirimor was applied on two separate occasions, it is not possible to relate the findings to any one specific application. Most findings originate from 2001, but pirimicarb-desmethyl-formamido was found in one drainage water sample and in one groundwater sample (M5) collected in June 2003.
- ***Metamitron***, ***metamitron-desamino***, ***ethofumesate*** and ***fluazifop (free acid)*** were found to leach from the root zone, reaching the drainage system, suction cups and one monitoring well. All four compounds were detected in high concentrations in the drainage system in June/August 2001 after an intense precipitation event, indicating rapid macropore transport (Figure 52). Drainage runoff was very low (<1 mm) during this period, however. Despite the high concentrations, the total mass of the four compounds that leached out was small. The concentrations in the drainage system decreased after a short time, and were 0.01–0.05 µg/l during autumn 2001. When runoff eventually started to increase in January 2002 the concentrations of all four compounds were below the detection limit and the compounds were not detected in drainage water in 2003. As a consequence the average concentrations were low, ranging from 0.01 to 0.06 µg/l (Table 12). These compounds were also frequently detected in one of the monitoring wells, M5 (Kjær *et al.*, 2003 and Appendix 10). Thus ethofumesate, metamitron and metamitron-desamino were found in all 3 screens starting in August 2001, when the groundwater table was about 2 m b.g.s. At the same time bromide was detected at M5 in slightly elevated concentrations, thus providing additional evidence that percolating water from the treated area had reached M5 (Figure 49). During autumn 2001, the compound was detected in concentrations exceeding 0.1 µg/l in several samples from M5, but not from any other monitoring wells. During 2002, ethofumesate, metamitron and metamitron-desamino were detected more frequently in M5, but never in concentrations exceeding 0.1µg/l. During 2003 metamitron-desamino was also found in M5 (Appendix 10).

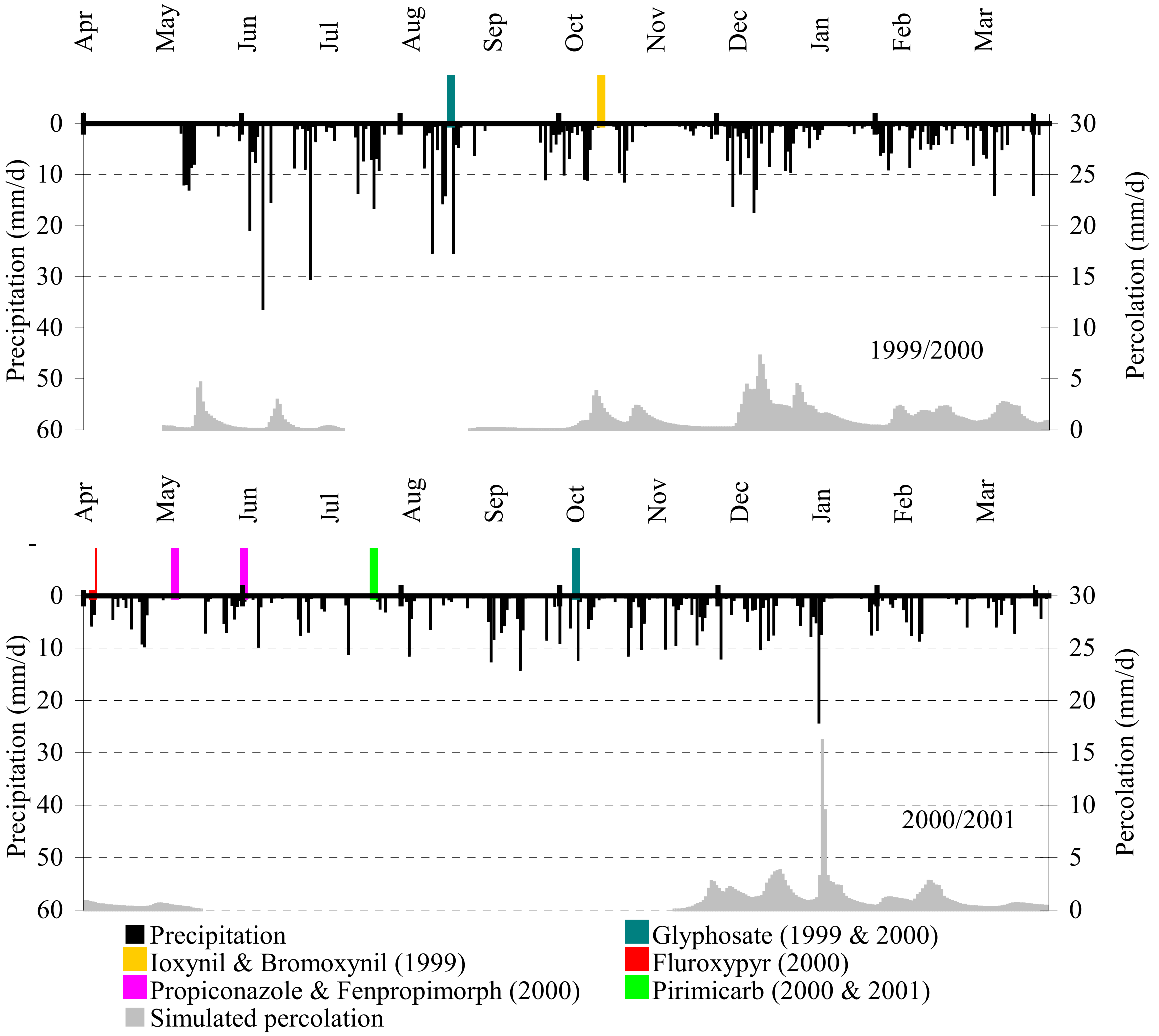

Figure 50. Pesticide application, precipitation (primary axis) together with simulated percolation (secondary axis) at Faardrup in 1999/2000 (upper) and 2000/2001 (lower).

When interpreting the detection of pesticides in M5, however, it should be kept in mind that the lower filters of M5 were hydraulically interconnected. Thus purging of the second-lowest filter (3.5–4.5 m b.g.s.) affected the overlying screen (2.5–3.5 m b.g.s.) in terms of a decreasing groundwater table. M5 is located downstream of the test site in till interbedded with thin sandy till lenses. The hydraulic connection between the filters is probably attributable to these lenses of sandy till (Lindhardt *et al.,* 2001). In conclusion, pesticides and their degradation products were transported through the unsaturated zone and reached the upper screen of M5. The detection of pesticides in the deeper screens should be interpreted with caution, however, as this might possibly be caused by screen purging. For further information see Kjær *et al.* (2003).

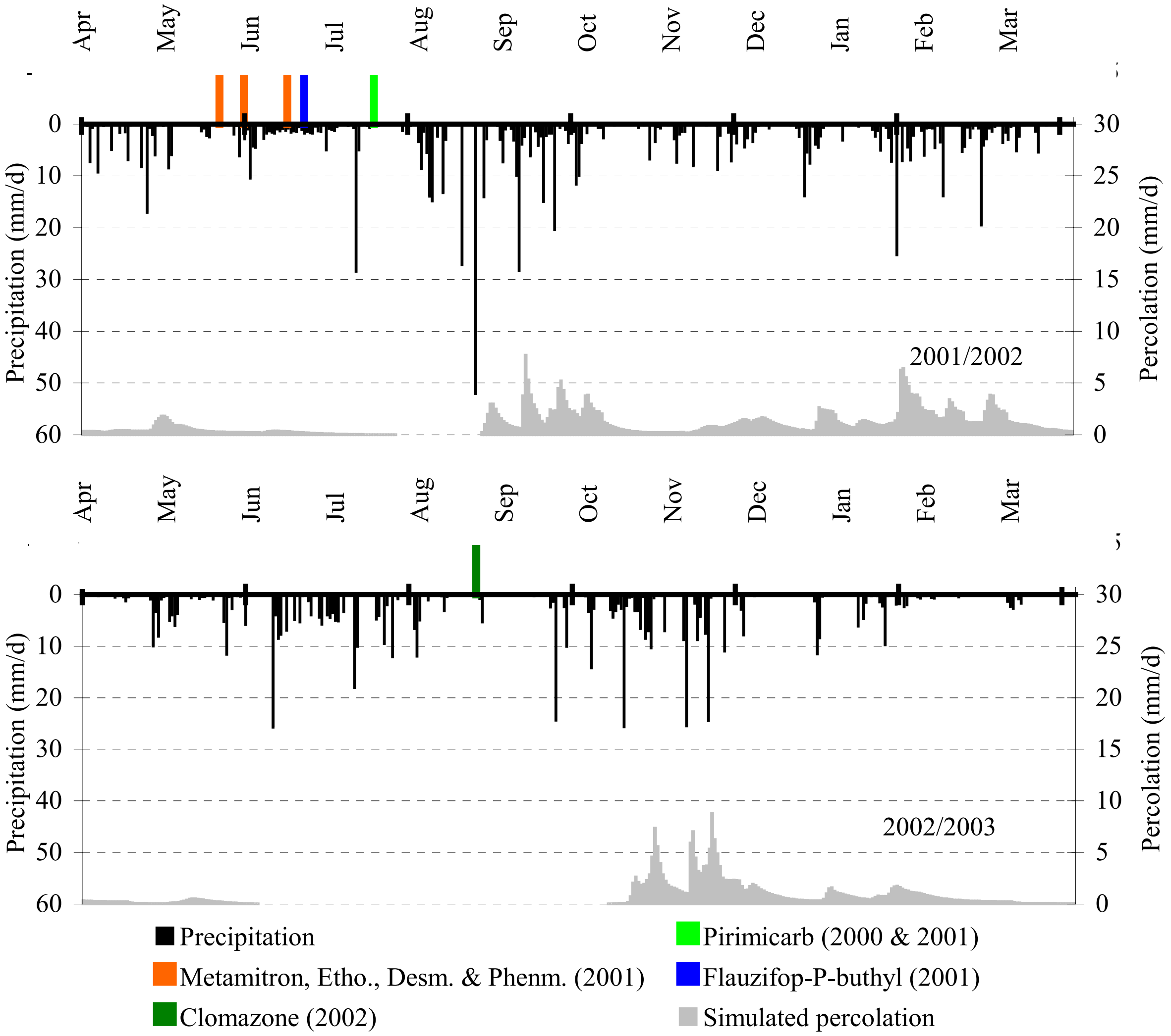

Figure 51. Pesticide application, precipitation (primary axis) together with simulated percolation (secondary axis) at Faardrup in 2001/2002 (upper) and 2002/2003 (lower). Pesticides applied later than April 2003 are not included). Etho.: Ethofumesate; Desm.: Desmedipham; Phenm.: Phenmedipham..

The leaching risk of pesticides applied in 2002 will not be fully evaluated until the 2004 monitoring results are available, i.e. when two years of monitoring data have been collated. Apart from one sample (drainage water sampled on 16 July 2002) containing 0.037 µg/l flamprop-M-isopropyl and 0.089 µg/l flamprop-M (free acid) and another (M5 sampled on 3 July 2002) containing 0.035 µg/l propiconazole, however, none of the applied pesticides or the degradation products listed in Table 12 have yet been detected.

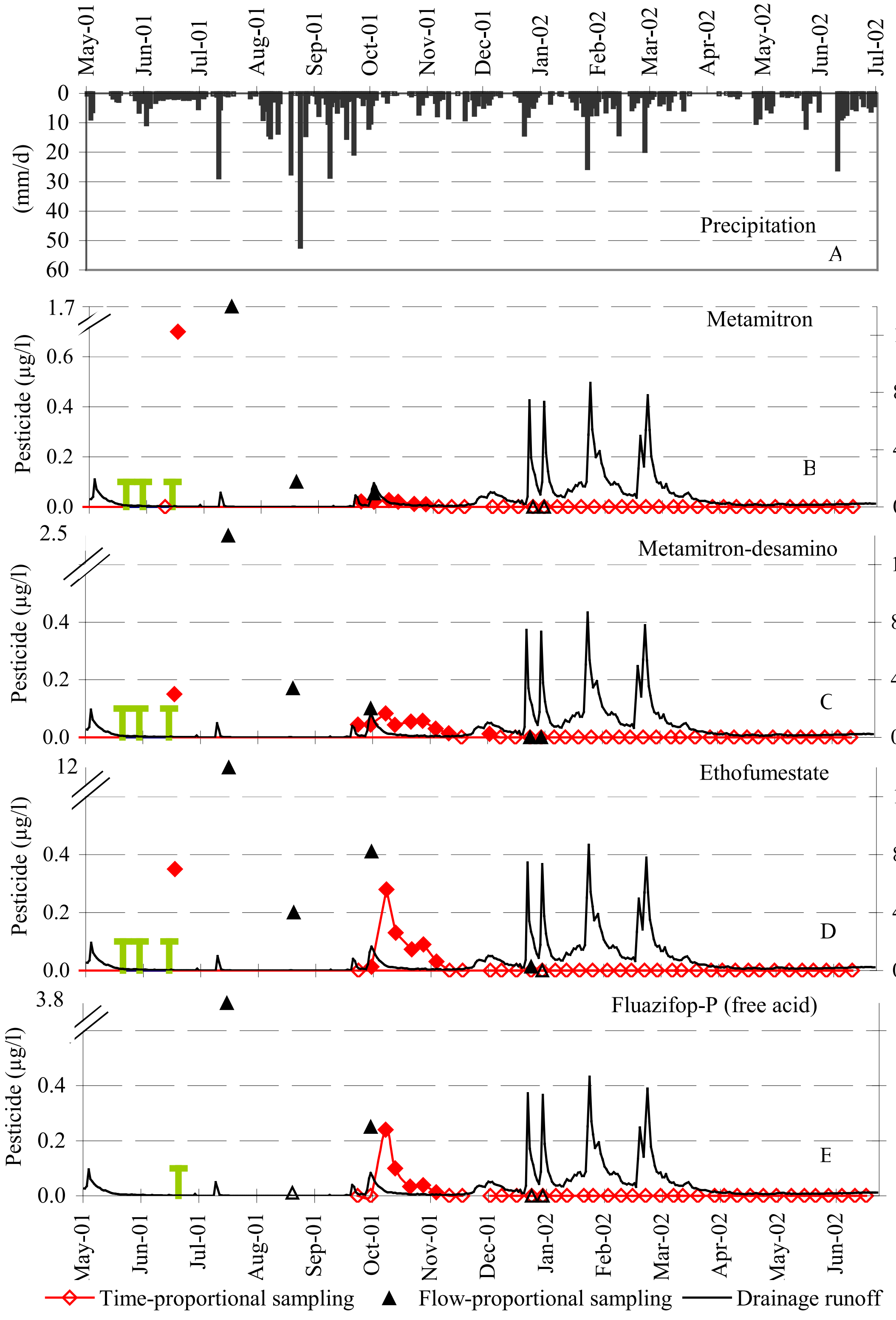

Figure 52. Precipitation (A) together with concentration of metamitron (B), metamitron-desamino (C), ethofumesate (D) and fluazifop-P (free acid) in the drainage runoff at Faardrup in 2001/2002. The green vertical lines indicate the dates of application. None of these pesticides were detected during the subsequent 2002/2003 drainage season.

7 Pesticide leaching at Slaeggerup

7.1 Materials and methods

7.1.1 Site description and monitoring design

The Slaeggerup test site is located on Zealand near the village of Slaeggerup northeast of Roskilde (Figure 1). The test field area is 2.2 ha (130 x 165 m). The ground surface within the test field slopes gently (1–4°) towards the northeast, the difference in altitude between highest and lowest levels being around 4.5 m (Figure 53). Three soil profiles were excavated on the site, all of which are classified as Typic Argiudoll (Soil Survey Staff, 1999). The topsoil content of clay within the three profiles was 20–24%, whereas the organic matter content was 1.8–2.4%. The sediments penetrated when drilling the piezometers and monitoring wells could be subdivided into three lithological units (Figure 54). The upper unit was generally up to 2.5 m thick. Its uppermost part (0–0.65 m) consisted of meltwater clay with numerous desiccation cracks and biopores. Further down, the unit consisted of sandy meltwater gravel and then gravely meltwater sand. Within these two parts there were only small vertical and horizontal fractures. The middle unit consisted of up to 4 m of clay till with numerous horizontal and vertical fractures. The largest of these fractures traversed the entire unit and ended at the lowest unit consisting of sand till. The sand had no fractures. The content of clay decreased with depth from around 55% in the meltwater clay of the upper unit to 16.3% in the sand till of the lowest unit. A brief description of the sampling procedure is provided in Appendix 2. The monitoring design and test site are described in detail in Lindhardt *et al.* (2001) and the analysis methods in Kjær *et al*. (2002).

7.1.2 Agricultural management

Management practice during the two most recent growing seasons is briefly summarised below and detailed in Appendix 3 (Table A3.6). For information about management practice during the first two monitoring periods see Kjær *et al*. (2003).

On 26 September 2001 the field was sprayed with glyphosate in the form of Roundup Bio (using 4.0 l/ha), at which time it still had not been possible to remove the pea residues. On 10 October it was decided to shred the residues and on 13 October the field was ploughed. Two days later the field was sown with winter wheat (cv. Bill). The wheat emerged on 1 November. One week later, ioxynil and bromoxynil were sprayed to combat weeds. Weeds were sprayed again on 22 April using amidosulfuron and on 15 May using flamprop-M-isopropyl. Fungicide spraying was carried out on 31 May and 14 June using propiconazole, and pests were sprayed using pirimicarb on 14 June. The winter wheat was harvested on 20 August 2002 yielding 72.3 hkg/ha of grain (85% dry matter). The yield was lower than normal for the area, probably due to the late sowing caused by the wet weather of autumn 2001.

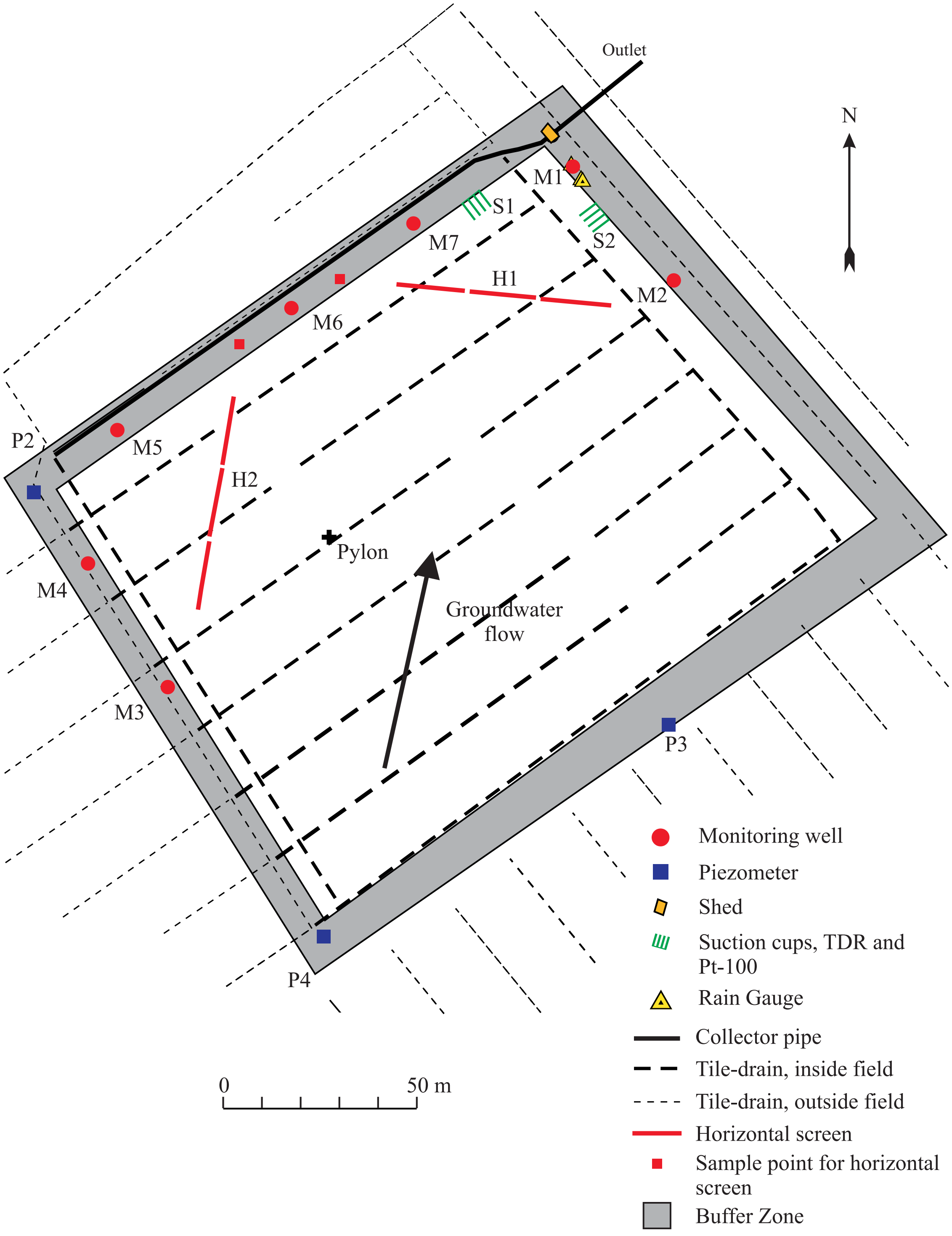

Figure 53. Overview of the Slaeggerup site. The innermost white area indicates the cultivated land, while the grey area indicates the surrounding buffer zone. The positions of the various installations are indicated, as is the direction of groundwater flow (by an arrow).

