The Danish Pesticide Leaching Assessment Programme

Monitoring results May 1999 – June 2001
Second report

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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 first phase of the programme from 1998–2001 was funded by the Danish Government, while a two-year prolongation from 2002–2003 was funded by the Ministry of Environment and the Ministry of Food, Agriculture and Fisheries.

This report presents the results of the monitoring period May 1999–June 2001. The report must be considered preliminary as the monitoring period is too short to fully evaluate the leaching risk of all applied pesticides. Preliminary results for three of the monitoring sites covering part of the monitoring period (May 1999–June 2000) have been reported previously (Kjær *et al.*, 2001) and the present report should therefore be seen as a continuation of that report.

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:

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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 registration procedures for pesticides in Denmark. The specific aim is to analyse whether pesticides applied in accordance with current regulations leach to the groundwater at levels exceeding the maximum allowable concentration of 0.1 µg/l.

The PLAP includes evaluation of the leaching risk of 24 pesticides at six agricultural sites (ranging from 1.1 to 2.4 ha) representing a wide range of Danish soil and climate conditions. The pesticides are all applied using the maximum permitted dosage. Initially, bromide tracer was applied and the concentrations of the bromide and pesticides 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 2001. The report must be considered preliminary as the monitoring period is too short to fully evaluate the leaching risk of all applied pesticides. A more complete evaluation integrating the monitoring data with both sorption and degradation studies and modelling of pesticide transport will be made once a more comprehensive data set covering the entire leaching period becomes available. The results hitherto obtained nevertheless suggest that:

- The majority of the applied pesticides (13 of 21) did not leach during the current monitoring period. It should be noted, though, that evaluation of the leaching risk of many of these pesticides is still preliminary as the potential leaching period extends beyond the current monitoring period.

- The monitoring data indicate unacceptable leaching by two of the applied pesticides. Thus glyphosate and its degradation product AMPA and two degradation products of metribuzin 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 the two 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 two years after application. Evidence was provided that the degradation products may still be present in the groundwater four years after application.

- Finally, the monitoring data indicate leaching of a further six pesticides, but it is too early to determine whether this will reach critical levels as the potential leaching period extends beyond the current monitoring period. 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 were supported by hydrological modelling (MACRO version 4.2) providing an overall water balance for each of the six sites. The model was parameterized using measured data or literature/default values, but – apart from at the Tylstrup site – it has not yet been calibrated. The uncalibrated models performed surprisingly well when comparing simulated and observed time series for groundwater table, soil water content and drainage flow.

Sorption and degradation parameters were determined on various combinations of pesticides and soil types representative of the PLAP programme. The results confirmed the low microbial activity, sorption and degradation rates generally found in subsoil. The findings also demonstrated very large variation in both degradation rates and sorption among soils, thereby underlining the importance of having site-specific parameters when modelling pesticide leaching. The rates of degradation were always better described by a two-compartment 1^{st} + 1^{st} order model than by the usual 1^{st} order model, especially with fenpropimorph. Thus degradation usually involved an initial fast degradation rate with a short half-life followed by a slower degradation rate with a longer half-life. An error is thus introduced if the simple 1^{st} order half-life is used in the evaluation of pesticide persistence. Further analysis of the significance of the introduced error for risk assessment of pesticide leaching is thus required.

The quality of the pesticide analyses was evaluated continuously using an intensive quality assurance (QA) system. This consisted of internal control samples prepared by the analysis laboratory as part of their standard method of analysis and both blank and spiked samples prepared in the field and analysed in the laboratory together with the routine samples. The overall quality of the pesticide analysis was considered satisfactory:

- Reproducibility of the pesticide analyses was good (SD 0.002–0.015 µg/l).
- Reproducibility of the degradation products was poorer than that of the mother compounds (SD 0.009–0.032 µg/l).
- Recovery of pesticides in both internal and external QA samples was acceptable for all pesticides detected in field samples.
- Variation in the recovery of the same compound in spiked samples from all field sites indicates uncertainty in analysis caused by differences in matrix composition.
- No contamination of samples generally occurred during collection, storage and analysis. However, two cases of "false positive" were observed in blank or spiked samples.
- Stability tests indicated that the majority of the analysed compounds did not exhibit stability problems. However, the occurrences of degradation products in some of the spiked samples indicates that a few of the compounds are unstable and that conditions during transport and storage are important.