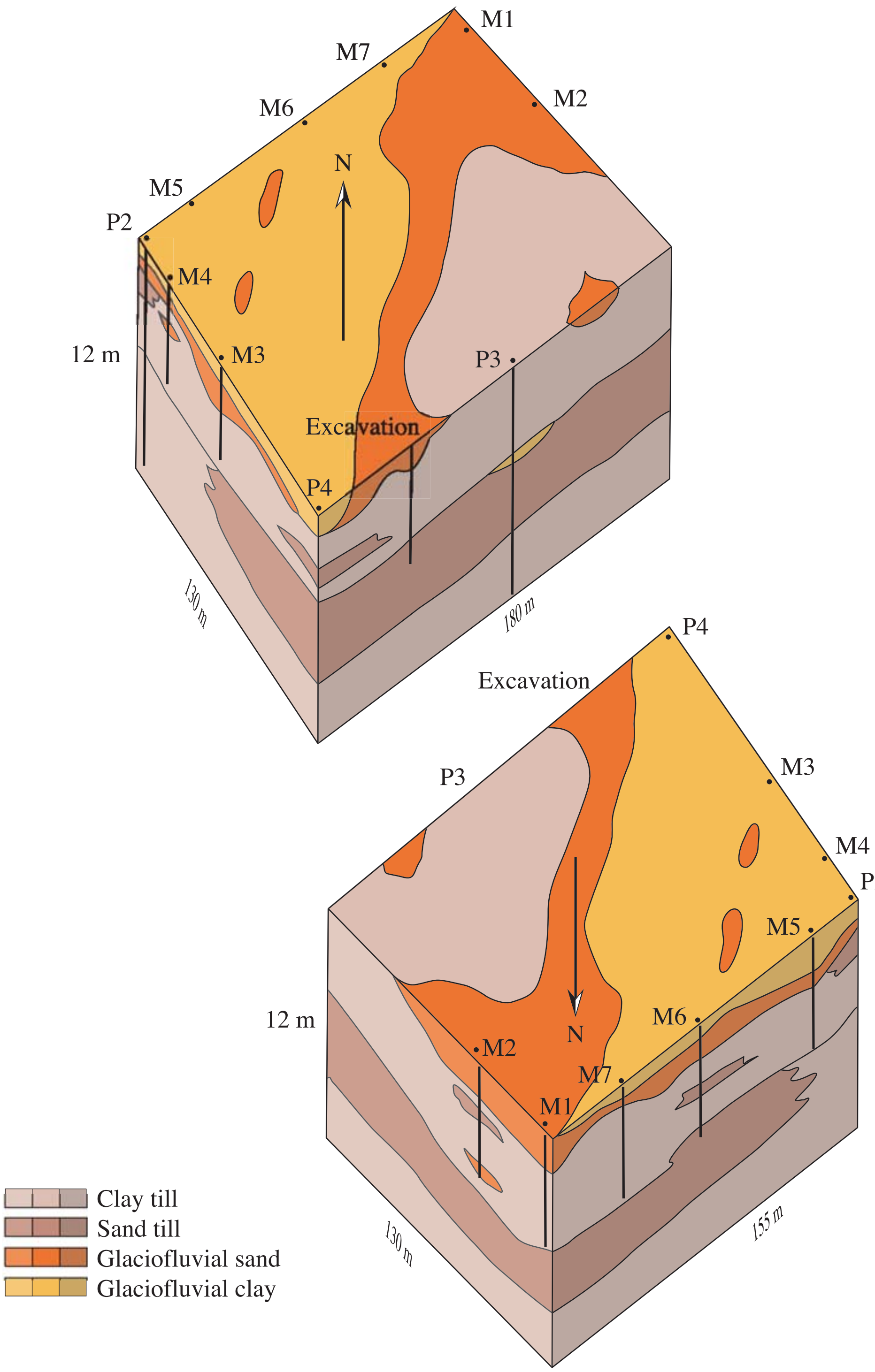

Figure 54. Geological description of the Slaeggerup site (Lindhardt *et al.,* 2001).

The 2003 crop was spring barley (cv. Prestige) sown on 26 March. The herbicide tribenuron methyl was sprayed out on 11 May when 4 leaves had unfolded. At the beginning of steam elongation, weeds were sprayed flamprop-m-isopropyl. The herbicide MCPA was applied on 4 June when the flag leaf was visible. Fungi and pests were sprayed on 10 June using propiconazole and dimethoate respectively. At harvest on 7 August the barley yielded 59.5 hkg/ha (85% dry matter), which is at the low end of the range for that year.

7.1.3 Model set-up and calibration

The MACRO model is applied to the Slaeggerup site covering the soil profile to a depth of 5 m b.g.s., always including the groundwater table. The model is used to simulate the water flow in the unsaturated zone during the full monitoring period April 2000–June 2003 and to establish an annual water balance.

The model was calibrated to the observed groundwater table measured in the piezometers located in the buffer zone as well as to three time series of soil water content measured at 25, 60 and 110 cm b.g.s. in the two profiles S1 and S2 (see Figure 53). A simple calibration procedure was applied that only necessitated adjustment of the empirical BGRAD parameter regulating the boundary flow and the drain depth, which was determined by the groundwater level during drainage periods. All remaining parameters were based on measured data or literature/default values. For a detailed description of data acquisition, model set-up and calibration procedures see Kjær *et al.* (2002) and (2003).

The latest year of the monitoring period, July 2002–June 2003, is considered a validation period and no further model calibration has therefore been performed. The model set-up is thus identical to that reported in Kjær *et al.* (2003), although with the precipitation, evapotranspiration and plant data having been prolonged by one year.

7.2 Results and discussion

7.2.1 Soil water dynamics and water balances

Model validation show that last model simulations, July 2002 to June 2003, are generally consistent with the observed data, thus indicating a good model description of the overall soil water dynamics in the unsaturated zone (Figure 55). As for previous years (Kjær *et al.*, 2003) the model is able to provide a good simulation of the measured groundwater table and the dynamics of the soil water as determined from the TDR probes. As the measured level of the uppermost groundwater table varies significantly at Slaeggerup, no average groundwater table has been calculated and instead measurements from P2 and P3 are shown in Figure 55. The simulated groundwater table captures the dynamics of the measured groundwater table and the simulated groundwater level lies within the range defined by measurements in P2 and P3. The measured variation in the groundwater table within the field indicates some of the limitations of applying a one-dimensional model to the larger field scale. Measured and simulated drainage flow are similar for the latest monitoring period (54 and 61 mm, respectively). As for previous years, however, the modelled drainage flow is delayed compared to the measured drainage flow. The measured drainage flow starts at the beginning of August, whereas the simulated flow starts in mid November (Figure 55C).

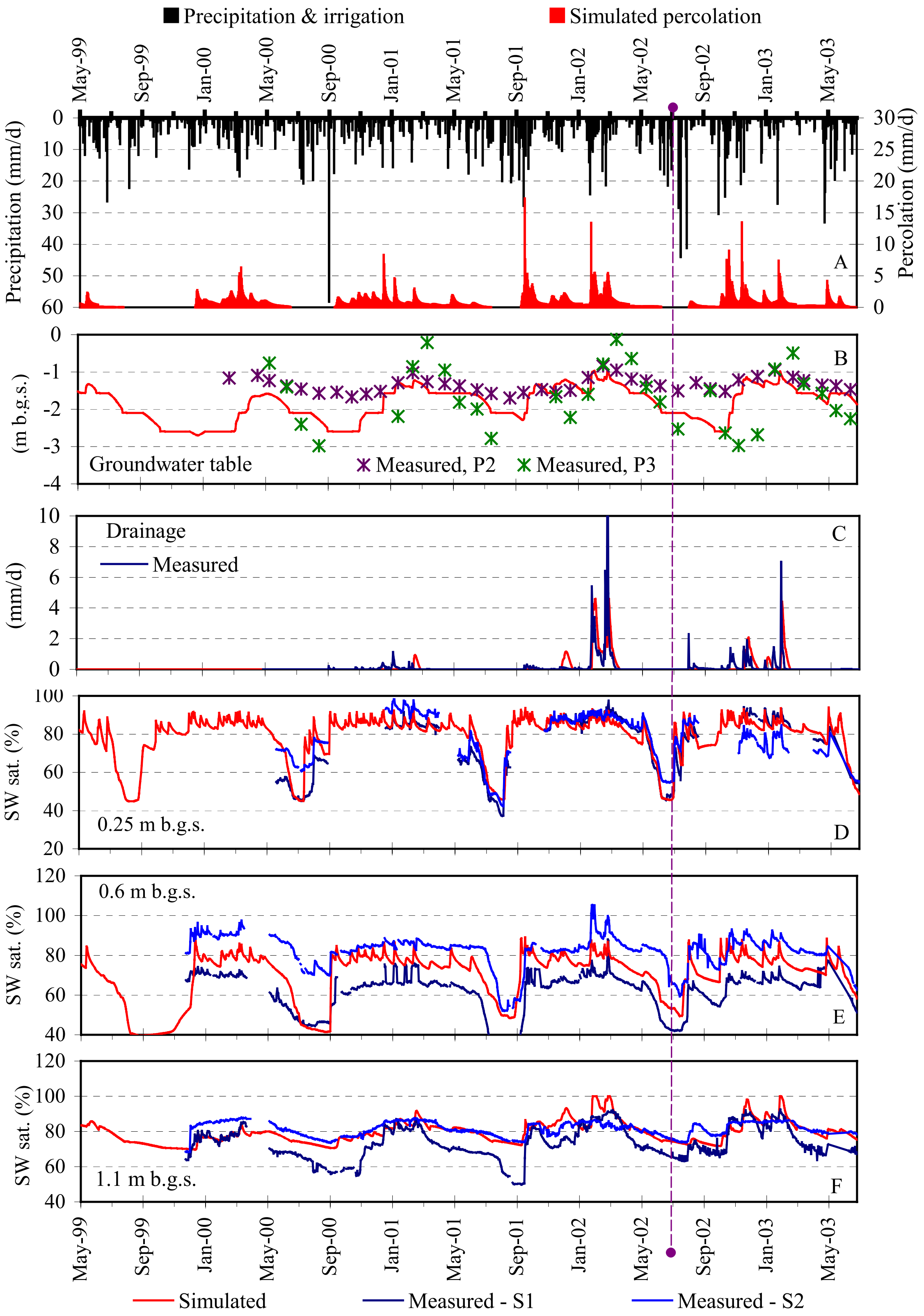

Figure 55. Soil water dynamics at Slaeggerup: Precipitation and simulated percolation at 1 m b.g.s. (A), simulated and measured groundwater level (B), simulated and measured drainage flow (C), and simulated and measured soil water saturation (SW sat.) at three different soil depths (D, E and F). The measured data in B derive from piezometers located in the buffer zone. The measured data in D, E and F derive from TDR probes installed at S1 and S2 (see Figure 53). The broken vertical line indicates the beginning of the validation period (July 2002–June 2003).

The resulting annual water balance is shown for each monitoring period (July–June) in Table 13. The latest monitoring period (July 2002–June 2003) received 17% more precipitation than "normal" and is characterized by high precipitation in summer 2002, low precipitation in the autumn (October–November), low precipitation in the winter/spring (February-March), and high precipitation in May (Appendix 4). Several precipitation events exceeding 20 mm/d occurred.

The high precipitation in summer 2002 resulted in drainage flow as early as the beginning of August, but the bulk of total drainage flow is observed from October through January. Because of the low precipitation in the winter/spring, drainage flow is absent from January to April 2003 and is observed again in May, when precipitation was high.

Table 13. Annual water balance for Slaeggerup (mm/year). Precipitation is corrected to the soil surface according to the method of Allerup and Madsen (1979).

	Normal Precipitation 1)	Precipitation	Actual evapotranspiration	Measured drainage	Modelled drainage	Groundwater recharge 2)
1.7.99–30.6.00 3)	660	511	392	–	0	119 4)
1.7.00–30.6.01	660	683	343	11	7	328
1.7.01–30.6.02	660	823	472	110	116	241
1.7.02–30.6.03	660	776	451	54	61	271

1) Normal values based on time series for 1961–1990

2) Groundwater recharge is calculated as precipitation - actual evapotranspiration - measured drainage

3) The monitoring was started in April 2000

4) Where drainage flow measurements are lacking, simulated drainage flow was used to calculate groundwater recharge

The high precipitation in summer 2002 also resulted in simulated percolation 1 m b.g.s. as early as the beginning of August, but the bulk of total percolation is simulated from October until mid February. Because of the low precipitation in the winter/spring, there is only very little or no percolation in March and April. In May, percolation is greater than observed in previous monitoring periods as a result of the high precipitation. After the high precipitation in the autumn, precipitation events exceeding approximately 20 mm/d are immediately reflected in the percolation (Figure 55A). For information about the water balance in previous monitoring periods see Kjær *et al.* (2003).

As in the previous monitoring periods, bromide tracer studies could not be carried out at Slaeggerup because the water supply authorities refuse permission due to the presence of a large municipal drinking water supply in the vicinity. Hence, no bromide data are available to verify water transport patterns.

7.2.2 Pesticide leaching

Monitoring at Slaeggerup began in April 2000 and presently encompasses 12 pesticides and 8 degradation products (Figure 56 and Table 14). It should be noted that precipitation in Table 14 is corrected to the soil surface according to Allerup and Madsen (1979), whereas percolation (1 m b.g.s.) refers to accumulated percolation as simulated with the MACRO model. It should also be noted that as tribenuron methyl (applied here as Express) degrades rapidly, the leaching risk is more associated with its degradation product, triazinamin-methyl. For the same reason it is the degradation product and not the parent compound that is monitored in the PLAP (Table 14).

Table 14. Pesticides analysed at Slaeggerup with the product used shown in parentheses. Degradation products are in italics. Precipitation (prec.) and percolation (perc.) are accumulated from the date of first application until the end of monitoring. 1st month perc. refers to accumulated percolation within the first month after application. C_{mean} refers to average leachate concentration in the drainage water the first drainage season after application (See Appendix 2 for calculation methods). The number of pesticide-positive samples is indicated in parentheses.

Crop and analysed pesticides	Application date	End of monitoring	Prec. (mm)	Perc. (mm)	1st month perc. (mm)	C_{mean} 1) (µg/l)
Spring barley 2000						
Metsulfuron-methyl (Ally)	May 00	Apr 03	2112	959	10	<0.01(0)
- triazinamin						<0.02(0)
Flamprop-M-isopropyl (Barnon Plus)	Jun 00	Jul 03	2300	1001	0	<0.01(5)
- flamprop (free acid)						<0.01 (2)
Propiconazole (Tilt Top)	Jun 00	Jul 03	2295	1000	0	<0.01 (0*)
Fenpropimorph (Tilt Top)	Jun 00	Jul 02	1519	655	0	<0.01 (0)
- fenpropimorphic acid						<0.01 (1)
Dimethoate (Perfection 500 S)	Jun 00	Jul 02	1519	655	0	<0.01 (0)
Triazinamin-methyl 1) (Express)	Jun 00	Apr 03	2080	647	0	<0.02 (0)
Peas 2001						
Pendimethalin (Stomp SC)	May 01	Jul 03	1703	752	22	<0.01 (1)
Bentazone (Basagran 480)	May 01	Jul 03	1703	752	22	0.02(14)
- 2-amino-N-isopropyl-benzamid						<0.02 (0)
Pirimicarb (Pirimor G)	Jul 01	Jul 03	1525	717	0	<0.01(1*)
- pirimicarb-desmethyl						<0.02(0)
- pirimicarb-desmethyl-formamido						<0.02(0)
Winter wheat 2002						
Glyphosate (Roundup Bio)	Sep 01	Jul 03	1302	658	50	0.04(21)
- AMPA						0.06(29)
Ioxynil (Oxitril)	Nov 01	Jul 03	1227	603	39	<0.01(3)
Bromoxynil (Oxitril)	Nov 01	Jul 03	1227	603	39	<0.01(2)
Amidosulfuron (Gratil)	Apr 02	Jul 03	946	353	6	< 0.01 (0)
Flamprop-M-isopropyl (Barnon Plus)	May 02	Jul 03	899	349	5	<0.01 (5*)
- flamprop-free acid						<0.01 (2*)
Propiconazole (Tilt 250 EC)	Jun 02	Jul 03	871	346	0	<0.01 (0*)
Pirimicarb (Pirimor G)	Jul 02	Jul 03	840	344	0	<0.01 (1*)
- pirimicarb-desmethyl						<0.01 (0)
- pirimicarb-desmethyl-formamido						<0.01 (0)

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

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

*) *The pesticide has been applied twice and the findings are not necessarily related to one specific application*

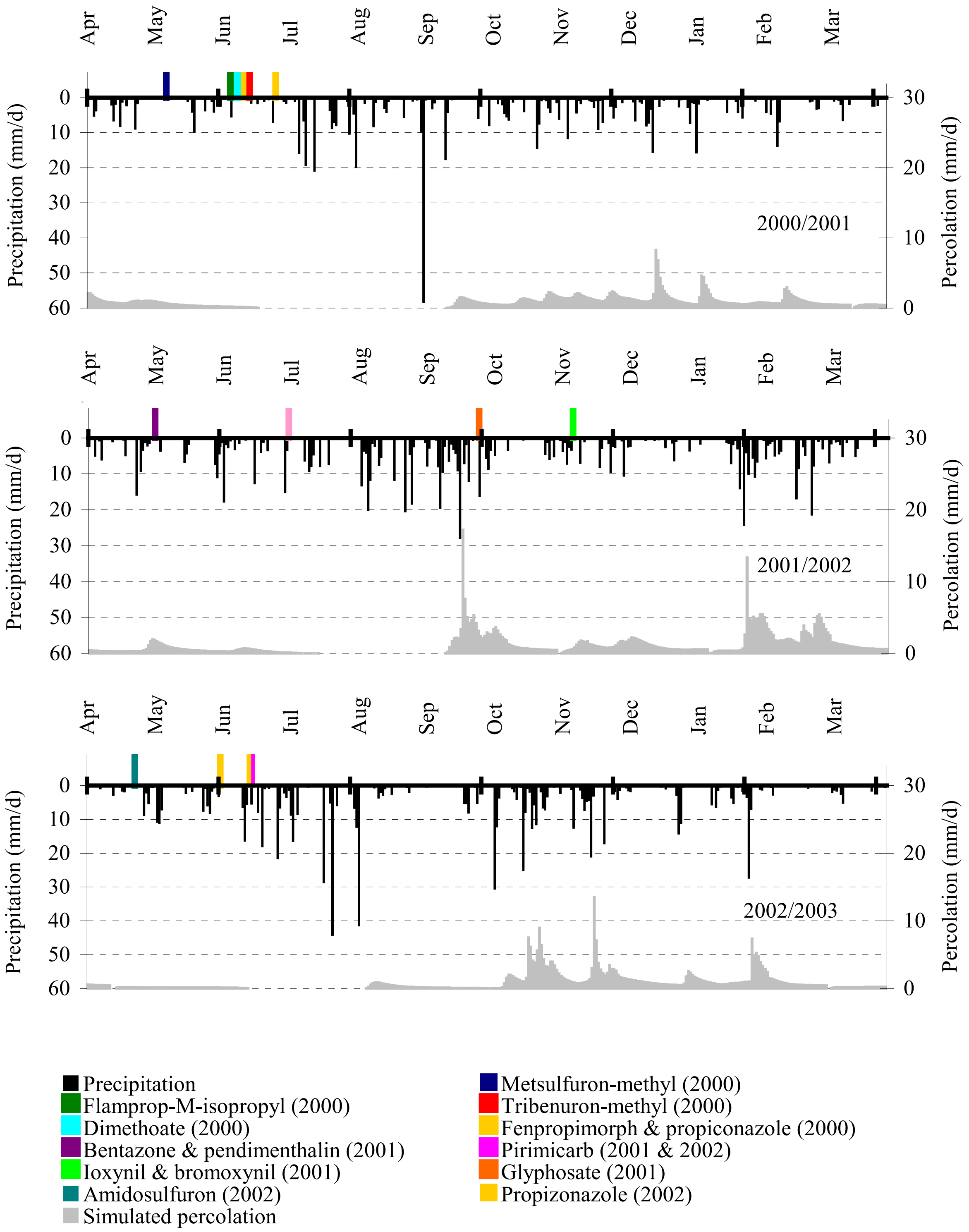

Figure 56. Pesticide application and precipitation (primary axis) together with simulated percolation 1 m b.g.s. (secondary axis) at Slaeggerup. Pesticides applied later than April 2003 are not included. As tribenuron methyl degrades rapidly it is the degradation product triazinamin-methyl that is monitored.

The leaching risk of pesticides applied during 2000 has been evaluated in Kjær *et al.* (2003). The findings regarding the pesticides applied during 2001 and 2002 are summarized below.

On 16 May, just 16 days after application, ***bentazone*** was detected at a concentration of 0.01 µg/l in soil water sampled 1 m b.g.s. at S2 as well as in the two uppermost screens of the vertical well M6. The following autumn, minor leaching of bentazone was detected. Bentazone was thus found in one flow-proportional sample of drainage water collected on 24 October 2001 (0.024 µg/l) and in five time-proportional samples collected between 6 February and 12 March 2002 (0.01–0.03 µg/l). In November/December 2002 and in January 2003, bentazone was found in three samples from the horizontal monitoring screen (0.019–0.024 µg/l).

On 27 November 2001, 13 days after application, ***ioxynil*** and ***bromoxynil*** were detected in a time-proportional drainage water sample at concentrations of 0.18 µg/l and 0.14 µg/l, respectively. Moreover, ioxynil was detected at a concentration of 0.02 µg/l in a time-proportional sample collected on 4 December 2001 and most recently in a flow-proportional sample collected on 1 March 2002. None of the substances were detected in any samples from the groundwater monitoring wells.