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. According to the Danish National Groundwater Monitoring Programme (GRUMO), pesticides and their degradation products have so far been detected in 30% of all screens monitored (Stockmarr, 2000).

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 and hence 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 potentially may 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 to the groundwater in unacceptable concentrations. The programme focuses on pesticides used in arable farming, monitoring 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 regulation leach to the groundwater at levels exceeding the maximum allowable concentration of 0.1 µg/l.

1.2 Structure of the PLAP programme

Soil type and climatic conditions are considered to be some of the most important parameters controlling pesticide leaching. The PLAP programme 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 to pesticide leaching (Table 1). Cultivation of the PLAP sites is in line with conventional agricultural practices applied 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 transformed products in the groundwater downstream of the sites can be related to the current approval conditions pertaining for the individual pesticides.

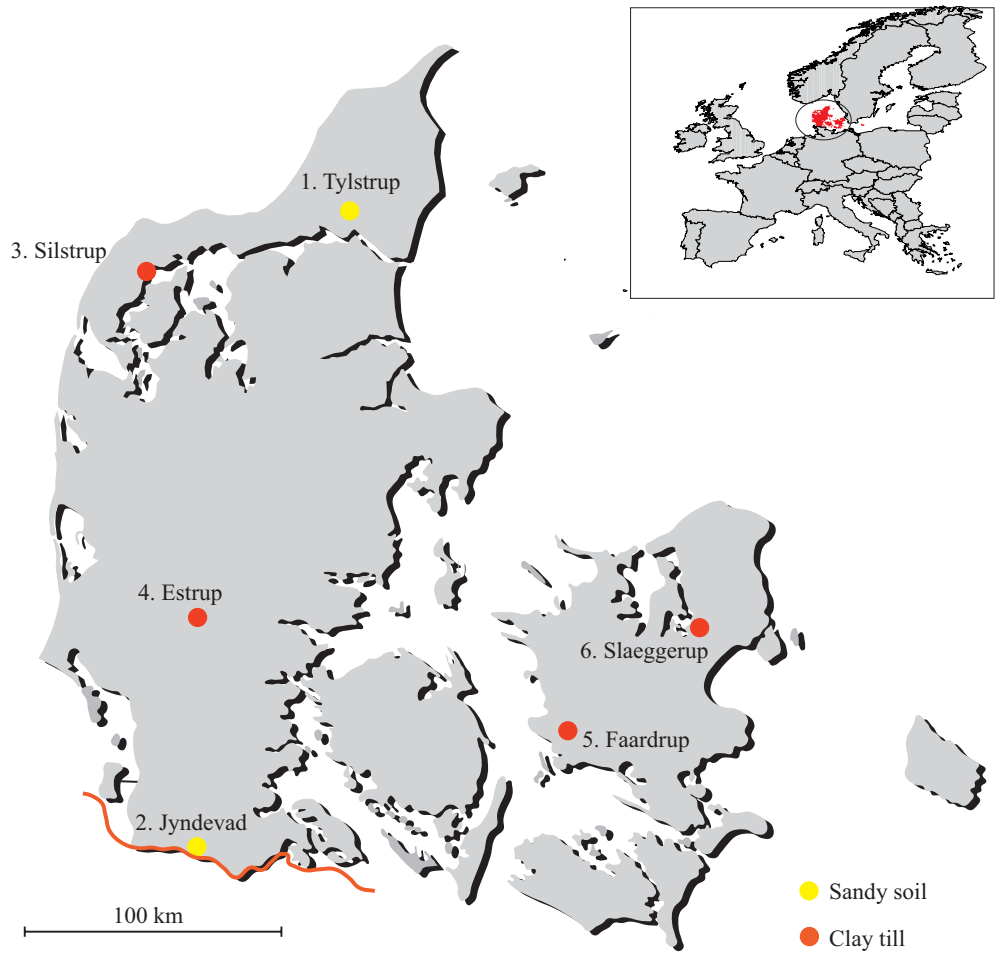

Figure 1. Location of the six PLAP sites Tylstrup, Jyndevad, Silstrup, Estrup, Faardrup and Slaeggerup.

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)	$2.0 \cdot 10^{-5}$	$1.3 \cdot 10^{-4}$	$3.4 \cdot 10^{-6}$	$8.0 \cdot 10^{-8}$	$7.2 \cdot 10^{-6}$	$3.1 \cdot 10^{-6}$
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 from 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

The PLAP programme was initiated in autumn 1998. During 1999, the six test sites were selected and established. The monitoring was initiated in 1999 at Tylstrup, Jyndevad and Faardrup, and in 2000 at Silstrup, Estrup and Slaeggerup (See Table 1).

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 2001. Preliminary results for three of the monitoring sites – Tylstrup, Jyndevad and Faardrup – covering part of the monitoring period (May 1999–June 2000) have been reported previously (Kjær *et al.*, 2001) and the present report should therefore be seen as a continuation of that report.

Within the PLAP programme, the evaluation of pesticide leaching risk is based upon at least two years of monitoring data. The present report must be considered preliminary for some pesticides as the monitoring period of these pesticides is as yet too short. A more complete evaluation of the data, including model simulation of the pesticide transport and

transformation processes, will thus be made once a more comprehensive data set covering the entire leaching period becomes available.