Glyphosate has been detected in 21 water samples from the drainage system and ***AMPA*** in 28 drainage water samples and one sample from the horizontal screen. August and in particular September 2001 were rainier than usual, causing drainage flow earlier than usual for the location (Figure 55; Appendix 4). When the field was sprayed with Roundup Bio (4.0 l/ha) on 26 September 2001, drainage flow had been going on for a little more than a week, although at very low levels (0.1 to 0.3 mm ha/day). When glyphosate and AMPA initially appeared in the drainage water just six days after application and after 34 mm of precipitation, the level of drainage flow was low. When the concentrations subsequently started to increase, the flow was still low due to a dry November and December (Figure 57; Appendix 4). Despite the very high concentrations detected (5.1 µg/l glyphosate and 5.4 µg/l AMPA), the amount leached during this period was thus very small. When runoff eventually started to increase due to the wetter than normal weather in January and February (Appendix 4), the concentration of both glyphosate and AMPA had decreased to low levels. During the 2001/2002 leaching season, the average drainage water concentration of glyphosate was 0.04 µg/l, while that of AMPA was 0.06 µg/l. During the 2003/2003 drainage season AMPA was detected at low concentrations (0.01 µg/l) during November 2002, whereas glyphosate was not detected (Figure 57). Apart from a single sample form the horizontal screen containing 0.017 µg/l AMPA, glyphosate and AMPA were not detected in samples from the groundwater monitoring wells.

No evidence was found to indicate leaching of the other pesticides applied in 2001 and 2002 since they were only detected in two drainage samples, one containing 0.01 µg/l pirimicarb and one containing 0.01 µg/l pendimethalin (Table 14). The flamprop-M-isopropyl detected was thus related to the previous application in 2000 (see Kjær *et al.,* 2002). It should be noted that the leaching risk of amidosulfuron is also associated with two of its degradation products. Methods for analysing these substances are not yet available, however.

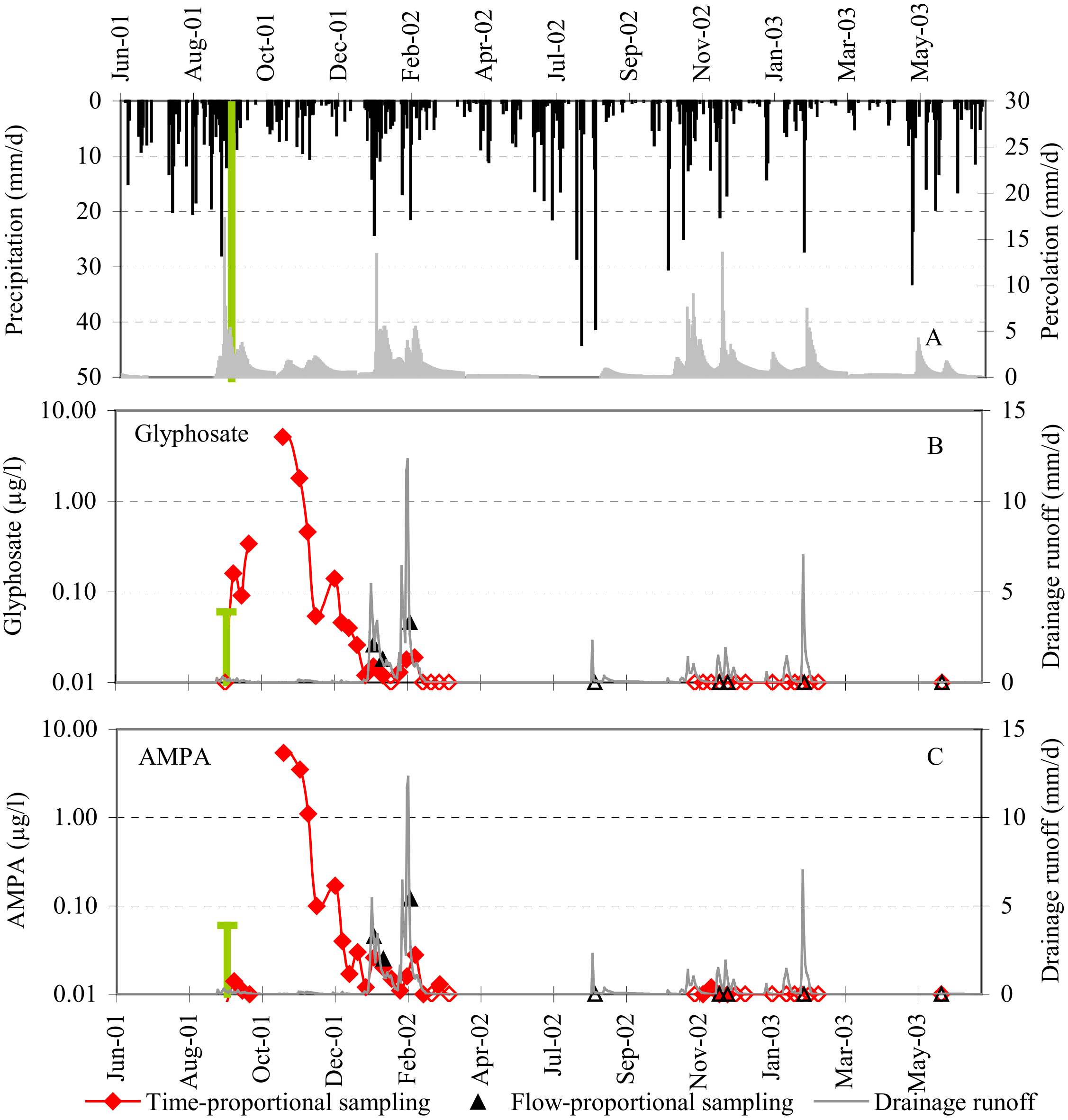

Figure 57. Precipitation and simulated percolation (A) together with the drainage water concentration of glyphosate (B) and AMPA (C) at Slaeggerup. The green vertical line indicates the date of application. Open diamonds and triangles indicate values below the detection limit of 0.01 µg/l.

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 has been supported by intensive quality assurance entailing continuous evaluation of the analyses employed. Two types of samples are used in the quality control – samples with known pesticide composition and concentration are used for *internal monitoring* of the laboratory method while *external spiked samples* are used to incorporate additional procedures such as sample handling, transport and storage. Pesticide analysis quality assurance (QA) data for the period July 2002–June 2003 are presented below while those for the preceding monitoring periods are given in Kjær *et al.* (2001, 2002, and 2003).

8.1 Materials and methods

The pesticide analyses were carried out at two commercial laboratories selected on the basis of a competitive tender. In order to assure the quality of the analyses, the call for tenders included requirements as to the laboratory's quality assurance (QA) system comprising both an internal and an external control procedure. In addition to specific quality control under the PLAP, each of the laboratories takes part in the proficiency test scheme employed by the Danish Environmental Protection Agency when approving laboratories for the Nationwide Monitoring and Assessment Programme for the Aquatic and Terrestrial Environments (NOVANA).

8.1.1 Internal QA

With each batch of samples the laboratories analysed one or two control samples prepared at each laboratory as a part of their standard method of analysis. The pesticide concentration in the internal QA samples was generally in the range 0.04 to 0.08 µg/l. Using these data it was possible to calculate and separate the analytical standard deviation into within-day (S_w), between-day (S_b) and total standard deviation (S_t). Total standard deviation was calculated using the following formula (Wilson 1970, Danish EPA 1997):

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

8.1.2 External QA

Every fourth month, two external control samples were analysed at the laboratories along with the various water samples from the six test sites. Two stock solutions of different concentrations were prepared from two standard mixtures in ampoules prepared by Promochem, Germany (Table 15). Fresh ampoules were used for each set of low and high standard solutions. 150 µl or 350 µl of the pesticide mixture was pipetted into a preparation glass containing 10 ml of ultrapure water. The glass was closed and shaken thoroughly and shipped to the staff collecting the samples. The staff finished the preparation of control samples in the field by quantitatively transferring the standard solution to a 3 l measuring flask. The standard solution was diluted and adjusted to the mark with groundwater from an upstream well. After thorough mixing, the control sample was transferred to a sample bottle and transported to the laboratories together with the regular samples. The standard solutions were prepared two days before a sampling day. The pesticide concentration in the solution is indicated in Table 15. Blank samples consisting of HPLC water were also included in the external QA procedure every month. All samples included in the control were labelled with coded reference numbers so that the laboratories were unaware of which samples were controls and blanks.

Table 15. Pesticide concentrations in the spike solution and in the high-level and low-level external control samples.

Compound	Spike solution (mg/l)	High-level control (ng/l)	Low-level control (ng/l)
Bentazone	1	117	50
Bromoxynil	1	117	50
Clomazone	1	117	50
Desmedipham	1	117	50
Dimethoate	1	117	50
Ethofumesate	1	117	50
Fenpropimorph	1	117	50
Flamprop (free acid)	1	117	50
Fluazifop (free acid)	1	117	50
Fluroxypyr (free acid)	1	117	50
Glyphosate	1	117	50
PPU	1	117	50
Ioxynil	1	117	50
Metamitron	1	117	50
Metribuzin	1	117	50
PHCP	1	117	50
Phenmedipham	1	117	50
Propiconazole	1	117	50
Pirimicarb	1	117	50
Terbuthylazine	1	117	50
Triazinamin-methyl	1	117	50
Triazinamin	1	117	50

8.2 Results and discussion

8.2.1 Internal QA

Ideally, the analytical procedure should provide precise and accurate results. However, the pesticide analyses that form the basis of the PLAP programme are subject to a certain standard deviation. Such standard deviation may be the combined result of several contributing factors. Overall, the accuracy of an analytical result reflects two types of error: random errors related to precision and systematic errors relating to bias. In a program like PLAP it is relevant to consider possible changes in analytical “reliability over time”. As these 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 result. To this end, control samples are included in the analytical process as described above. Thus, by means of statistical analysis of the internal QA data it is possible to separate and estimate the different causes of the analytical variation in two categories: day-to-day variation and within-day variation (Miller *et al.,* 2000; Funk *et al.*, 1995) This kind of analysis can provide an indication of the reliability of the analytical results used in the PLAP. The statistical tool used is an analysis of variance (ANOVA) and encompasses all duplicate pesticide analyses, single analyses being excluded. The analysis can be divided into three stages:

1. NORMALITY: An initial test for normality is made as this is an underlying assumption for the one-way ANOVA
2. BETWEEN-DAY CONTRIBUTION: Explained simply, this test will reveal any day-to-day contribution to the variance in the measurements. If there is none, the total standard deviation can be considered to be attributable to the within-day error of the analysis. For this purpose an ANOVA based test is used to determine if the between-day standard deviation (S_b) differs significantly from 0 (this test is made as an F-test with the $H_{0:}$ between-day mean square = within-day mean square).
3. CALCULATING STANDARD DEVIATIONS. If the F-test described above reveals a contribution from the between-day standard deviation (S_b) it is relevant to calculate three values: The within-day standard deviation S_w, the between-day standard deviation S_b, and the total standard deviation S_t.

As the error associated with the analytical result is likely to be highly dependent on the compound analysed, the QA applied is pesticide specific. The results of the internal QA statistical analysis for each pesticide are presented Table 16 and Table 17. For reference, estimated S_b values are listed for all pesticides, including those for which the between-day variance is not significantly greater than the within-day variance. ANOVA details and variance estimates are also included, even in the case of pesticides where the requirement for normality is not fulfilled. Such data should obviously be interpreted with caution.

As a "rule of thumb" the between-day standard deviation should be no more than double the within-day standard deviation. From Table 16 and Table 17 it can be seen that S_b/S_w ratios greater than two were observed for several compounds. As mentioned, the analysis is only conclusive for pesticide data that meet the normality requirement. Among the pesticides meeting the requirement, the Sb/Sw ratio is highest for fenpropimorph and pendimethalin . Overall, the results indicate a relative large contribution by the day-to-day variation.

The total standard deviations (S_t) of the various pesticide analyses lie within the range 0.002–0.053 µg/l (only data with $n \geq 3$ are included in the analysis). The overall mean S_t was 0.016 µg/l. S_t was in the range 0.001–0.053 µg/l for the pesticides and 0.002–0.051 µg/l for the degradation products. The three pesticides with the poorest reproducibility were fluazifop-P (free acid), MCPA and pirimicarb. Analysing S_t with a *t*-test revealed no significant differences between pesticides and degradation products (*t*-test, equal variances, $\alpha = 0.05$). However, S_t differed significantly within laboratories (*t*-test, Satterthwaite unequal variances, $\alpha = 0.05$). In interpreting the observed difference between laboratories it should be noted the selection of pesticides and number of duplicate samples varies between the two laboratories.

Table 16 Internal QA of pesticide analyses from laboratory 1. Results of the test for normality, one-way analysis of variance (ANOVA), and the estimated values of standard deviations (w: within day, b: between-day, t: total – see text for details), and number of duplicate samples (n) is given for each pesticide. Degradation products are indicated with 'D' following the compound name. For tests the P value α=0.05 was used. Only data for n≥3 are included.

Pesticide / Degradation product		Normal distribution α=0.05	Significant S_b between-day contribution ANOVA α=0.05	S_w (µg/l)	S_b (µg/l)	S_t (µg/l)	Ratio Sb/Sw	n
2-hydroxy-desethyl-terbuthylazine	D	yes		0.008	0.007	0.011	0.92	11
2-hydroxy-terbuthylazine	D	yes		0.011	0.006	0.013	0.51	12
4-chlor-2-methylphenol	D			0.038	0.014	0.041	0.38	29
AMPA	D	yes	yes	0.006	0.005	0.007	0.84	40
EHPC	D		yes	0.012	0.046	0.048	3.74	43
Propanamide-clomazone	D		yes	0.010	0.047	0.048	4.53	32
PPU	D		yes	0.003	0.004	0.005	1.13	10
PPU-desamido	D	yes	yes	0.002	0.005	0.005	2.24	10
MCPA			yes	0.011	0.047	0.049	4.25	31
MHPC	D		yes	0.009	0.035	0.036	3.73	43
Bentazone			yes	0.006	0.025	0.026	4.51	6
Clomazone			yes	0.009	0.041	0.042	4.34	29
Desethylterbuthylazine	D	yes	yes	0.001	0.004	0.004	2.54	33
Desisopropylatrazine	D	yes	yes	0.008	0.010	0.013	1.20	13
Desmedipham			yes	0.008	0.035	0.036	4.61	40
Dimethoat			yes	0.009	0.038	0.039	4.42	44
Ethofumesate			yes	0.008	0.030	0.031	3.68	43
Fenpropimorph		yes	yes	0.003	0.006	0.006	2.17	25
Fenpropimorph acid	D		yes	0.003	0.011	0.012	3.35	25
Flamprop (free acid)			yes	0.007	0.034	0.035	4.82	44
Flamprop-M-isopropyl			yes	0.010	0.044	0.045	4.32	44
Fluazifop-P (free acid)			yes	0.012	0.052	0.053	4.39	26
Fluazifop-P-butyl			yes	0.007	0.031	0.032	4.38	31
Glyphosate			yes	0.003	0.004	0.004	1.37	41
Metamitron			yes	0.009	0.032	0.033	3.71	43
Pendimethalin		yes	yes	0.002	0.004	0.004	2.46	3
Phenmedipham			yes	0.008	0.035	0.036	4.44	42
Pirimicarb			yes	0.011	0.046	0.047	4.12	42
Pirimicarb-desmethyl-formamido	D		yes	0.013	0.049	0.051	3.85	23
Propiconazole			yes	0.008	0.027	0.028	3.50	52
Terbuthylazine			yes	0.003	0.007	0.007	2.57	33
Triazinamin-methyl	D		yes	0.007	0.030	0.031	4.13	44

Table 17. Internal QA of pesticide analyses from laboratory 2. Results of the test for normality, one-way analysis of variance (ANOVA), and the estimated values of standard deviations (w: within day, b: between-day, t: total – see text for details), and number of duplicate samples (n) is given for each pesticide. Degradation products are indicated with 'D' following the compound name. For tests the P value $\alpha=0.05$ was used. Only data for $n\geq3$ are included.

Pesticide / Degradation product		Normal distribution $\alpha=0.05$	Significant S_b between-day contribution ANOVA $\alpha=0.05$	S_w (µg/l)	S_b (µg/l)	S_t (µg/l)	Ratio Sb/Sw	N
2-amino-N-isopropylbenzamid	D			0.016	0.006	0.017	0.39	7
4-chlor-2-methylphenol	D	yes		0.004	0.004	0.006	0.87	6
Amidosulfuron	D	yes		0.005	0.002	0.005	0.38	6
EHPC	D	yes		0.002	0.002	0.003	1.18	3
Propanamide-clomazone	D			0.008	0.003	0.009	0.42	10
MCPA		yes		0.003	0.001	0.003	0.29	9
MHPC	D	yes		0.006	0.007	0.009	1.19	3
Bentazone		yes		0.002	0.002	0.002	1.00	10
Bromoxynil			yes	0.002	0.004	0.005	2.82	12
Clomazone				0.004	0.004	0.006	0.93	6
Clopyralid		yes		0.002	0.003	0.003	1.11	8
Desmedipham		yes		0.006	0.008	0.010	1.34	3
Dimethoat		yes		0.001	0.002	0.002	1.44	4
Ethofumesate		yes		0.001	0.002	0.002	1.49	4
Fenpropimorph		yes	yes	0.001	0.004	0.004	2.53	9
Fenpropimorph acid	D	yes	yes	0.003	0.004	0.005	1.57	6
Flamprop (free acid)		yes	yes	0.001	0.003	0.003	2.26	14
Flamprop-M-isopropyl				0.003	0.001	0.004	0.36	14
Ioxynil		yes	yes	0.002	0.004	0.005	2.02	12
Metamitron		yes		0.003	0.001	0.003	0.42	3
Metamitron-desamino	D	yes	yes	0.000	0.003	0.003	6.71	3
Metribuzin-desamino-diketo	D	yes	yes	0.004	0.005	0.006	1.08	10
Metribuzin-diketo	D	yes		0.008	0.005	0.009	0.63	10
Metsulfuron methyl		yes		0.005	0.006	0.008	1.04	5
Pendimethalin			yes	0.002	0.002	0.002	1.06	19
Phenmedipham			yes	0.001	0.003	0.003	5.72	3
Pirimicarb		yes	yes	0.002	0.002	0.002	1.16	13
Pirimicarb-desmethyl	D	yes	yes	0.005	0.007	0.008	1.49	18
Pirimicarb-desmethyl-formamido	D		yes	0.003	0.005	0.005	1.94	17
Propiconazole			yes	0.002	0.003	0.004	1.61	20
Triasulfuron		yes	yes	0.003	0.005	0.006	1.90	5
Triazinamin	D			0.008	0.001	0.008	0.15	10
Triazinamin-methyl	D			0.005	0.003	0.006	0.75	8

8.2.2 External QA

Table 18 provides an overview of the recovery of all externally spiked samples based on one to three observations. Recovery of the spiked samples is generally good (>70%). Exceptions are the pesticides desmedipham, fluroxypyr and phenmedipham, for which recovery was low at some of the field sites.

As the results are based on only one to three observations, this should not be interpreted rigorously. However, the data may indicate possible recovery problems for pesticides at one or several sites. A possible cause of the low recovery observed may be hydrolysis. Thus, both phenmedipham and desmedipham are easily hydrolysed in water, particularly at high pH. In contrast, the degradation products MHPC from phenmedipham and EHPC from desmedipham are rather stable to hydrolysis. In agreement with the hydrolysis hypothesis, some degradation products were observed in a few samples even if these compounds were not included in the spike solution: EHPC, MHPC, and PPU-desamido (indicated by asterisks in Table 18). These degradation products were not observed when testing the blank matrix used for spiking. Thus, the findings support the theory that in some instances, spiked compounds may have degraded during transport, storage or analysis. The compounds likely to have degraded are the rimsulfuron degradation product PPU due to detection of PPU-desamido, desmedipham due to detection of EHPC, and phenmedipham due to detection of MHPC.

The extent of degradation is related to the soil matrix as can be seen comparing samples from Faardrup with Silstrup. Low recovery is observed for desmedipham and phenmedipham at Faardrup indicating stability problems for these two compounds. However, even if degradation products were observed in samples from Silstrup the recovery of these compounds is within the acceptable range. Low recovery and possible degradation of these, particular compounds at Faardrup has been observed previously (Kjær *et al*., 2002*)*.

With some samples a rather high recovery was observed (>125%). At some sites particular large values were observed for bentazone and the degradation products triazinamin-methyl and triazinamin. As for the low recovery extremes, the high recovery values are also likely to be related to a matrix effect. This assumption is based on the observation that within-range recoveries of these substances were observed at other sites. When available, the external and internal QA results are shown for all substances that have been detected in Appendix 11.

During the 2002/2003 monitoring period a total of twelve pesticides and fourteen degradation products were detected in samples from the experimental fields and QA data relating to these particular pesticides/degradation products are of special interest. These data are therefore described in detail in Appendix 11.

No pesticides were detected in blank samples, thus indicating that no contamination of the samples occurred in the laboratory. Samples found to contain pesticides and their degradation products are thus regarded as true positive findings. All the pesticides in the spiked samples were detected in all samples.

Table 18. External spiked samples. Average recovery (%) of the nominal concentration at low/high concentration level indicated for each site.