The monitoring data were supported by hydrological modelling of the unsaturated zone. The MACRO model (version 4.2) was applied to each site in order to establish an overall water balance. The modelling results shown in this report are based on the first model set-up, which has not yet been calibrated except for the Tylstrup site.

The risk of pesticide leaching is highly dependent on the degradation and sorption processes occurring in the root zone. To improve the interpretation of the data, sorption and degradation studies have been conducted on selected combinations of pesticides and soil types representative for the PLAP programme. The methodology and initial results are presented in Section 8.

Scientifically valid methods of analysis are essential for the integrity of the PLAP programme. The field monitoring work has therefore been supported by intensive quality assurance entailing continuous evaluation of the analyses employed. The quality assurance methodology and initial results are presented in Section 9.

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 (Figure 3). 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 and analysis methods is provided in Appendixes 1–2. The monitoring design and test site are described in detail in Lindhardt *et al.* (2001).

2.1.2 Agricultural management

The 1999 crop was potato for starch production. The cultivar used was Dianella, which is a commonly used variety. During the growing season the field was sprayed with the herbicides linuron and metribuzin, and with the fungicide mancozeb. Potassium bromide tracer was applied on 27 May. The potatoes were harvested on 20 October. The yield of tubers was 475 hkg/ha (24% dry matter), which is somewhat less than the average for the location. During the autumn of 1999 the field was disc harrowed several times in order to reduce problems of waste potatoes in the subsequent crop. The 2000 crop was spring barley (cv. Bartok), which emerged on 10 April. On 13 May, when the crop had 3 tillers, it was sprayed with the herbicide triasulfuron. Stem elongation and heading began in mid May and June, respectively. Combined fungicide and insecticide spraying was carried out on 19 June, in the middle of heading, using propiconazole, fenpropimorph and pirimicarb. The crop was harvested on 21 August yielding 73.3 hkg/ha of grain (85% dry matter) – somewhat above the average for that year and location. The 2001 crop was winter rye, which emerged on 7 October. On 2 November, when the crop had 2 leaves, it was sprayed with the herbicides tribenuron-methyl and pendimethalin. Spraying of fungus was done twice on 14 May and 13 June using propiconazole and fenpropimorph. At harvest on 28 August the grain yield was 63.6 hkg/ha. Management practice at the site is detailed in Appendix 3, Table A3.1.