	Tylstrup		Jyndevad		Silstrup		Estrup		Faardrup		Slaeggerup	
	Low	High	Low	High	Low	High	Low	High	Low	High	Low	High
Bromoxynil	82	107					86	91			79	82
Desmedipham [1)]					81	73			32	40		
Dimethoat	68	67	100	94	98	93			92	88		
Ethofumesate					98	89	78	82	92	91		
Fenpropimorph	70	69			79	77						
Fluroxypyr	40	34										
Glyphosate					103	128	88	79	87	85	104	64
Ioxynil	100	129					100	102			82	110
Metamitron					122	102	66	68	76	82		
Pendimethalin	91	87			98	84	103	109			100	94
Phenmedipham [1)]					85	73			42	43		
Pirimicarb	89	79			106	102	72	79	86	96	80	66
Propiconazole	74	78			90	90	96	95	71	83	83	93
Terbuthylazine			108	96	94	86						
Flamprop (free acid)	82	80			92	91	75	85	92	89	97	82
Bentazone					168	119	85	85			82	82
Triazinamin	134	108					110	126			87	90
MHPC *					*	*			*	*		
Triazinamin-methyl	19	19			110	95			99	91	131	145
EHPC *					*	*			*	*		
PHCP			142	122	140	119						
Clomazone	99	93							109	105		
PPU [1)]			78	81								
PPU-desamido *			*	*								
Fluazifop-P (free acid)									86	87		

[1)] The compound may have partly degraded as degradation products were detected at one or several sites

** Indicates that the compound was detected even if it was not included in the spiking solution – see text for details*

8.3 Summary

The overall quality of the pesticide analysis was considered satisfactory. The QA system showed that:

- Reproducibility of the pesticide analyses was good, total standard deviation being in the range 0.001-0.053 µg/l.
- No differences in reproducibility were observed between pesticides and degradation products
- Recovery was generally good (70–125%) in external spiked samples. Low recovery of the pesticides desmedipham, fluroxypyr and phenmedipham was observed at single sites. High recovery was observed for bentazone and the degradation products triazinamin-methyl and triazinamin at single sites.
- Variation in recovery of the same compound in spiked samples from different field sites indicates that uncertainties in analysis are partly attributable to differences in matrix composition.
- Contamination of samples was not observed during collection, storage and analysis.

9 Summary of monitoring results

The monitoring data identified three different leaching patterns for the applied pesticides – no leaching, slight leaching and unacceptable leaching (see Table 19). Unacceptable leaching is here defined as root zone leaching exceeding average concentration of 0.1 µg/l. It should be noted, though, that the present evaluation of the leaching risk of some of these pesticides is still preliminary as their potential leaching period extends beyond the current monitoring period. This applies to those pesticides marked with a single asterisk in Table 19. The monitoring results indicate a marked degree of leaching by four of the applied pesticides or their degradation products.

- Two degradation products of metribuzin – metribuzin-diketo and metribuzin-desamino-diketo – leached from the root zone (1 m b.g.s.) at average concentrations exceeding 0.1 µg/l at the sandy soil at Tylstrup. Both degradation products appear to be relatively stable and leached throughout the entire monitoring period. Average concentrations reaching 0.1 µg/l were thus seen as much as three years after application. Evidence was also found that their degradation products might be present in the groundwater several years after application. At both sandy sites (Tylstrup and Jyndevad), previous application of metribuzin has caused marked groundwater contamination with its degradation products (Kjær *et al.,* 2002; Kjær *et al.,* 2003).

- The findings indicate that glyphosate can leach through the root zone at high average concentrations on loamy soils. At the loamy sites Estrup and Silstrup, glyphosate leached from the root zone into the drainage water at average concentrations exceeding 0.1 µg/l. At Estrup its degradation product AMPA leached at an average concentration exceeding 0.1 µg/l. The leaching of glyphosate was mainly governed by pronounced macropore flow occurring within the first months after application. AMPA was frequently detected more than one and a half-years after application. That leaching of AMPA occurs a relatively long time after application is indicative of 1) AMPA being retained in the soil for a rather long time before it is further degraded, and 2) a minor release occurring from the uppermost metre of the soil. So far, the marked leaching of AMPA and glyphosate has mainly been confined to the depth of the drainage system and they have rarely been detected in monitoring screens located below the depth of the drainage system. At the two other loamy sites, Faardrup and Slaeggerup, glyphosate and AMPA were also detected in drainage water, but in acceptable levels. Evidence of glyphosate leaching was only seen in the loamy soil and the leaching risk was negligible at the coarse, sandy soil site at Jyndevad. Infiltrating water passed through a matrix rich in aluminium and iron thereby providing good conditions for sorption and degradation.

Table 19. Pesticide leaching at the 6 PLAP sites. Pesticides included in the monitoring programme for less than two years are indicated by an asterisk. The colours indicate the degree of leaching and the letters H, F and I indicate the type of pesticide: herbicide, fungicide and insecticide respectively. Pesticides applied in spring 2003 are not included in the table.

	Tylstrup (Sandy soil)	Jyndevad (Sandy soil)	Silstrup (Loamy soil)	Estrup (Loamy soil)	Faardrup (Loamy soil)	Slaeggerup (Loamy soil)
Glyphosate (H)		▒	🟥	🟥	🟦	🟦
Metribuzin (H)	🟥	🟥 1)				
Rimsulfuron (H)		🟥 *				
Terbuthylazine (H)		🟦	🟥 *			
Bentazone (H)				🟦		🟦
Bromoxynil (H)	▒ *			🟦	▒	🟦
Dimethoate (I)			🟦	▒	▒ *	▒
Ethofumesate (H)			🟦		🟦	
ETU (Mancozeb) (F)	🟦					
Fenpropimorph (F)	▒	▒	▒	▒	▒	🟦
Flamprop-M-isopropyl (H)			🟦	🟦	▒ *	🟦
Fluazifop-P (H)			▒		🟦	
Fluroxypyr (H)					🟦	
Ioxynil (H)	▒ *			🟦	▒	🟦
MCPA (H)				🟦 *	▒ *	
Metamitron (H)			🟦		🟦	
Pendimethalin (H)	▒			🟦		▒
Phenmedipham (H)			▒		🟦	
PHCP (Pyridate) (H)		▒	🟦 *			
Pirimicarb (I)	▒		🟦	🟦	🟦	▒
Propiconazole (F)	▒	▒	🟦	🟦	▒	▒
Amidosulfuron (H)				▒ *		▒ *
Clomazone (H)	▒				▒ *	
Desmedipham (H)			▒		▒	
Linuron (H)	▒					
Metsulfuron-methyl (H)				▒		▒
Triazinamin-methyl (Tribenuron methyl) (H)	▒	▒	▒		▒ *	▒
Triasulfuron (H)	▒					

1) Derived from previous application (see Kjær *et al.,* 2002)

🟥 Pesticide (or its degradation products) leached from the root zone (1 m b.g.s.) in average concentrations exceeding 0.1 µg/l.

🟦 Pesticide (or its degradation product) was detected in either several (more than three) consecutive samples or in a single sample in concentrations exceeding 0.1 µg/l; average concentration below 0.1 µg/l

▒ Pesticide either not detected or only detected in very few samples in concentrations below 0.1 µg/l

Table 20. Number of samples in which the various pesticides were detected at each site with the maximum concentration (µg/l) in parentheses. Degradation products are indicated in italics The table only encompasses those pesticides/degradation products detected in either several (more than three) consecutive samples or in a single sample in concentrations exceeding 0.1 µg/l. Pesticides applied in spring 2003 are not included.

	Tylstrup	Jyndevad	Silstrup	Estrup	Faardrup	Slaeggerup
Glyphosate		0	51(4.7)	121(2.1)	8(0.093)	21(5.1)
- *AMPA*		3(0.022)	80(0.35)	136(0.83)	17(0.11)	29(5.4)
Metribuzin	3(0.024)					
- *metribuzin-desamino-diketo*	305(2.1)	20(1.831)				
- *metribuzin-diketo*	505(0.69)	29(1.372)				
Rimsulfuron		0				
- *PPU*		23(0.21)				
- *PPU-desamido*		17(0.092)				
Terbuthylazine		0	70(1.55)			
- *desethylterbuthylazine*		28(0.056)	85(1.08)			
- *desisopropylatrazine*			18(0.047)*			
- *2-hydroxy-desethyl-terbuthylazine*			16(0.036)*			
- *2-hydroxy-terbuthylazine*			12(0.026)*			
Bentazone				52(0.73)		14(0.03)
- *2-amino-N-isopropylbenzamid*				1(0.026)		0
Bromoxynil	0			3(0.6)	0	2(0.14)
Dimethoate			2(1.417)	0	0	0
Ethofumesate			24(0.227)		45(12)	
ETU[1]	9(0.038)					
Fenpropimorph	0	2(0.038)	0	1(0.01)	1(0.015)	0
- *fenpropimorph-acid*	0	0	1(0.019)	0	0	1(0.25)
flamprop-M-isopropyl			13(0.109)	20(0.069)	1(0.037)	5(0.035)
- *flamprop (free acid)*			7(0.096)	13(0.031)	1(0.089)	2(0.35)
fluazifop-P (free acid)[2]			1(0.072)		17(3.8)	
fluroxypyr					1(0.19)	
ioxynil	0			20(0.25)	2(0.011)	3(0.18)
MCPA				12(3.894)	0	
- *4-chlor-2-methylphenol*				1(0.046)	0	
metamitron			69(0.551)		35(1.7)	
- *metamitron-desamino*			61(0.67)		63(2.5)	
pendimethalin				4(0.042)		1(0.01)
phenmedipham			0		2(0.025)	
- *MHPC*			0		3(0.19)	
PHCP[3]		0	18(2.69)			
pirimicarb	0		17(0.054)	28(0.077)	9(0.056)	1(0.012)
- *pirimicarb-desmethyl*	0		1(0.052)	0	9(0.053)	0
- *pirimicarb-desmethyl-formamido*	0		0	6(0.035)	5(0.076)	0
propiconazole	0	0	6(0.033)	26(0.862)	1(0.035)	0

[1] *degradation product of mancozeb*

[2] *degradation product of fluazifop-P-butyl*

[3] *degradation product of pyridate*

**) Included in the monitoring at Silstrup from February 2003*

- The degradation product of terbuthylazine - desethylterbuthylazine - also leached through the root zone at high average concentrations in loamy soils. At the loamy site Silstrup, desethylterbuthylazine leached from the root zone into the drainage water at average concentrations exceeding 0.1 µg/l. Moreover, desethylterbuthylazine was frequently detected in the monitoring screen situated beneath the drainage system. Apart from a few samples the concentrations here were all below 0.1 µg/l. Minor leaching of desethylterbuthylazine was also seen at the sandy soil at Jyndevad, where desethylterbuthylazine was frequently detected in low concentration (< 0.1 µg/l) in the soil water sampled 1 m b.g.s. Desethylterbuthylazine has not yet reached the groundwater monitoring screens located downstream of the Jyndevad test site.

- The degradation product of rimsulfuron – PPU – leached from the root zone (1 m b.g.s.) in average concentrations of 0.06–0.13 µg/l at the sandy soil at Jyndevad. PPU has not yet reached the groundwater monitoring screens located downstream of the test site. It should be noted that the concentration of PPU might be underestimated due to stability problems. Results from the field-spiked samples thus indicated that PPU are unstable and may have further degraded to PPU-desamido during subsequent storage and transport. The concentration was still elevated towards the end of the current monitoring period, thus indicating that leaching of the compound from the uppermost metre of the soil has not yet ceased. The present evaluation of the leaching risk is thus preliminary.

The monitoring data also indicate leaching of a further 17 pesticides, but not in unacceptable levels. Although the concentration exceeded 0.1 µg/l in several samples, the average concentration did not. This is summarized in Table 20, which shows the number of samples in which the various pesticides were detected at each site and the maximum concentration. Apart from the sandy soil site at Tylstrup, where slight leaching of ETU was observed (Kjær *et al.,* 2002), leaching within this group of pesticides was only observed at the loamy soil sites, where leaching was associated with pronounced macropore transport that resulted in very rapid movement of pesticides through the unsaturated zone.

On several occasions, single precipitation events caused leaching to the drainage water in high concentrations. In most cases the concentration decreased to a low level after a short period of time, and leached mass and average concentration in the drainage water were generally low. The observed leaching was typically confined to a 6–9 month period following pesticide application, exceptions being metamitron-desamino and bentazone. With these two compounds there was evidence of slight leaching one year after application.

Seven of the 28 pesticides applied – about 25% – did not leach during the monitoring period. This group includes the three different sulfonylureas – metsulfuronmethyl, triasulfuron and tribenuron methyl – that were applied at several sites. For example, tribenuron methyl was applied at 4 different sites under different hydrological conditions with percolation (1 m b.g.s.) during the first month after application ranging from 0 to 114 mm. The monitoring results provide no evidence of leaching of any of the applied compounds or their degradation products, including triazinamin and triazinamin-methyl.

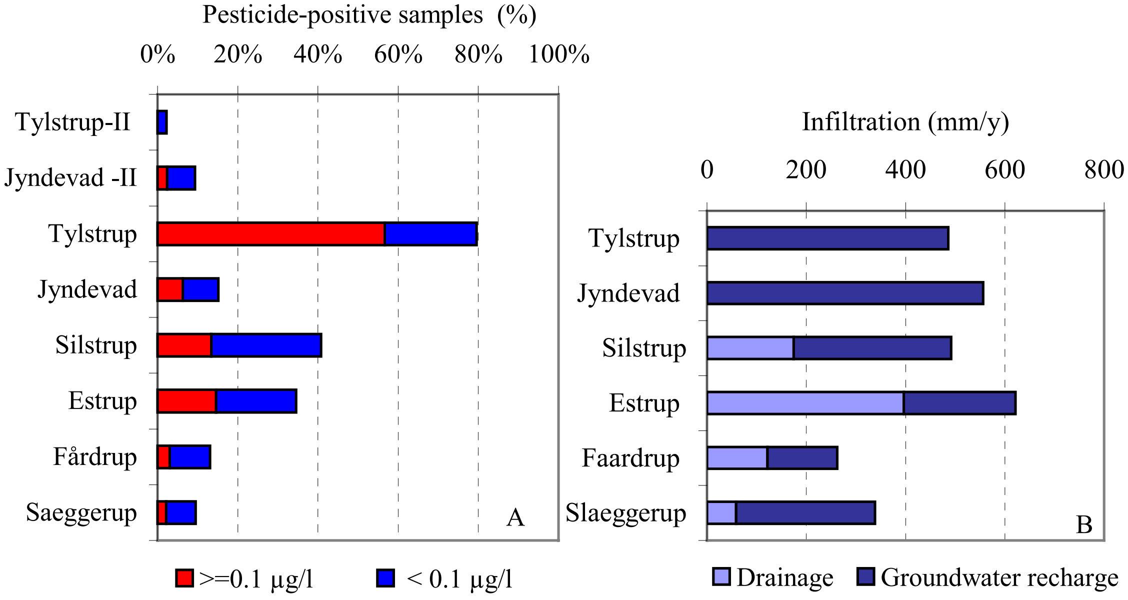

Figure 58. A: Percentage of all analysed samples containing one or more pesticides. In Tylstrup-II and Jyndevad-II metribuzin-diketo and metribuzin-desamino-diketo, have been excluded from the analyses. B: Infiltration apportioned as estimated groundwater recharge and measured drainage runoff (loamy soils).

The difference between the six field sites is further illustrated in Figure 58, which shows the percentage of analysed samples containing one or more pesticides. At the sandy sites the predominant pesticides detected were the degradation products of metribuzin (Figure 58 A). Excluding these degradation products from the analysis (Tylstrup-II and Jyndevad-II) revealed that very few samples from Tylstrup contained other pesticides (Figure 58A). At Jyndevad the percentage of pesticide-positive samples was slightly higher due to the incipient leaching of desethylterbuthylazine (degradation product of terbuthylazine) and PPU and PPU-desamido (degradation products of rimsulfuron).

At the loamy sites the number of pesticide-positive samples tends to be higher than at the sandy sites. At present, the differences between sandy and loamy soils are not necessarily due to the sandy soil being less vulnerable to pesticide leaching than the loamy soil. The differences should be seen in relation to differences in the pesticides tested on the different sites. Thus many of the pesticides that leached at the loamy sites have not yet been tested at the sandy soils (Table 19). Moreover, the differences should also be seen in relation to the different ways of examining root zone leaching. At the loamy sites the drainage system provides frequent and integrated water samples, continuously capturing water infiltrating during the drainage runoff season. In fact, the sampling procedure allowed all major storm event to be captured in separate samples (Appendix 2). At the sandy sites, groups of suction cups provide less frequent sampling in the form of discrete samples, which once a month were collected within a week.

Within the loamy sites the pesticide-positive samples was markedly higher at Silstrup and Estrup than at Faardrup and Slaeggerup. The hydrological conditions play an important role for these differences since precipitation and subsequent infiltration was markedly higher at

Silstrup and Estrup than at Faardrup and Slaeggerup (Figure 58B). In fact, the amount of percolation occurring within the first month after application was generally higher at Silstrup and Estrup than at Silstrup and Slaeggerup (Table 8, Table 10, Table 12 and Table 14).

At the loamy sites, several pesticides were frequently detected in the drainage system, whereas the amount of pesticide reaching the monitoring screen situated beneath the drainage system is limited and varies considerably between the four sites (Figure 59 - Figure 60). Once again, these differences should be seen in relation to the different sampling procedures applied. The drainage system provides frequent and integrated water samples, continuously capturing water infiltrating during the drainage runoff season. On the other hand the monitoring screens situated beneath the drainage systems were sampled less frequently (monthly samples from a limited number of monitoring screens; Appendix 2). Moreover the frequencies shown in Figure 59 and Figure 60 are based on the entire monitoring period and the time that the different pesticides have been included in the programme and the number of analysed samples thus vary considerably among the different pesticides. While transport to the drainage system occurs rapidly, the subsequent transport to the monitoring screen is generally much slower. For some pesticides the monitoring period might not have been sufficiently long for them to reach the monitoring screen.

Nevertheless, evidence of pesticide leaching was frequently found in selected monitoring screens at Faardrup (Kjær *et al.,* 2003) and in particular at Silstrup, where detection in monitoring screens were most pronounced. On the other hand, pesticide leaching at Estrup has hitherto mainly been confined to the depth of the drainage system. Apart from seven detections of glyphosate, pesticides have only sporadically been detected in monitoring screens located below the depth of the drainage system. Again, the hydrological conditions play an important role for these differences. The amount of leached pesticide leaving the system through drainage runoff is much higher at Estrup for example than at Silstrup, since the amount of percolation leaving the system through drainage runoff is far higher at Estrup than at Silstrup (Figure 58).

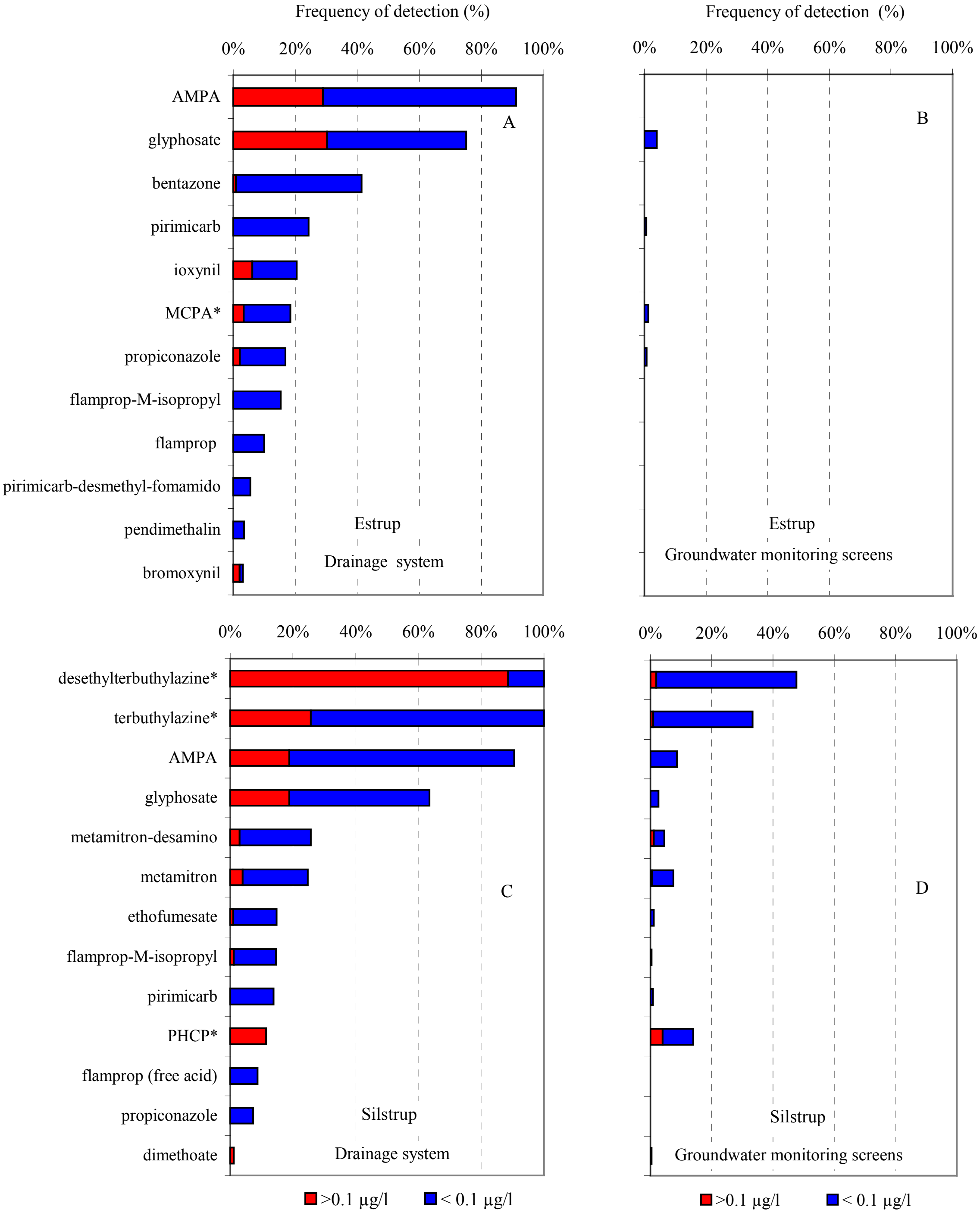

Figure 59. Frequency of detection in samples from the drainage system (left) and groundwater monitoring screen situated beneath the depth of the drainage system (right) at the loamy soils Silstrup (A, B) and Estrup (C,D). Frequency is estimated for the entire monitoring period and the time that the different pesticides have been included in the programme and the number of analysed samples thus vary considerably among the different pesticides. Pesticides monitored for less than two years are indicated by an asterisk. Pesticides either monitored for less than one year, or detected in less than two samples are not included.