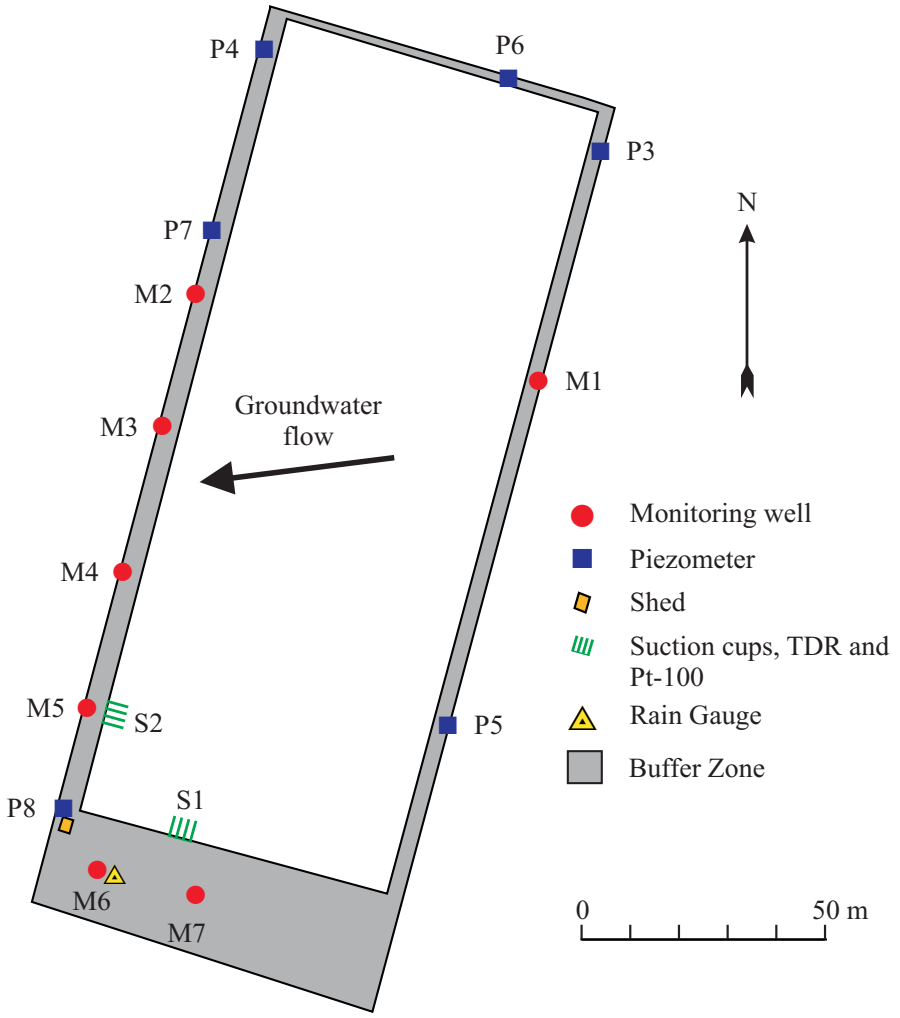

Figure 2. Overview of the Tylstrup test site. The innermost white area indicates the cultivated land, while the grey area indicates the surrounding buffer zone. The positions of the various installations are indicated, as is the direction of groundwater flow.

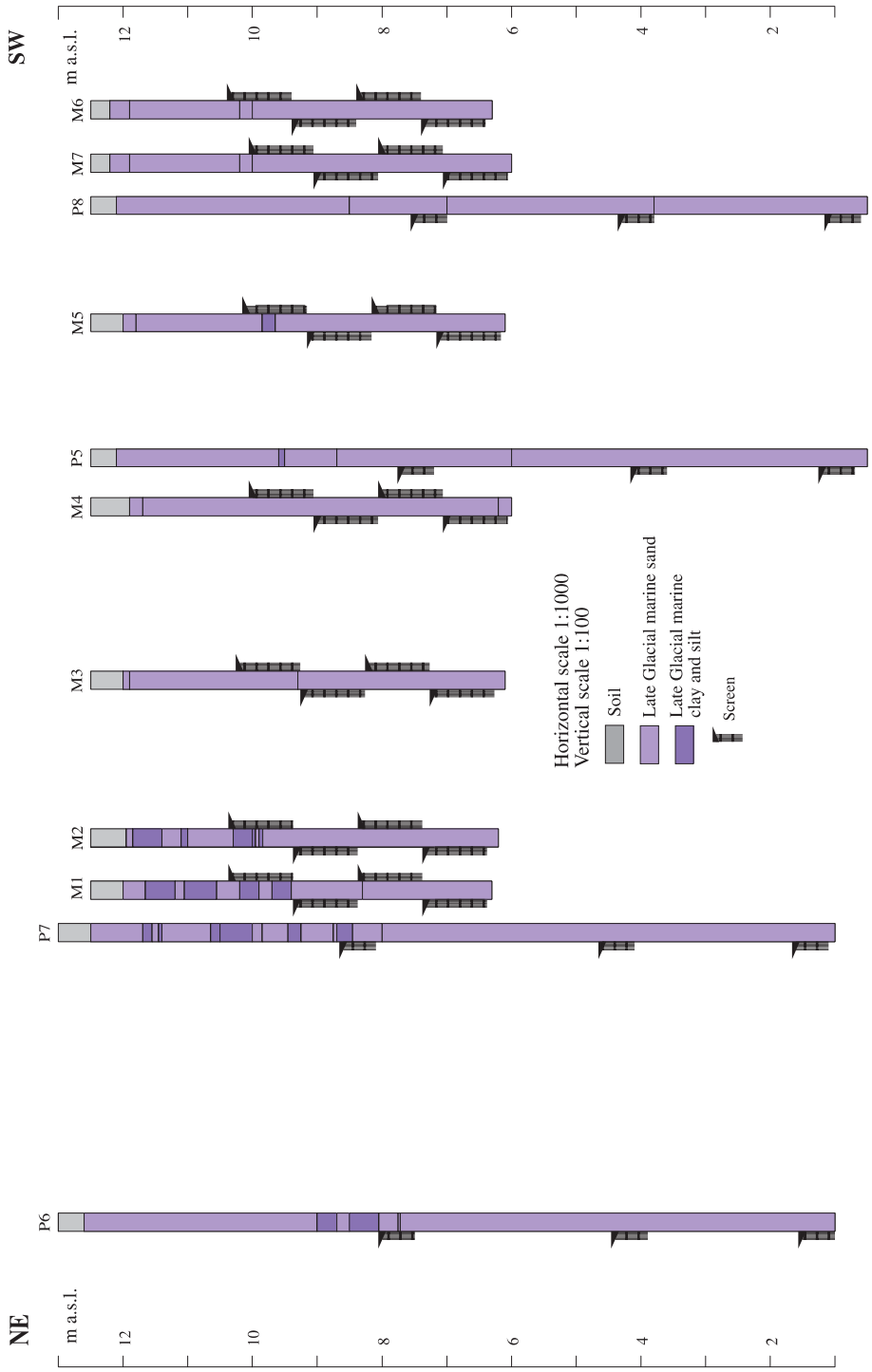

Figure 3. NE-SW cross sections based on wells at the Tylstrup site (Lindhardt *et al.,* 2001). The location of the wells is indicated in Figure 2.

2.1.3 Model set-up and calibration

The MACRO model was 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 was used to simulate the water and bromide transport in the unsaturated zone during the full monitoring period May 1999–June 2001. Data acquisition and model set-up are described in Appendix 5.