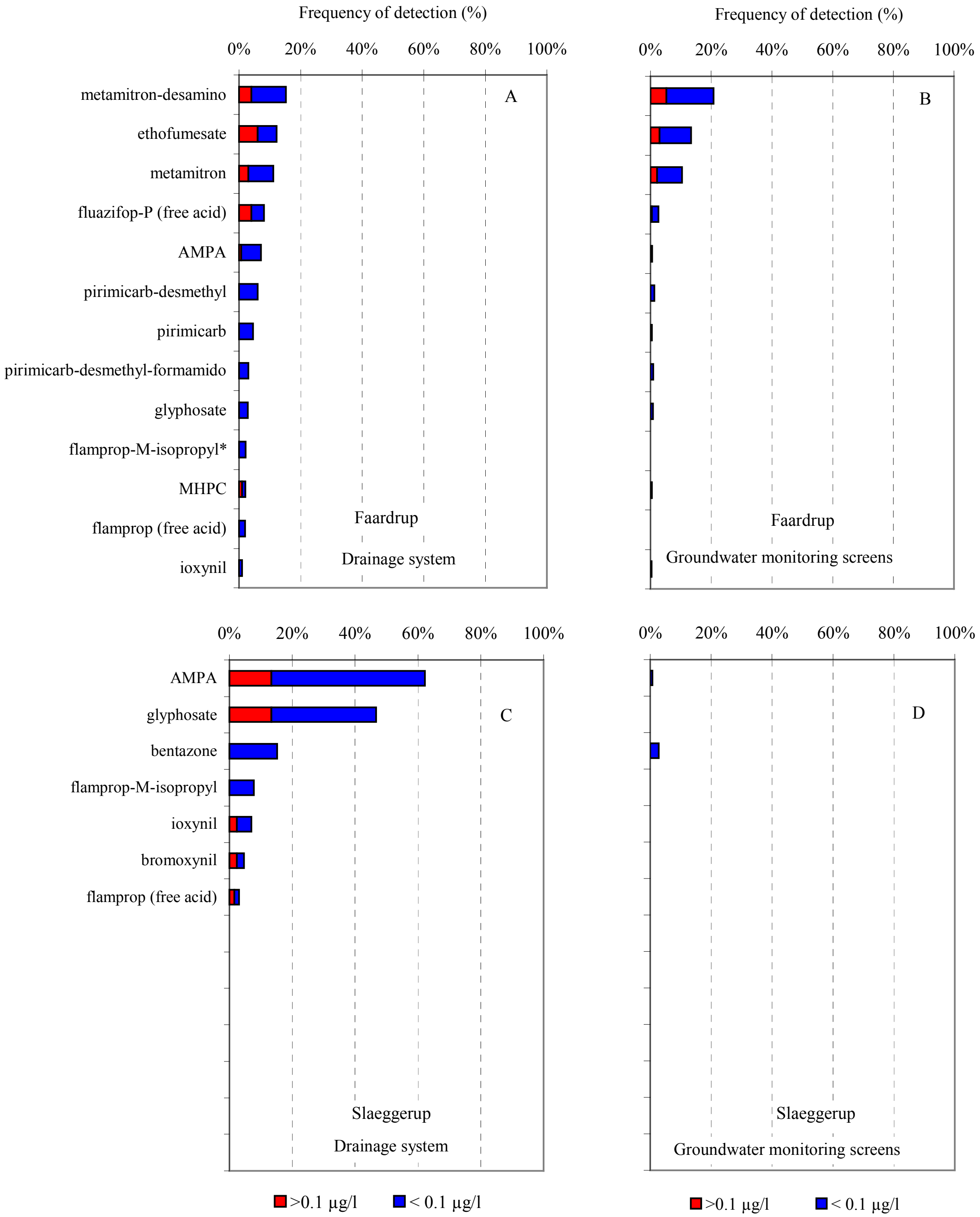

Figure 60. Frequency of detection in samples from the drainage system (left) and groundwater monitoring screen situated beneath the depth of the drainage system (right) at the loamy soils Faardrup (A, B) and Slaeggerup (C, D). Frequency is estimated for the entire monitoring period and the time that the different pesticides have been included in the programme and the number of analysed samples thus vary considerably among the different pesticides. Pesticides monitored for less than two years are marked indicated by an asterisk. Pesticide either monitored for less than one year, or detected in less than two samples are not included.

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

Table A1.1 Systematic chemical nomenclature for the pesticides and degradation products encompassed by the PLAP.

Parameter	Systematic chemical nomenclature
AMPA	Amino-methylphosphonic acid
Amidosulfuron	N-[[[[(4,6-dimethoxy-2-pyrimidinyl)amino]carbonyl]-amino]sulfonyl]-N-methylmethanesulfonamide
Bentazone	3-(1-methylethyl)-1H-2,1,3-benzothiadiazin-4(3H)-one 2,2 dioxide
Bromoxynil	3,5-dibromo-4-hydroxybenzonitrile
Clomazone	2-[(2-chlorphenyl)methyl]-4,4-dimethyl-3-isoxazolidione
Desethylterbuthylazine *	6-chloro-N-(1,1-dimethylethyl)-1,3,5,triazine-2,4-diamine
Desisopropylatrazine *	6-chloro-N-ethyl-1,3,5,triazine-2,4-diamine
Desmedipham	Ethyl 3-(phenylcarbamoyloxy)phenylcarbamate
Dimethoate	O,O-dimethyl S-methylcarbamoylmethyl-phosphorodithioate
EHPC*	Ethyl 3-hydroxy-phenylcarbamate
Ethofumesate	(±)-2-ethoxy-2,3-dihydro-3,3-dimethylbenzofuran-5-yl-methanesulfonate
ETU*	Ethylenethiourea
Fenpropimorph	Cis-4-[3-[4-(1,1-dimethylethyl)-phenyl]-2-methylpropyl]-2,6-dimethylmorpholine
Fenpropimorphic acid*	Cis-4-[3-[4-(2-carboxypropyl)-phenyl]-2-methylpropyl]-2,6-dimethylmorpholine
Flamprop (free acid)	N-benzoyl-N-(3-chloro-4-flourophenyl)-D-alanine
Flamprop-M-isopropyl	Isopropyl N-benzoyl-N-(3-chloro-4-flourophenyl)-D-alaninate
Fluazifop-P-butyl	Butyl (R)-2-[4-(5-trifuoromethyl-2-pyridyloxy)phenoxy]propionate
Fluazifop-P (free acid)*	(R)-2-[4-(5-trifluoromethyl-2-pyridyloxy)phenoxy]propanoic acid
Fluroxypyr	(4-amino-3,5-dichloro-6-fluro-2-pyridinyl)oxy]acetic acid
Glyphosate	N-(phosphonomethyl)glycine
Hydroxyterbuthylazine*	6-hydroxy-N-(1,1-dimethylethyl)-N´-ethyl-1,3,5,triazine-2,4-diamine
Hydroxydesethylterbuthylazine*	6-hydroxy-N-(1,1-dimethylethyl)-1,3,5,triazine-2,4-diamine
PPU-desamido*	N-((3-(ethylsulfonyl)-2-pyridyl)-4,6 dimethoxy-2 pyrimidinamine (IN70942)
PPU*	N-(4,6-dimethoxy-2-pyrimidinyl-N-((3-ethylsulfonyl)-2-pyridinyl)urea (IN70941)
Ioxynil	4-hydroxy-3,5-diiodobenzonitrile
Linuron	3-(3,4-dichlorophenyl)-1-methoxy-1-methylurea
MCPA	(4-cloro-2-methylphenoxy)acetic acid
Metamitron	4-amino-4,5-dihydro-3-methyl-6-phenyl-1,2,4-triazin-5-one
Metamitron-desamino*	4,5-dihydro-3-methyl-6-phenyl-1,2,4-triazin-5-one
Metribuzin	4-amino-6-tert-butyl-4,5-dihydro-3-methylthio-1,2,4-triazin-5-one
Metribuzin-desamino-diketo*	6-tert-butyl-4,5-dihydro-3-methylthio-1,2,4-triazin-3,5-dione

*Degradation product

Table A1.1 (continued) Systematic chemical nomenclature for the pesticides and degradation products encompassed by the PLAP.

Parameter	Systematic chemical nomenclature
Metribuzin-diketo*	4-amino-6-tert-butyl-4,5-dihydro-1,2,4-triazin-3,5-dione
Metsulfuron-methyl	Methyl2-[[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]=carbonyl]amino]-sulfonyl]benzoic acid
MHPC*	Methyl-N-(3-hydoxyphenyl)-carbamate
Pendimethalin	N-(1-ethyl)-2,6-dinitro-3,4-xynile
Phenmedipham	3-[(methoxycarbonyl)amino]phenyl (3-methylphenyl)carbamate
PHCP*	3-phenyl-4-hydroxy-6-chloropyridazine
Pirimicarb	2-(dimethylamino)-5,6-dimethyl-4-pyrimidinyldimethylcarbamate
Pirimicarb-desmethyl*	2-(dimethylamino)-5,6-dimethyl-4-pyrimidinylmethylcarbamate
Pirimicarb-desmethyl-formamido*	2-methylformamido-5,6-dimethylpyrimidine-4-yl dimethylcarbamate
Propanamide-clomazone*	(N-[2- chlorophenol)methyl] -3-hydroxy-2,2- dimethyl propanamide
Propiconazole	1-[[2-(2,4-dichlorophenyl)-4-propyl-1,3-dioxolan-2-yl]methyl]-1H-1,2,4-triazole
Rimsulfuron	N-[[(4,6-dimethoxy-2-pyrimidinyl)amino]carbonyl]-3-(ethylsulfonyl)-2-pyridinesulfonamide
Terbuthylazine	6-chloro-N-(1,1-dimethylethyl)-N-ethyl-1,3,5,triazine-2,4-diamine
Triasulfuron	1-[2-(2-chloroethoxy)phenylsulfonyl]-2-(4-methoxy-6-methyl-1,3,5-triazin-2-yl)-urea
Triazinamin	4-methoxy-6-methyl-1,3,5-triazin-2-amin
Triazinamin-methyl*	1,3,5-triazin-2-2-amine 4-methoxy-N, 6-dimethyl

*) Degradation product

From each of the PLAP sites, samples were collected of groundwater, drainage water and soil water in the unsaturated zone. A full description of the monitoring design is provided in Lindhardt *et al*. (2001). The sampling procedures are briefly summarized below:

Groundwater samples are collected monthly from vertical and horizontal monitoring wells. To facilitate sample collection from the vertical monitoring wells, a whale pump was permanently installed in each screen. Sampling from the horizontal monitoring wells was performed using a peristaltic pump. At the two sandy sites (Tylstrup and Jyndevad), each well was purged by removing a volume of water equivalent to three times the volume of the saturated part of the well prior to water sampling. At the four clayey sites, the well was purged by emptying it the day before sampling.

Soil water samples are collected monthly using 16 Teflon suction cups each connected via a single length of PTFE tubing to a sampling bottle located in a refrigerator in the instrument shed. The soil water was extracted by applying a continuous vacuum (of about 0.8 bar) to each of the suction cups one week prior to sampling. The 16 suction cups were clustered in four groups installed 1 m b.g.s. and 2 m b.g.s. at locations S1 and S2. Each group of suction cups consists of four individual cups covering a horizontal distance of 2 m. The chemical analysis for each group was performed on a single, pooled water sample.

Drainage water samples are collected using ISCO 6700 samplers equipped with eight 1,800-ml glass bottles (boron silicate), teflon suction tubes and intakes of stainless steel. The intakes are located a few centimetres into the inlet of the drainpipe to ensure sampling of flowing drain water and particulate matter. Two samplers are used at each site – one for time-proportional sampling and one for flow-proportional sampling:

- The time-proportional sampler is equipped with seven refrigerated bottles such that the water samples can be collected over a 7-day period. Hence during the period of continuous drainage runoff, a 70-ml sample is collected every hour independent of flow rate. 24 samples are collected per bottle giving 1,680 ml per day. Pesticides and inorganic chemicals (Br, Cl, K, Ca, Mg, Mn, Na, NO_3, PO_4, total-N, PO_4, total-P, dissolved total-P and suspended matter) are then analysed on a weekly basis on a pooled sample derived from the seven bottles.

- The flow-proportional sampler is only activated during storm events and sampling is carried out for 1–2 days depending on the intensity of the event. Hence each flow event is activated by a predefined rise in water level/runoff within the preceding 12-hour period. Sampling is controlled by the flow rate, where collection of each sample is initiated when the accumulated flow rate exceeds a predefined level depending on the month of the year. Levels of predefined rise and accumulated flow rate are set/adjusted individually for each site by experience. Each sample volume is 200 ml yielding nine samples per bottle and a maximum of 72 samples per storm event. For each storm event, analysis of pesticides and inorganic chemicals (Br, Cl, K, NO_3, DOC, PO_4, total-N, PO_4, total-P, dissolved total-P and suspended matter) is performed on pooled water samples deriving from all seven bottles. In addition, tracer analysis (Br, Cl, Ca and K) is performed on additional water samples deriving from each of the seven individual bottles.

The weighted average concentration of pesticides in the drainage water was calculated according to the following equation:

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

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

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

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

The monitoring programme encompasses the analysis of both inorganic parameters and selected pesticides:

Inorganic analysis is performed monthly on water samples derived from all monitoring wells and from the suction cups located at 1 m b.g.s. and 2 m b.g.s. Br, Cl, K, Ca, NO_3, NO_2, PO_4, SO_4, pH and conductivity are measured monthly. Until March 2002, HCO_3, Fe, Mg, Mn, DOC, Na, NO_3, NO_2, PO_4, total-P, dissolved total-P, suspended matter and SO_4 were measured four times a year. At the loamy sites the inorganic analysis is also performed on drainage water samples.

Until March 2002, pesticide analysis was performed monthly on water samples from the suction cups located both 1 m b.g.s. and 2 m b.g.s., from two screens of the horizontal monitoring wells and from two of the downstream vertical monitoring wells. In addition, more intensive monitoring encompassing all four groups of suction cups, six screens of the horizontal monitoring wells and five monitoring wells was performed every fourth month (Kjær *et al.*, 2002). At the loamy sites, the pesticide analysis was also performed on drainage water samples.

The monitoring programme was revised in March 2002 and the number of pesticide analyses was reduced. At the loamy sites, pesticide analysis of water sampled from the suction cups was ceased, and the monthly monitoring was restricted to just one monitoring well. At Jyndevad, pesticide analysis of the suction cups located 2 m b.g.s. was ceased and the interval for the intensive monitoring encompassing the larger number of monitoring screen was extended to six months except for the suction cups 2 m b.g.s. at Tylstrup, where the 4-month interval was retained (Table A2.1).

Table A2.1 Pesticide monitoring programme in the suction cups (S), horizontal monitoring wells (H) and vertical monitoring (M) wells as of March 2002.

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

*) *Measured every fourth month*

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

Table A3.1 Management practice at Tylstrup during the 2002 and 2003 growing seasons. The active ingredients of the various pesticides are indicated in parentheses.

Date	Management practice
03.09.01	Winter rape sown – cultivar Artus
05.09.01	Herbicide – 0.25 l/ha Command CS (clomazone)
16.10.01	Herbicide – 1.0 l/ha Matrigon (clopyralid)
22.03.02	Fertilization – 155 kg N/ha, 20 kg P/ha and 72 kg K/ha
24.04.02	Irrigation – 24 mm/ha
16.05.02	Irrigation – 22 mm/ha
31.05.02	Irrigation – 34 mm/ha
27.07.02	Winter rape harvested (seed yield 25.9 hkg/ha; 91% dry matter)
12.08.02	Disk harrowed – 6 cm depth
19.09.02	Winter wheat sown – cultivar Solist
09.10.02	Herbicide – 3.0 l/ha Boxer EC (prosulfocarb) + 1.0 l/ha Oxitril (ioxynil+bromoxynil)
17.03.03	Tracer application – 30 kg/ha potassium bromide
17.03.03	Fertilization – 61.1 kg N/ha, 8.7 kg P/ha and 29.1 kg K/ha
08.05.03	Herbicide application – 0.8 l/ha Starane 180 (fluroxypyr)
13.05.03	Fertilization – 76.4 kg N/ha, 10.9 kg P/ha and 36.4 kg K/ha
15.05.03	Herbicide – 3.0 l/ha Barnon Plus (flamprop-m-isopropyl)
28.05.03	Fungicide – 0.25 l/ha Tilt 250 EC (propiconazole)
17.06.03	Fungicide – 0.25 l/ha Tilt 250 EC (propiconazole)
24.06.03	Irrigation – 23 mm/ha
08.07.03	Insecticide – 0.6 l/ha Perfection 500 S (dimethoate)
20.08.03	Winter wheat harvested (grain yield 54.5 hkg/ha, 85% dry matter. Straw yield 35.0 hkg/ha, 100% dry matter)

Table A3.2 Management practice at Jyndevad during the 2002 and 2003 growing seasons. The active ingredients of the various pesticides are indicated in parentheses.

Date	Management practice
01.04.02	Ploughed – 20 cm depth
20.04.02	Seed bed preparation – 15 cm depth
22.04.02	Potatoes planted – cultivar Oleva
13.05.02	Herbicide – 0.2 kg/ha Sencor WG (metribuzin)
23.05.02	Herbicide – 30 g/ha Titus (rimsulfuron)
01.06.02	Fertilization – 30 kg N/ha
13.06.02	Irrigation – 20 mm/ha
18.06.02– 05.08.02	Eight fungicide applications – each comprising 0.2 l/ha Shirlan (fluazinam)
24.09.02	Potatoes harvested (tuber yield 515.8 hkg/ha; 23.0% dry matter)
01.10.02	Stubble harrowed – 12 cm depth
12.03.03	Tracer application – 30.0 kg/ha potassium bromide
07.04.03	Ploughed – 20 cm depth (furrow packed)
08.04.03	Fertilization – 128 kg N/ha, 19 kg P/ha and 64 kg K/ha
09.04.03	Spring barley sown – cultivar Otira
06.05.03	Herbicide – 0.020 kg/ha Ally (metsulfuron-methyl)
03.06.03	Herbicide – 2.0 l/ha Metaxon (MCPA)
06.06.03	Fungicide – 0.25 l/ha Tilt 250 EC (propiconazole)
07.06.03	Irrigation – 26 mm/ha
25.06.03	Insecticide – 0.6 l/ha Perfection 500 S (dimethoate)
25.06.03	Fungicide – 0.25 l/ha Tilt 250 EC (propiconazole)
04.08.03	Spring barley harvested (seed yield 73.3 hkg/ha; 85% dry matter. Straw yield 26.5 hkg/ha; 100% dry matter)

Table A3.3 Management practice at Silstrup during the 2002 and 2003 growing seasons. The active ingredients of the various pesticides are indicated in parentheses.

Date	Management practice
25.04.02	Seedbed preparation – 8 cm depth
25.04.02	Maize sown – cultivar Loft
19.05.02	Herbicide – 1.5 l/ha Lido (terbuthylazine + pyridate)
03.06.02	Herbicide – 1.5 l/ha Lido (terbuthylazine + pyridate)
19.06.02	Herbicide – 1.5 l/ha Matrigon (clopyralid)
23.09.02	Maize harvested (total yield 134.3 hkg/ha; 100% dry matter. Left on field 27.5 hkg/ha in stubble)
08.10.02	Stubble harrowed – 5 cm depth
11.11.02	Ploughed – 24 cm depth
07.04.03	Fertilization – 8.7 kg P/ha and 45.4 kg K/ha
07.04.03	Seedbed preparation – 3 cm depth
14.04.03	Peas sowing – cultivar Attica
17.05.03	Herbicide – 1.0 l/ha Basagran 480 (bentazone) + 1.5 l/ha Stomp SC (pendimethalin)
10.08.03	Peas harvested (seed yield 39.8 hkg/ha; 86% dry matter. Straw yield 30.0 hkg/ha; 100% dry matter)

Table A3.4 Management practice at Estrup during the 2002 and 2003 growing seasons. The active ingredients of the various pesticides are indicated in parentheses.

Date	Management practice
19.10.01	Winter wheat sown – cultivar Ritmo
20.11.01	Herbicide – 1.0 l/ha Oxitril CM (ioxynil + bromoxynil)
22.03.02	Fertilization – 73.5 kg N/ha, 10.5 kg P/ha and 35 kg K/ha
24.04.02	Fertilization – 73.5 kg N/ha, 10.5 kg P/ha and 35 kg K/ha
25.04.02	Herbicide – 20 g/ha Gratil 75 WP (amidosulfuron)
13.05.02	Herbicide – 2.0 l/ha Metaxon (MCPA)
27.05.02	Fungicide – 0.25 l/ha Tilt 250 EC (propiconazole)
17.06.02	Fungicide – 0.25 l/ha Tilt 250 EC (propiconazole)
24.06.02	Insecticide – 0.25 kg/ha Pirimor G (pirimicarb)
09.08.02	Winter wheat harvested (grain yield 69.4 hkg/ha; 85% dry matter)
19.08.02	Straw removed (straw yield 41.4 hkg/ha; 100% dry matter)
02.09.02	Herbicide – 4.0 l/ha Roundup Bio
14.04.03	Cattle slurry – 60.8 tonnes/ha: 265.7 kg Total-N/ha, 60.2 kg P/ha, 266.3 kg K/ha and 169.0 kg NH_4-N/ha
15.04.03	Ploughed – 20 cm depth
16.04.03	Seedbed preparation – 5 cm depth
16.04.03	Fodder beet sown – cultivar Magnum,
08.05.03, 22.05.03 & 16.06.03	Herbicide – 1.0 l/ha Goltix SC700 + 1.0 l/ha Betanal Optima (metamitron, phenmedipham, desmedipham and ethofumesate)
28.07.03	Insecticide – 0.3 kg/ha Pirimor G (pirimicarb)

Table A3.5 Management practice at Faardrup during the 2002 and 2003 growing seasons. The active ingredients of the various pesticides are indicated in parentheses.

Date	Management practice
27.03.02	Fertilization – 95 kg N/ha, 13 kg P/ha and 35 kg K/ha
28.03.02	Spring barley sown – cultivar Barke
07.05.02	Herbicide – 15 g/ha Express (tribenuron methyl)
22.05.02	Herbicide – 2.0 l/ha Metaxon (MCPA)
25.05.02	Herbicide – 3.0 l/ha Barnon Plus (flamprop-M-isopropyl)
04.06.02	Insecticide – 0.4 l/ha Perfection 500 S (dimethoate)
04.06.02	Fungicide – 0.5 l/ha Tilt 250 EC (propiconazole)
09.08.02	Spring barley harvested (grain yield 65.6 hkg; 85% dry matter. Straw yield 60.2 hkg/ha; 100% dry matter)
19.08.02	Ploughed – 25 cm depth
20.08.03	Fertilization – 30 N kg/ha
22.08.03	Winter rape sown – cultivar Canberra
23.08.03	Herbicide – 0.33 l/ha Command CS (clomazone)
25.09.02	Herbicide – 1.0 l/ha Matrigon (clopyralid)
24.03.03	Fertilization – 145 kg N/ha, 20 kg P/ha and 53 kg K/ha
24.04.03	Insecticide – 0.5 l/ha Fastac (alpha-cypermethin)
28.07.03	Winter rape harvested (seed yield 28.7 hkg/ha; 9% dry matter. Straw yield 38.9 hkg/ha; 100% dry matter).

Table A3.6 Management practice at Slaeggerup during the 2002 and 2003 growing seasons. The active ingredients of the various pesticides are indicated in parentheses.

Date	Management Practice
05.04.02	Fertilization – 64 kg N/ha, 19 kg P/ha and 53 kg K/ha
22.04.02	Herbicide – 20 g/ha Gratil 75 WG (amidosulfuron)
02.05.02	Fertilization – 69 kg N/ha, 16 kg P/ha and 58 kg K/ha
15.05.02	Herbicide – 3.0 l/ha Barnon Plus 3 (flamprop-M-isopropyl)
31.05.02	Fungicide – 0.25 l/ha Tilt 250 EC (propiconazole)
14.06.02	Insecticide – 0.25 kg/ha Pirimor G (pirimicarb)
14.06.02	Fungicide – 0.25 l/ha Tilt 250 EC (propiconazole)
20.08.02	Winter wheat harvested (seed yield 72.3 hkg/ha; 85% dry matter)
28.08.02	Straw removed (straw yield 21.87 hkg/ha fresh weight)
04.09.02	Stubble harrowed – 8 cm depth
01.11.02	Ploughed – 22 cm depth
20.03.03	Clods broken
25.03.03	Fertilization 105 kg N/ha, 18.6 kg P/ha and 74 kg K/ha
26.03.03	Spring barley sown – cultivar Prestige
11.05.03	Herbicide – 0,015kg/ha Express (tribenuron methyl)
27.05.03	Herbicide – 3.0 l/ha Barnon Plus 3 (flamprop-M-isopropyl)
04.06.03	Herbicide – 2.0 l/ha Metaxon 750 (MCPA)
10.06.03	Fungicide – 0.5 l/ha Tilt 250 EC (propiconazole)
10.06.03	Insecticide – 0.6 l/ha Perfection 500 S (dimethoate)
07.08.03	Spring barley harvested (grain yield 59.5 hkg; 85% dry matter)
10.08.03	Straw removed (straw yield 27.2 hkg/ha fresh weight)

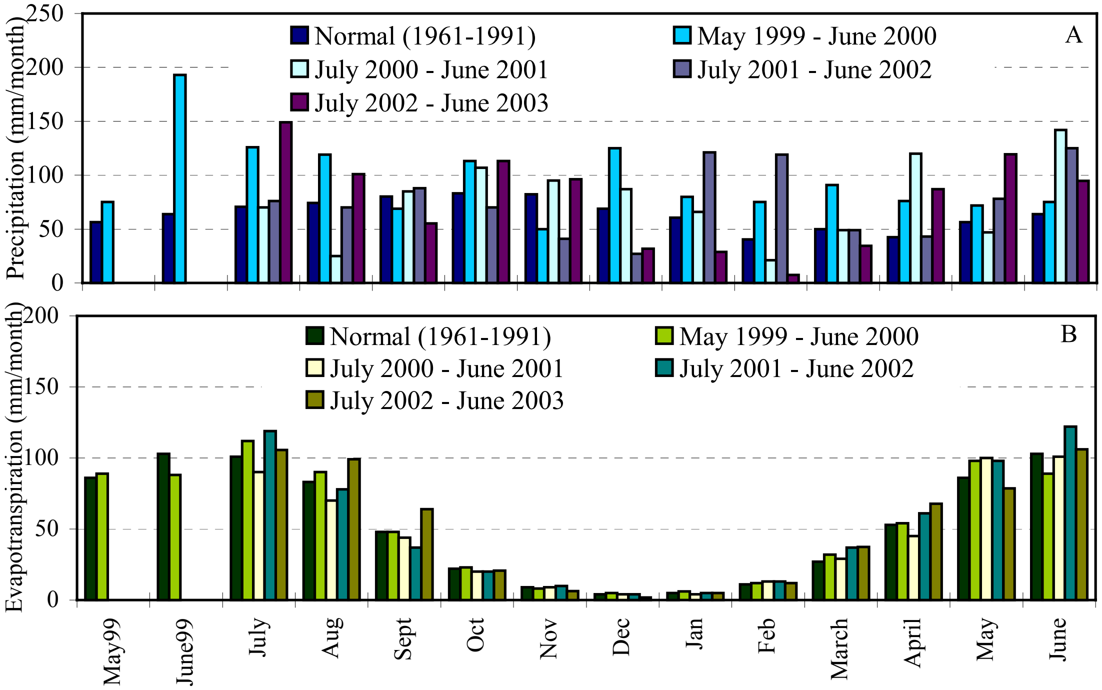

Figure A4.1. Monthly precipitation (A) and potential evapotranspiration (B) at Tylstrup for the monitoring period May 1999–June 2003. Normal values (1961–1990) compared to locally measured (precipitation) or calculated (evapotranspiration).

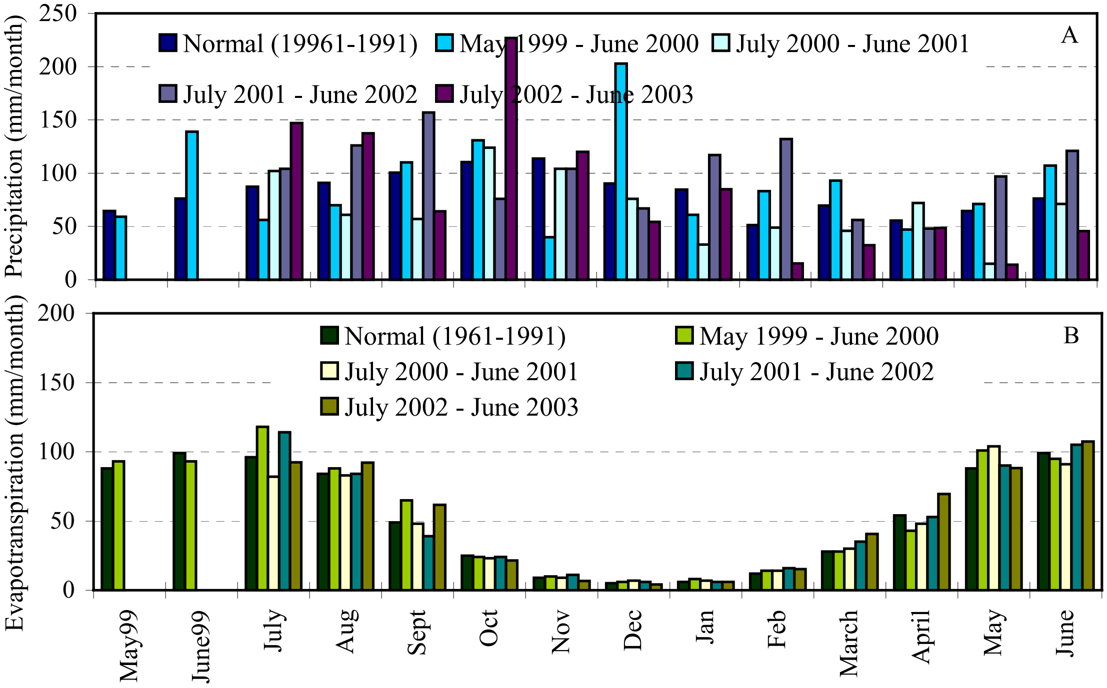

Figure A4.2. Monthly precipitation (A) and potential evapotranspiration (B) at Jyndevad for the monitoring period May 1999–June 2003. Normal values (1961–1990) compared to locally measured (precipitation) or calculated (evapotranspiration).

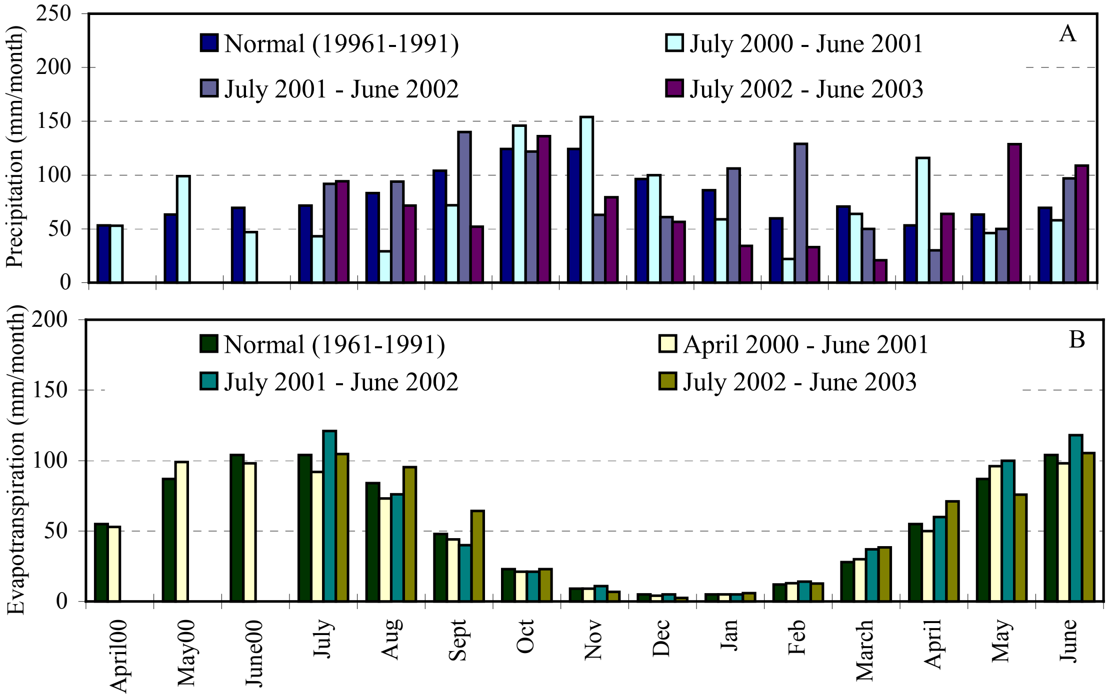

Figure A4.3. Monthly precipitation (A) and potential evapotranspiration (B) at Silstrup for the monitoring period April 2000–June 2003. Normal values (1961–1990) compared to locally measured (precipitation) or calculated (evapotranspiration).

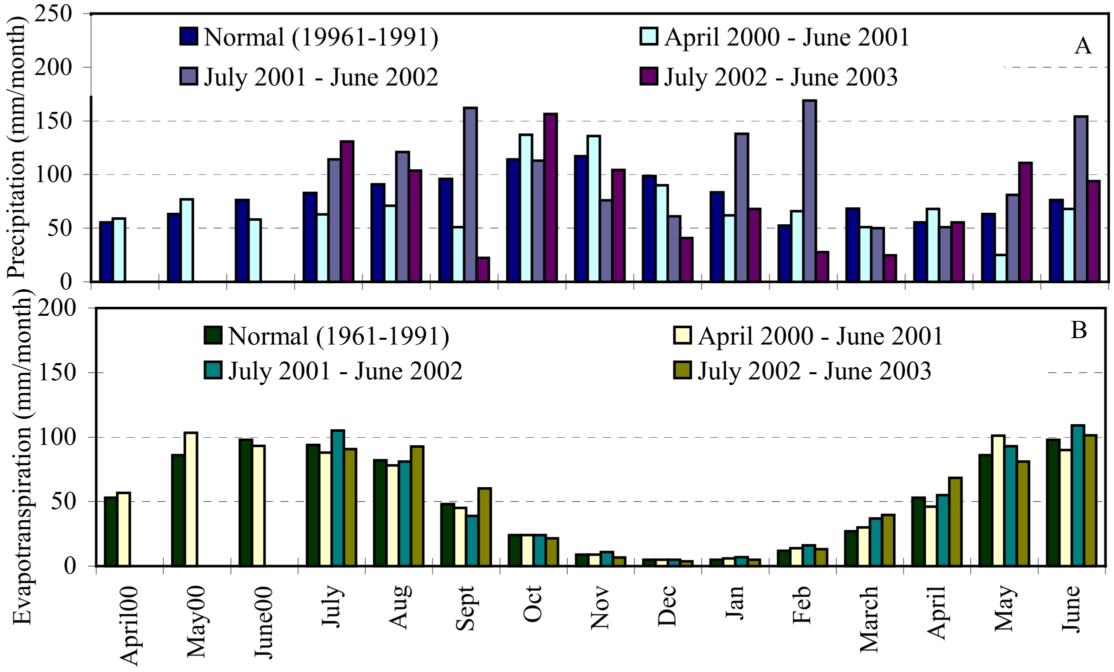

Figure A4.4. Monthly precipitation (A) and potential evapotranspiration (B) at Estrup for the monitoring period June 2000–June 2003. Normal values (1961–1990) compared to locally measured (precipitation) or calculated (evapotranspiration).

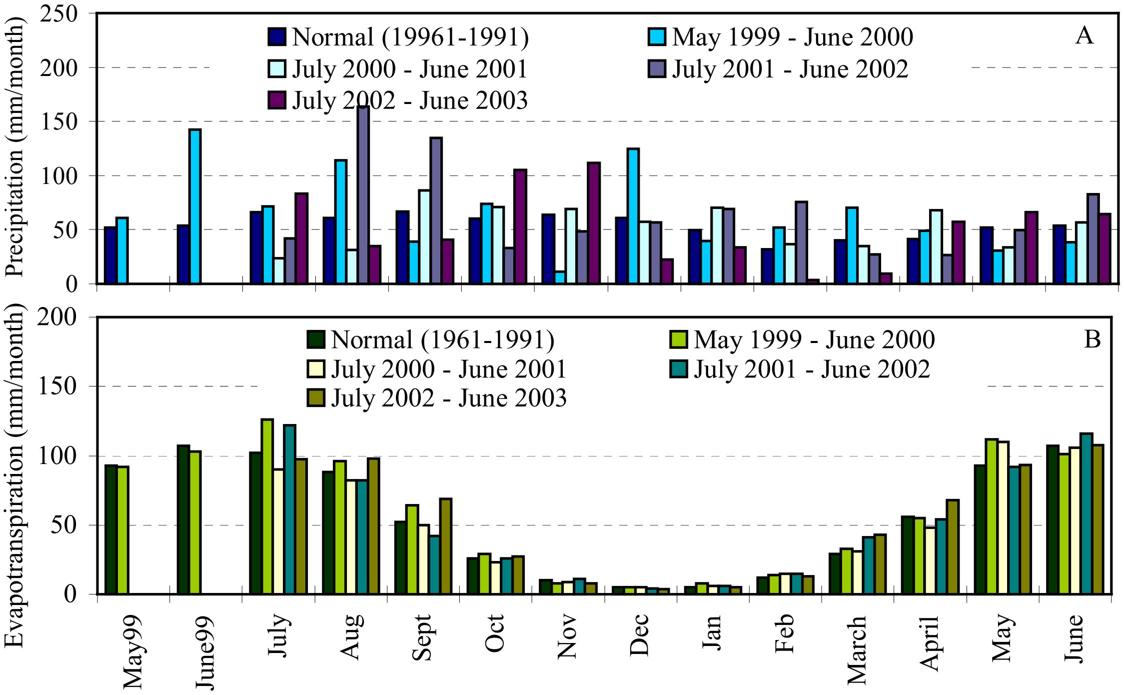

Figure A4.5. Monthly precipitation (A) and potential evapotranspiration (B) at Faardrup for the monitoring period May 1999–June 2003. Prior to July 2002 precipitation measured at the nearby Flakkebjerg site was used instead of precipitation at Faardrup due to noise in the measurements. Normal values (1961–1990) compared to locally measured (precipitation) or calculated (evapotranspiration).

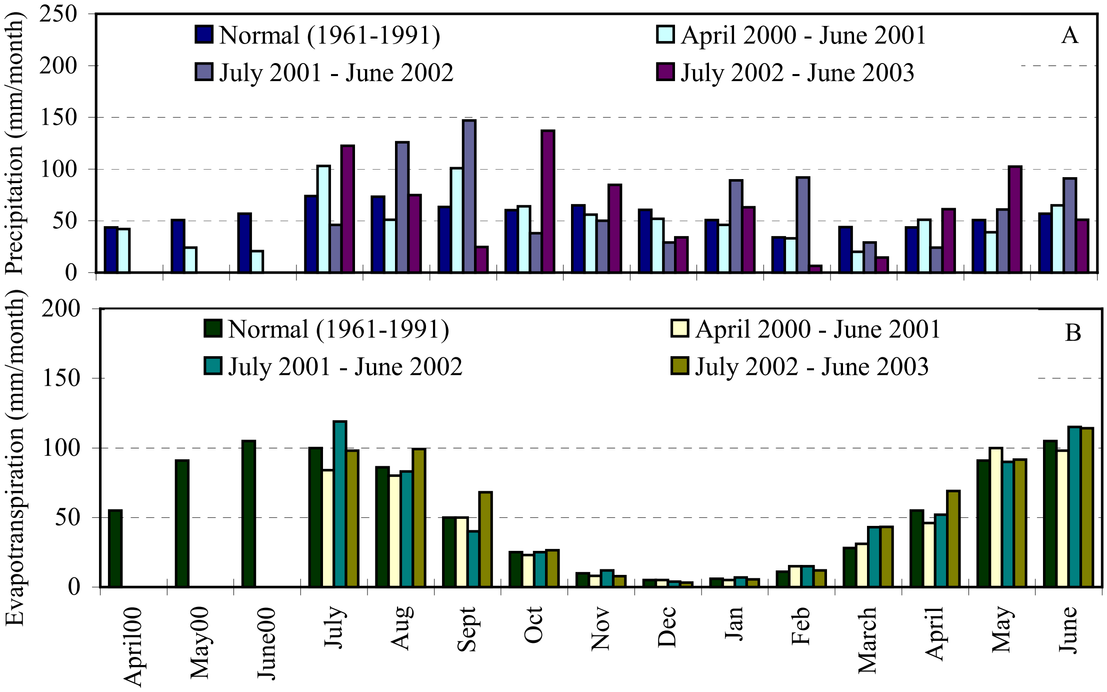

Figure A4.6. Monthly precipitation measured (A) and potential evapotranspiration (B) at Slaeggerup for the monitoring period April 2000–June 2003. Normal values (1961–1990) compared to locally measured (precipitation) or calculated (evapotranspiration).

The average concentration of pesticides 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 cup S1 and suction cup S2. For each of the measured concentrations, the corresponding percolation (Perc.) was estimated according to the equation:

$$P_i = \sum_{t_1}^{t_2} P_t$$

Where

t = sampling date

$t_1 = 0.5(t_{i-1}+t_i)$; $t_2=0.5(t_i+t_{i+1})$

P_t = Daily percolation at 1 m b.g.s. as estimated by the MACRO model (mm)

The average concentration was estimated according to the equation:

$$C = \frac{\sum C_i \cdot P_i}{\sum P_i}$$

where

C_i = measured pesticide concentration in the suction cups located 1 m b.g.s.

As the analysis methods for these degradation products were developed during the present project, results are only available from September 1999 onwards. The bromide transport studies indicate that the degradation products are unlikely to have reached the suction cups before late August 1999. The percolate concentration was therefore assumed to be zero during the period 1.6.99–23.8.99. Some of the analyses were also subject to some uncertainty due to the high detection limit. . For some years the average concentration is therefore given as a range representing the maximum and minimum concentrations estimated by applying a concentration equal to either zero or the detection limit.

Table A5.1 Estimated percolation rate (Perc.) and measured concentration of metribuzin-diketo (DK) and metribuzin-desamino-diketo (DADK) at Tylstrup. The estimated average concentrations for each monitoring period are also shown.

Suction cup S1 – 1 m b.g.s.				Suction cup S2 – 1 m b.g.s.			
Date t_i	Perc. (mm) P_i	DADK (µg/l) C_i	DK (µg/l) C_i	Date t_i	Perc. (mm) P_i	DADK (µg/l) C_i	DK (µg/l) C_i
23.08.99	93	n.a.	n.a.	23.08.99	93	n.a.	n.a.
09.09.99	47	*	*	09.09.99	47	*	<0.2
04.11.99	98	*	<0.2	04.11.99	98	*	<0.2
08.12.99	87	0.25	0.22	08.12.99	87	0.32	<0.04
10.01.00	98	0.72	0.62	10.01.00	98	0.25	0.08
03.02.00	54	2.05	0.39	03.02.00	54	0.23	0.11
02.03.00	67	2.10	0.17	02.03.00	67	0.23	0.07
06.04.00	56	1.96	0.50	06.04.00	56	0.20	0.14
10.05.00	26	1.39	n.a.	10.05.00	26	0.21	0.09
07.06.00	38	1.06	0.48	07.06.00	38	0.21	<0.02
03.10.00	10	0.28	0.15	03.10.00	39	0.11	0.09
31.10.00	91	0.10	0.17	05.12.00	165	0.30	0.12
05.12.00	212	0.11	<0.2	04.01.01	71	0.24	0.08
30.04.01	93	0.74	0.20	07.02.01	42	0.37	0.10
30.05.01	20	0.56	0.18	06.03.01	19	0.30	0.11
04.07.01	12	0.21	0.09	03.04.01	19	0.42	0.12
08.08.01	1	0.07	0.21	30.04.01	56	0.66	0.23
13.09.01	5	0.03	0.09	04.07.01	26	0.52	0.13
10.10.01	40	0.03	0.15	08.08.01	1	0.37	0.18
06.11.01	27	<0.04	0.15	13.09.01	5	0.18	0.08
04.12.01	31	0.04	0.09	10.10.01	40	0.14	0.05
07.01.02	26	0.06	0.10	06.11.01	27	0.14	<0.02
06.02.02	138	0.05	0.16	04.12.01	31	0.12	0.06
05.03.02	75	0.07	<0.1	07.01.02	26	0.12	0.11
03.04.02	24	0.20	0.08	06.02.02	138	0.19	0.13
30.04.02	17	0.06	0.14	05.03.02	75	0.23	0.08
28.05.02	30	<0.02	0.11	03.04.02	24	0.16	0.04
02.07.02	78	0.05	0.12	30.04.02	17	0.12	0.11
07.08.02	56	<0.06	0.071	28.05.02	30	0.12	0.12
03.09.02	15	0.041	0.295	02.07.02	78	0.06	0.068
01.10.02	14	<0.02	<0.1	07.08.02	56	0.14	0.11
29.10.02	71	<0.05	0.11	03.09.02	15	0.10	0.15
03.12.02	108	<0.06	0.07	01.10.02	14	0.027	0.12
04.02.03	51	<0.06	<0.06	29.10.02	71	0.04	0.10
04.03.03	8	<0.06	0.08	03.12.02	90	<0.02	0.02
02.04.03	11	0.03	<0.1	07.01.03	36	<0.03	0.08
07.05.03	32	<0.04	0.06	04.02.03	33	0.04	0.06
03.06.03	32	<0.02	0.10	04.03.03	8	0.02	0.08
				02.04.03	11	<0.02	<0.05
				07.05.03	32	0.02	0.08
				03.06.03	32	0.02	0.22
1.7.99–30.6.00		**0.87–0.97**	**0.26–0.36**	**1.7.99–30.6.00**		**0.19–0.31**	**0.05–0.11**
1.7.00–30.6.01		**0.33**	**0.13–0.23**	**1.7.00–30.6.01**		**0.33**	**0.12**
1.7.01–30.6.02		**0.06**	**0.11–0.13**	**1.7.01–30.6.02**		**0.19**	**0.09**
1.7.02–30.6.03		**<0.05**	**0.07-0.09**	**1.7.02–30.6.03**		**0.04–0.05**	**0.08**

**Degradation product detected in the range 0.05–0.5 µg/l; n.a.: Not analysed*

Table A6.1 Estimated percolation rate (Perc.) and measured concentration of PPU and PPU-desamido at Jyndevad. The estimated average concentrations for each monitoring period are also shown.

		Suction cup S1 – 1 m b.g.s.		Suction cup S2 – 1 m b.g.s.	
Date t_i	Perc. (mm) P_i	PPU (µg/l) C_i	PPU-desamido (µg/l) C_i	PPU (µg/l) C_i	PPU-desamido (µg/l) C_i
30.04.02		< 0.01	< 0.01	< 0.01	< 0.01
29.05.02		< 0.01	< 0.01	< 0.01	< 0.01
03.07.02	124	0.022	< 0.01	0.028	< 0.01
06.08.02	30	0.058	0.071	< 0.01	0.041
03.09.02	37	0.21	0.04	0.17	< 0.01
01.10.02	47	0.096	0.044	0.023	0.092
29.10.02	209	0.16	0.037	0.048	< 0.01
03.12.02	58	0.18	0.031	0.075	0.025
08.01.03	85	0.17	0.043	0.086	< 0.01
05.02.03	41	0.16	0.03	0.096	< 0.01
04.03.03	19	0.12	0.026	0.09	< 0.01
02.04.03	0	0.11	0.033	0.11	0.026
06.05.03	13	0.088	0.036	0.11	0.036
03.06.03	0	0.12	0.036	0.11	0.022
1.7.02–30.6.03		**0.13**	**0.03**	**0.06**	**0.01-0.02**

The calculation method is explained in Appendix 5. When the average concentration is given as a range it represents the maximum and minimum concentrations estimated by applying a concentration equal to either zero or the detection limit in the case of samples for which the concentration was below the detection limit.

Table A7.1 Detection of glyphosate and AMPA in groundwater monitoring screens at Silstrup during the period from 25.10.01 (date of application) until 01.07.03 (µg/l). The location of the monitoring installations is indicated in Figure 25.

Monitoring well	H1.2[1]	H1.3[2]	M5[1]			M12[2]	M13[2]
Screen depth (m b.g.s..)	3.5	3.5	1.5–2.5	2.5–3.5	3.5–4.5	1.5–2.5	2.5–3.5
AMPA							
06.11.01	<		0.011	0.08	<		
04.12.01	<		<	0.01	<		
08.01.02	0.014		0.012	<	<		
05.02.02	<		<	<	<		
05.03.02	0.01		0.014	<	<		
14.01.03	<	0.011	0.019	<	<	0.012	<
04.02.03	<		0.01	<	<		
Glyphosate							
09.10.01	<	<	<	<	<		
06.11.01	<		0.01	0.03	<		
04.12.01	<	<	<	0.01	<		
03.07.02	<	<	<	<	<	<	0.014

<: concentration was below the detection limit of 0.01 µg/l, [1] Monitored monthly, [2] Monitored half-yearly

Table A7.3 Detection of PHCP in groundwater monitoring screens at Silstrup during the period from 19.05.02 (date of first application) until 01.07.03 (µg/l). The location of the monitoring installations is indicated in Figure 25.

Monitoring well	H1.1[2]	H1.2[1]	H1.3[2]	M5[1]				M9[2]	M13[2]
Screen depth (m b.g.s.)	3.5	3.5	3.5	1.5-2.5	2.5-3.5	3.5-4.5	4.5-5.5	1.5-2.5	1.5-2.5
28-05-02		<		<	<	<			
03-07-02	0.042	0.035	<	0.309	0.197	0.091		0.048	0.041
05-08-02		<		0.11	0.059	0.121			
03-09-02		<			<	0.093			
02-10-02		<			<	0.054	0.059		
29-10-02		<		<	<	0.033			

<: concentration was below the detection limit of 0.01 µg/l, [1] Monitored monthly, [2] Monitored half-yearly

Table A7.2 Detection of terbuthylazine and desethylterbuthylazine in groundwater monitoring screen at Silstrup during the period from 19.05.02 (date of first application) until 01.07.03 (µg/l). The location of the monitoring installations is indicated in Figure 25.

Monitoring well	H1.1[2]	H1.2[1]	H1.3[2]	M5[1]				M9[2]
Screen depth (m b.g.s.)	3.5	3.5	3.5	1.5-2.5	2.5-3.5	3.5-4.5	4.5-5.5	1.5-2.5
Desethylterbuthylazine								
28.05.02		<		<	<	<		
03.07.02	0.02	0.018	0.016	0.143	0.051	0.011		0.022
05.08.02		0.028		0.131	0.07	0.038		
03.09.02		0.015			0.05	0.045		
02.10.02		<			0.037	0.045	0.011	
29.10.02		0.026		0.062	0.046	0.043		
03.12.02		0.014		0.046	0.04	0.042		
14.01.03	0.012	0.011	0.013	0.075	0.042	0.045		0.019
04.02.03		0.029		0.064	0.048	0.043		
12.03.03		0.014		0.052	0.054	0.044		
01.04.03		0.017		0.067	0.047	0.047		
05.05.03		0.011		0.056	<	0.049		
03.06.03		0.015		0.066	<	0.051		
01.07.03		0.017		0.068	0.048	0.046		
Terbuthylazine								
28.05.02		<		<	<	<		
03.07.02	0.014	0.011	0.012	0.124	0.03			<
05.08.02		0.011		0.082	0.033			
03.09.02		<			0.022	0.01		
02.10.02		<			0.013	0.011	<	
29.10.02		<		0.025	0.014	<		
03.12.02		<		0.016	0.012	0.011		
14.01.03	<	<	<	0.025	0.011	0.01		<
04.02.03		0.012		0.022	0.014	0.01		
12.03.03		<		0.016	0.013	0.01		
01.04.03		<		0.019	0.01	0.01		
05.05.03		<		0.013	<	<		
03.06.03		<		0.02	0.012	0.012		
01.07.03		<		0.014	<	<		

<: concentration was below the detection limit of 0.01 µg/l, [1] Monitored monthly, [2] Monitored half-yearly

Appendix 8. Concentration of AMPA and glyphosate in the drainage water at Estrup

Table A8.1 Measured concentrations of AMPA and glyphosate in drainage water at Estrup. Drainage runoff refers to the accumulated runoff for each of the analysed samples. Glyphosate was applied to the field on 02.09.02. Detection before this data refers to the previous application on 13.10.00.

Time-proportional sampling				Flow-proportional sampling			
Date	Glyphosate (µg/l)	AMPA (µg/l)	Drainage runoff (mm)	Date	Glyphosate (µg/l)	AMPA (µg/l)	Drainage runoff (mm)
09.07.02	<0.01	<0.01	28	09.07.02	0	0	4
16.07.02	<0.01	<0.01	4	16.07.02	0	0	3
06.08.02	<0.01	<0.01	23	06.08.02	0	0	3
13.08.02	<0.01	<0.01	13				
20.08.02	<0.01	<0.01	4				
27.08.02	<0.01	0.010	2	27.08.02	0.017	0.036	7
03.09.02	<0.01	0.020	20	29.08.02	0.013	0.077	6
10.09.02	1.1	0.058	3				
22.10.02	0.62	0.130	9	22.10.02	0.78	0.32	8
29.10.02	1.2	0.480	50	28.10.02	1.7	0.83	13
06.11.02	<0.01*	<0.01*	17	06.11.02	0.53	0.24	9
12.11.02	0.23	0.14	12	12.11.02	0.47	0.28	9
19.11.02	0.2	0.15	16	19.11.02	0.27	0.2	12
26.11.02	0.27	0.12	13				
03.12.02	0.22	0.096	14	28.11.02	0.33	0.63	8
11.12.02	0.066	0.038	4				
19.12.02	0.091	0.070	1				
03.01.03	0.91	0.53	7	03.01.03	1.2	0.66	7
09.01.03	0.24	0.14	<1				
16.01.03	1.6	0.63	6	16.01.03	1.4	0.63	9
22.01.03	0.23	0.11	15	23.01.03	0.27	0.25	10
28.01.03	0.058	0.050	13				
04.02.03	0.061	0.057	12	04.02.03	0.1	0.11	4
11.02.03	0.081	0.056	12	11.02.03	0.18	0.12	7
18.02.03	0.039	0.034	1				
11.03.03	0.17	0.098	4				
18.03.03	0.018	0.030	7				
25.03.03	0.021	0.026	1				
06.05.03	0.032	0.044	2	06.05.03	0.033	0.067	2
13.05.03	0.072	0.019	1				
20.05.03	0.028	0.021	<1	22.05.03	0.017	0.034	4
27.05.03	0.025	0.051	19	26.05.03	0.038	0.062	10
03.06.03	0.024	0.036	4				
10.06.03	0.025	0.031	<1				
17.06.03	0.026	0.052	1	13.06.03	0.039	0.049	<1
24.06.03	0.083	0.210	1	25.06.03	0.084	0.25	1
01.07.03	0.043	0.030	1	03.07.03	0.057	0.16	1

**: Considered to be incorrectly analysed and therefore excluded from Figure 43 and Figure 44*

Table A9.2 Detection of pesticides in groundwater monitoring screens at Estrup during the period from date of pesticide application until 01.07.03 (µg/l). The location of the monitoring installations is indicated in Figure 36.

Monitoring well		H1.2[1]	M1[2]	M5[1]	M5[1]	M5[1]	M1[2]	M6[2]
Screen depth (m b.g.s.)		3.5	3.5-4.5	2.5-3.5	3.5-4.5	4.5-5.5	1.5-2.5	2.5-3.5
Glyphosate	20-03-02				0.033			
	16-04-02				0.014	0.036		
	18-12-02				0.014	0.013		
	22-01-03							0.015
	19-02-03				0.011			
MCPA	14-05-02			0.019				
Pirimicarb	22-01-03		0.015					
Propiconazole	22-01-03		0.022				0.017	
Triazinamin	16-04-02			0.042				
2-amino-N-isopropylbenzamid	18-09-02	0.026						

[1] *Monitored monthly;* [2] *Monitored half-yearly*

Table A10.1 Concentration (µg/l) of ethofumesate, metamitron and metamitron-desamino in the vertical monitoring wells at Faardrup. The location of the monitoring installations is indicated in Figure 45.

Monitoring well	M2				M4				M5				M6			
Screen number	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4
Ethofumesate																
03.05.01	<	<	<		<	<	<		<	<	<		<	<	<	
30.05.01									<	<	<		<	<	<	
04.07.01									<	<	<		<	<	<	
08.08.01		<	<	<	<	<		<	1.40	0.29	0.44		<	<		<
12.09.01									0.03	0.07	0.10				<	<
10.10.01									0.33	0.15	0.14		<	<	<	
05.12.01									0.07	0.04	0.06		<	<	<	
07.02.02			<	<	<	<	<		0.01	0.02	0.02					
06.03.02									0.01	0.01	0.02					
04.04.02									0.01	0.01	0.01					
28.05.02									0.00	0.01	0.02		<	<	<	
03.07.02									0.01	0.01	0.01		<	<	<	
03.07.02									0.01	0.01	0.01		<	<	<	
07.08.02		<	<	<	<	<	<		0.01	0.01	0.01			<	<	<
04.09.02										0.01	0.01	<		<	<	<
02.10.02				<						<	<	<		<	<	<
30.10.02							<	<		<	<	<				
04.12.02					<	<	<		<	<	<					
15.01.03					<	<	<		<	<	<					
04.02.03	<	<	<		<	<	<		<	<	<		<	<	<	
04.03.03					<	<	<		<	<	<					
02.04.03					<	<	<		<	<	<					
07.05.03					<	<	<		<	<	<					
04.06.03						<	<	<	<	<	<					
Metamitron																
03.05.01	<	<	<		<	<	<		<	<	<		<	<	<	
30.05.01									<	<	<		<	<	<	
04.07.01									<	<	<		<	<	<	
08.08.01		<	<	<	<	<		<	0.63	0.15	0.21		<	<		<
12.09.01									0.27	0.08	0.10				<	<
10.10.01									0.08	0.05	0.05		<	<	<	
05.12.01									0.03	0.04	0.03		<	<	<	
07.02.02			<	<	<	<	<		0.02	0.01	0.01					
06.03.02									<	<	0.01					
04.04.02									0.01	0.01	0.01					
28.05.02									<	0.01	0.01		<	<	<	
03.07.02									0.01	<	<		<	<	<	
03.07.02									0.01	<	<		<	<	<	
07.08.02		<	<	<	<	<	<		0.01	<	<			<	<	<
04.09.02										<	<	<		<	<	<
02.10.02				<						0.012	<	<		<	<	<
30.10.02							<	<		<	<	<				
04.12.02					<	<	<		<	<	<					
15.01.03					<	<	<		<	<	<					

**) Screens 1,2,3 and 4 are located 1.5–2.5, 2.5–3.5, 3.5–4.5, and 4.5–5.5 m b.g.s., respectively*

<) Below the detection limit of 0.01 µg/l

Table A10.1 (Continued) Concentration (µg/l) of ethofumesate, metamitron and metamitron-desamino in the vertical monitoring wells at Faardrup. The location of the monitoring installations is indicated in Figure 45.

Monitoring well	M2				M4				M5				M6			
Screen number	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4
Metamitron																
04.02.03	<	<	<		<	<	<		<	<	<		<	<	<	
04.03.03					<	<	<		<	<	<					
02.04.03					<	<	<		<	<	<					
07.05.03					<	<	<		<	<	<					
04.06.03						<	<	<	<	<	<					
Metamitron-desamino																
03.05.01	<	<	<		<	<	<		<	<	<		<	<	<	
30.05.01									<	<	<		<	<	<	
04.07.01									<	<	<		<	<	<	
08.08.01		<	<	<	<	<		<	1.30	0.33	0.62		<	<		<
12.09.01									0.50	0.18	0.21				<	<
10.10.01									0.23	0.16	0.15		<	<	<	
05.12.01				<					0.16	0.27	0.15		<	<	<	
07.02.02			<		<	<	<		0.04	0.05	0.05					
06.03.02									0.03	0.04	0.04					
04.04.02									0.02	0.02	0.02					
28.05.02									0.00	0.02	0.02		<	<	<	
03.07.02									0.01	0.02	0.02		<	<	<	
04.04.01									<	<	<		<	<	<	
03.05.01	<	<	<		<	<	<		<	<	<		<	<	<	
03.07.02									0.01	0.02	0.02		<	<	<	
07.08.02		<	<	<	<	<	<		0.02	0.02	0.02			<	<	<
04.09.02										0.019	0.02	0.01		<	<	<
02.10.02				<						0.02	0.02	0.02		<	<	<
30.10.02							<	<		0.01	0.01	0.02				
04.12.02					<	<	<		0.01	0.01	0.011					
15.01.03					<	<	<		0.01	0.01	<					
04.02.03	<	<	<		<	<	<		<	0.01	<		<	<	<	
04.03.03					<	<	<		<	<	<					
02.04.03					<	<	<		<	<	<					
07.05.03					<	<	<		0.01	0.01	0.01					
04.06.03						<	<	<	<	0.01	<					

**) Screens 1,2,3 and 4 are located 1.5–2.5, 2.5–3.5, 3.5–4.5, and 4.5–5.5 m b.g.s., respectively*
<) Below the detection limit of 0.01 µg/l

None of the compounds listed in Table A10.1 were detected in any of the water samples from the horizontal monitoring wells. Moreover, fluazifop (free acid) was only detected on two occasions in monitoring well M5, as indicated in Table A10.2.

Table A10.2 detection of fluazifop (free acid) in groundwater monitoring screen at Faardrup

Well number	M5[1]		
Screen depth (m b.g.s.)	1.5 -2.5	2.5-3.5	3.5-4.5
08-08-01	0.011	0.01	0.015
10-10-01	0.17	0.095	0.091

[1] monitored monthly

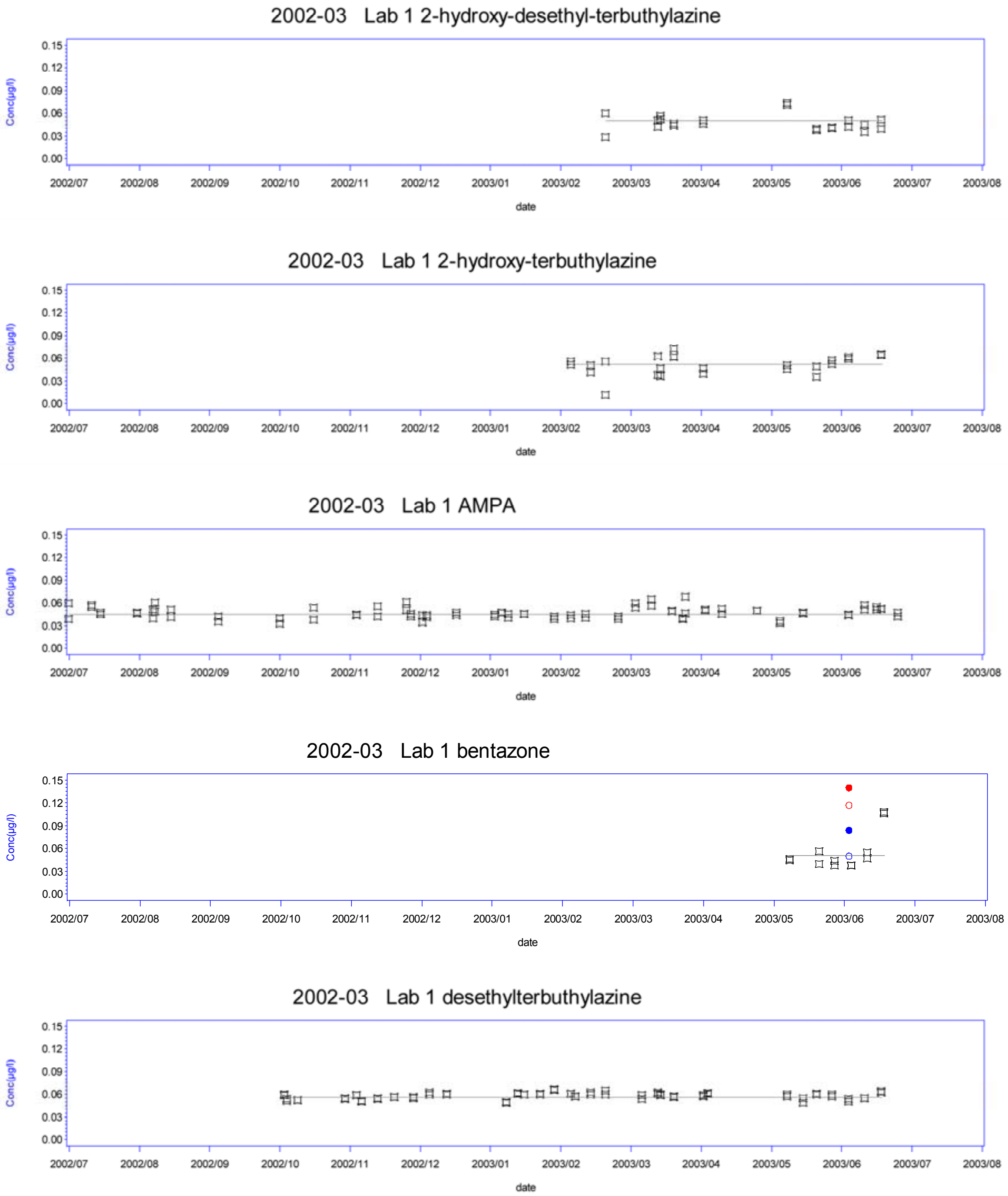

Figure A11.1 Quality control data for pesticide analysis by laboratory 1. Internal laboratory control samples are indicated by square symbols and the nominal level is indicated by the solid grey line (⌑ IQ measured, — IQ nominal concentration). External control samples are indicated by circles. Open circles indicates the nominal level (○ EQ nominal low, ○ EQ nominal high), and filled circles the observed concentration (● EQ measured low, ● EQ measured high).

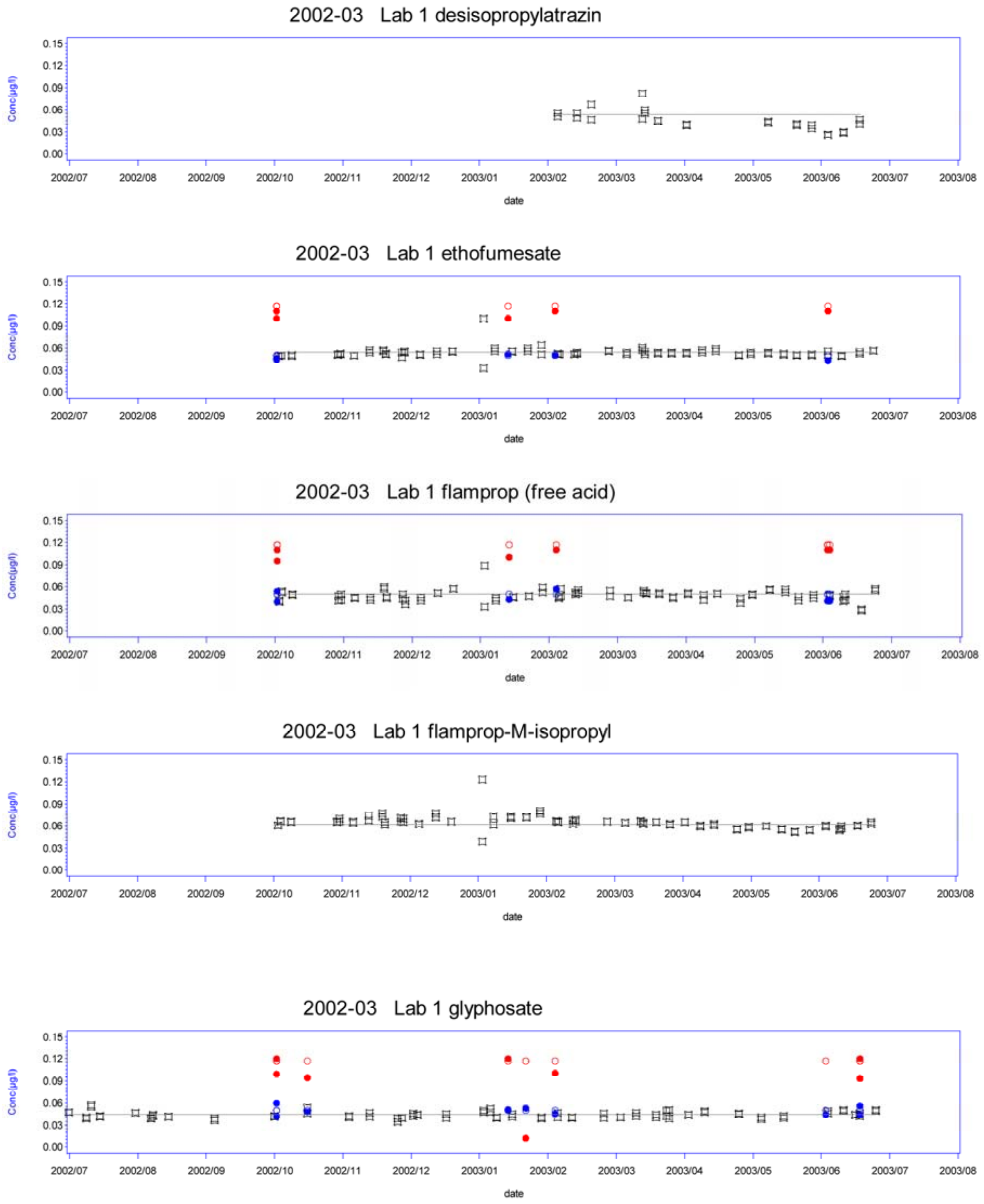

Figure A11.1 (Cont.) Quality control data for pesticide analysis by laboratory 1. Internal laboratory control samples are indicated by square symbols and the nominal level is indicated by the solid grey line (⌑ IQ measured, — IQ nominal concentration). External control samples are indicated by circles. Open circles indicates the nominal level (○ EQ nominal low, ○ EQ nominal high), and filled circles the observed concentration (● EQ measured low, ● EQ measured high).

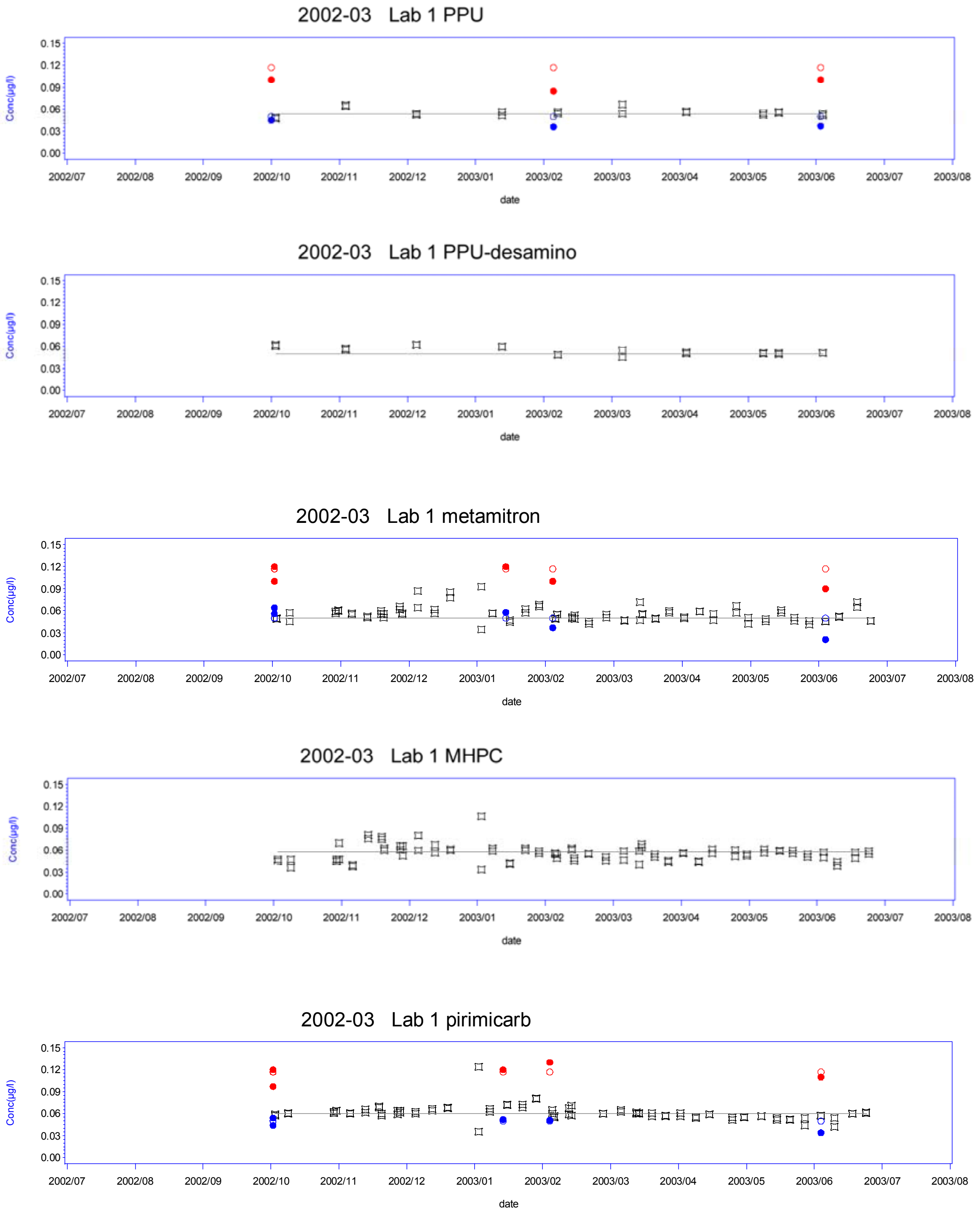

Figure A11.1 (Cont.) Quality control data for pesticide analysis by laboratory 1. Internal laboratory control samples are indicated by square symbols and the nominal level is indicated by the solid grey line (⌑ IQ measured, — IQ nominal concentration). External control samples are indicated by circles. Open circles indicates the nominal level (○ EQ nominal low, ○ EQ nominal high), and filled circles the observed concentration (● EQ measured low, ● EQ measured high).

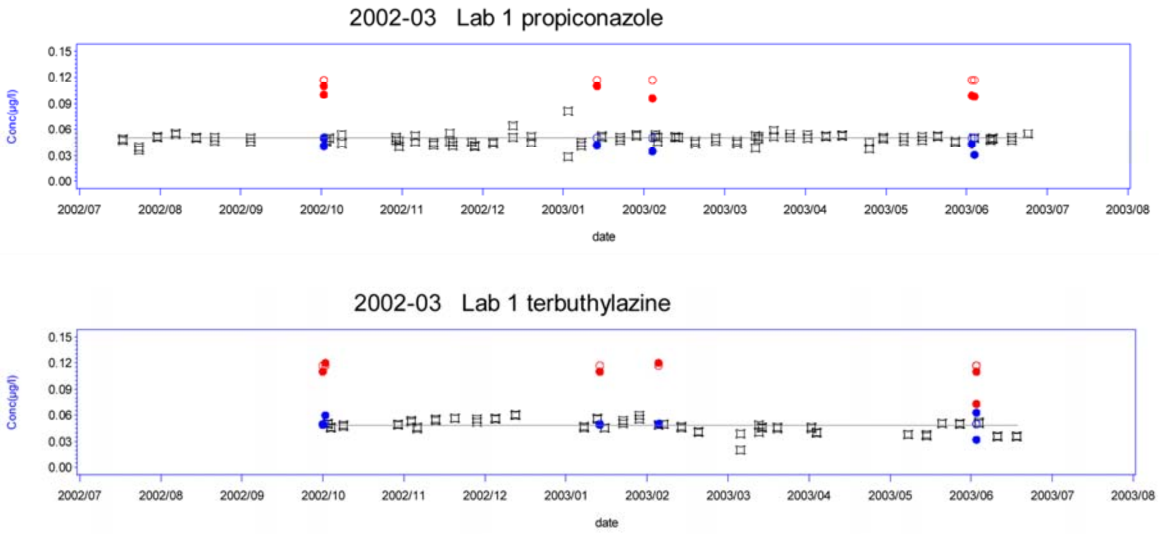

Figure A11.1 (Cont.) Quality control data for pesticide analysis by laboratory 1. Internal laboratory control samples are indicated by square symbols and the nominal level is indicated by the solid grey line (⌑ IQ measured, — IQ nominal concentration). External control samples are indicated by circles. Open circles indicates the nominal level (○ EQ nominal low, ○ EQ nominal high), and filled circles the observed concentration (● EQ measured low, ● EQ measured high).

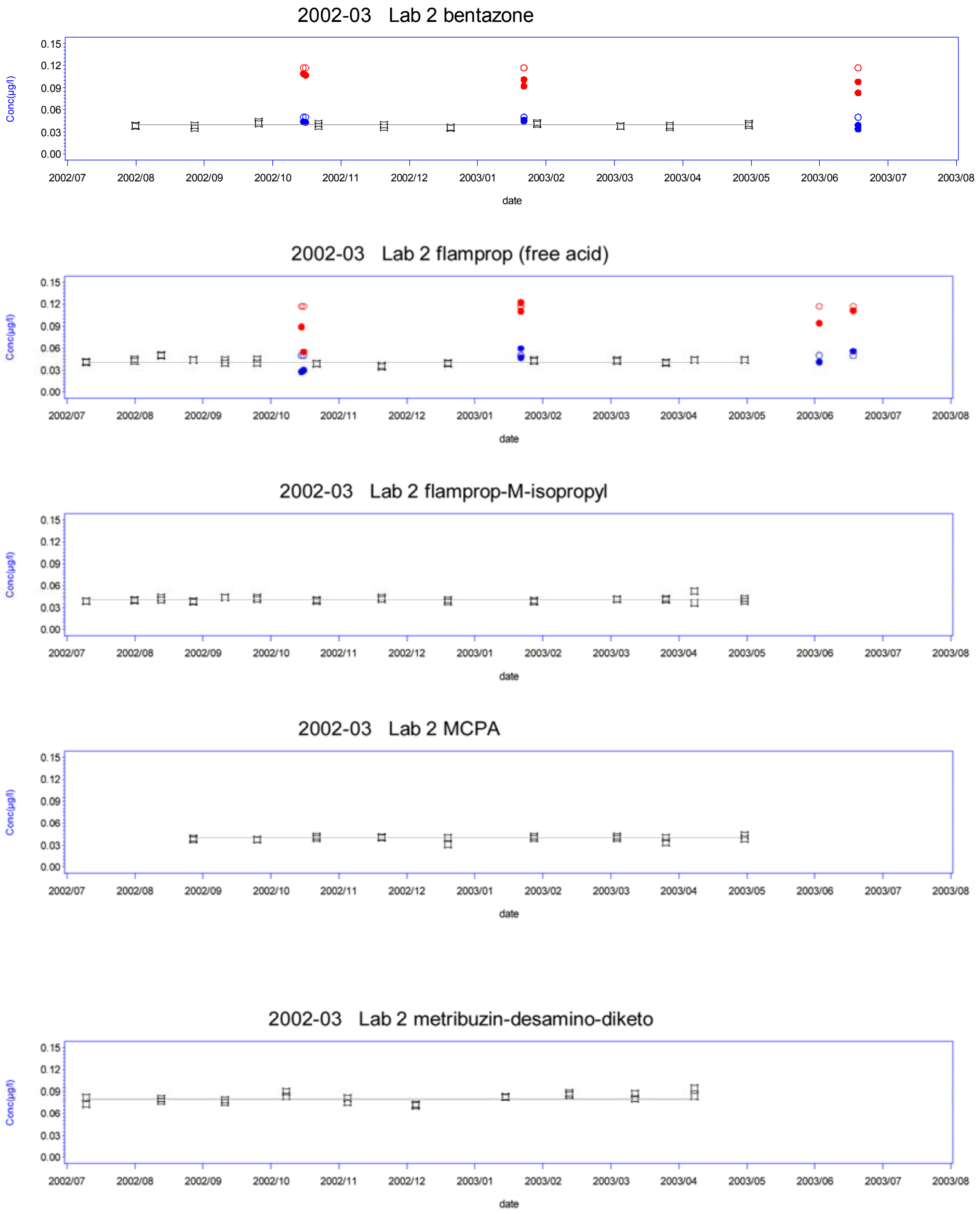

Figure A11.2 Quality control data for pesticide analysis by laboratory 2. Internal laboratory control samples are indicated by square symbols and the nominal level is indicated by the solid grey line (⌑ IQ measured, — IQ nominal concentration). External control samples are indicated by circles. Open circles indicates the nominal level (○ EQ nominal low, ○ EQ nominal high), and filled circles the observed concentration (● EQ measured low, ● EQ measured high).

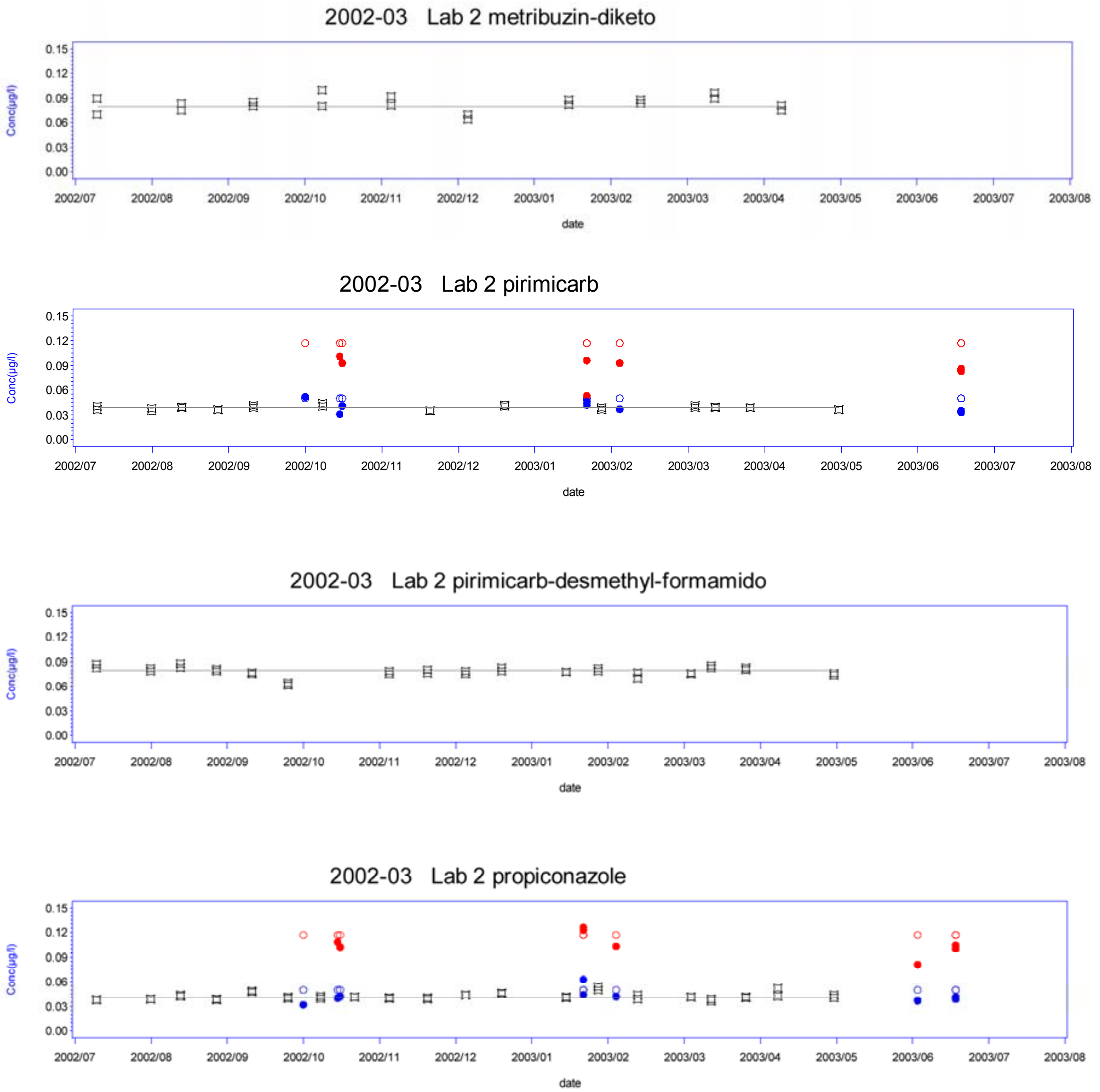

Figure A11.2 Quality control data for pesticide analysis by laboratory 2. Internal laboratory control samples are indicated by square symbols and the nominal level is indicated by the solid grey line (⌑ IQ measured, — IQ nominal concentration). External control samples are indicated by circles. Open circles indicates the nominal level (○ EQ nominal low, ○ EQ nominal high), and filled circles the observed concentration (● EQ measured low, ● EQ measured high).