The calibration procedure employed at Tylstrup involved three steps:

- Firstly, a good description of the overall water balance was obtained. The model was thus calibrated to the observed groundwater table measured in the piezometers located in the buffer zone (see Figure 2). The calibration parameter only involved the empirical BGRAD parameter regulating the boundary flow.

- Secondly, the model description of soil water dynamics was improved. The model was thus calibrated to the observed soil water content measured with TDR probes. Calibration data comprised measured time series of soil water content at six different depths (25, 60, 90, 110, 190 and 210 cm b.g.s.) from the two profiles S1 and S2 (see Figure 2). This calibration step involved a sensitivity analysis of selected crop and soil physical parameters. Important crop and soil hydraulic properties were selected according to findings of Dubus *et al.* (2000) for a similar sandy soil and these parameters then changed as defined in Table 2.

- Finally, the model description of solute transport was improved. The model was thus calibrated to the measured bromide concentration in the suction cups. The parameter related to the solute exchange between matrix and macropores was also calibrated, but this had very little effect on the results. Dispersive parameters were not calibrated.

Soil water dynamics within the root zone was sensitive to all of these parameters to some extent as they directly relate to the soil hydraulic parameterization of the applied model. For instance, at low values of the pore size distribution factor λ in matrix the groundwater level decreased more dynamically during drying to satisfy the evaporative demand, whereas it was virtually unaffected during soil wetting. Moreover, root water uptake for transpiration exhibited some sensitivity towards the crop-related parameters in Table 2.

As a result of the calibration, the minimum root depth $z_{r(min)}$ and minimum leaf area index $GLAI_{min}$ were changed from 0.01 to 0.1 to more closely match the observed soil water decrease. Moreover the root adaptability factor ω_c^* was corrected to allow enhanced water uptake from well-supplied soil layers to compensate for stress-induced reductions in others. The root distribution ζ, which refers to the percentage of root length in the top 25% of the total root depth, remained at 60%.

Table 2. Parameters included in the sensitivity analysis

Parameter	Description	Final value	Parameter change (-/+%)
Crop parameters			
	Root adaptability factor (ω_c *)	0.5	-50 / +100
	Minimum leaf area index ($GLAI_{min}$)	0.1	-50 / +100
	Maximum root depth ($z_{r(max)}$)	0.4 m	-25 / +25
	Minimum root depth ($z_{r(min)}$)	0.1 m	-25 / +25
	Root distribution (ζ)	60%	-15 / +15
Hydraulic parameters			
	Saturated water content (θ_s)	48 vol%*)	-10 / +10
	Boundary soil water content (θ_b)	25 vol%*)	-10 / +10
	Pore size distribution factor, micropores (λ)	0.35*)	-50 / +100
	Tortuosity factor, matrix (n)	0.5	-50 / +100
	Saturated hydraulic conductivity ($K_{s(min)}$)	15 mm/h*)	-75 / +300
	Pore size distribution factor and tortuosity factor, macropores (n*)	6*)	-10 / +10

*) *for A horizon*

2.2 Results and discussion

2.2.1 Soil water dynamics and water balances

The model simulations were generally consistent with the observed data, thus indicating a good model description of the overall soil water dynamics in the unsaturated zone. The model is thus able to well match the measured groundwater table, the maximum difference between the measured and simulated groundwater level being 0.5 meter. The dynamics is captured, whereas the amplitude of the fluctuations is less well described.

The overall trends in soil water content could be modelled successfully, although the model did not satisfactorily capture soil water dynamics at all levels. For example, modelling of a period from the end of April to mid May 2000 is inadequate due to the absence of precipitation in combination with a high evaporative demand (Figure 4C).

A water balance was determined for each monitoring year (July to June). Because the Tylstrup site was initiated in May 1999, the two months preceding the hydrological year is included as a separate period (Table 3).

Table 3. 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)	115	251	0	138	114
1.7.99–30.6.00	752	991	33	528	496
1.7.00–30.6.01	752	866	31	494	403

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*

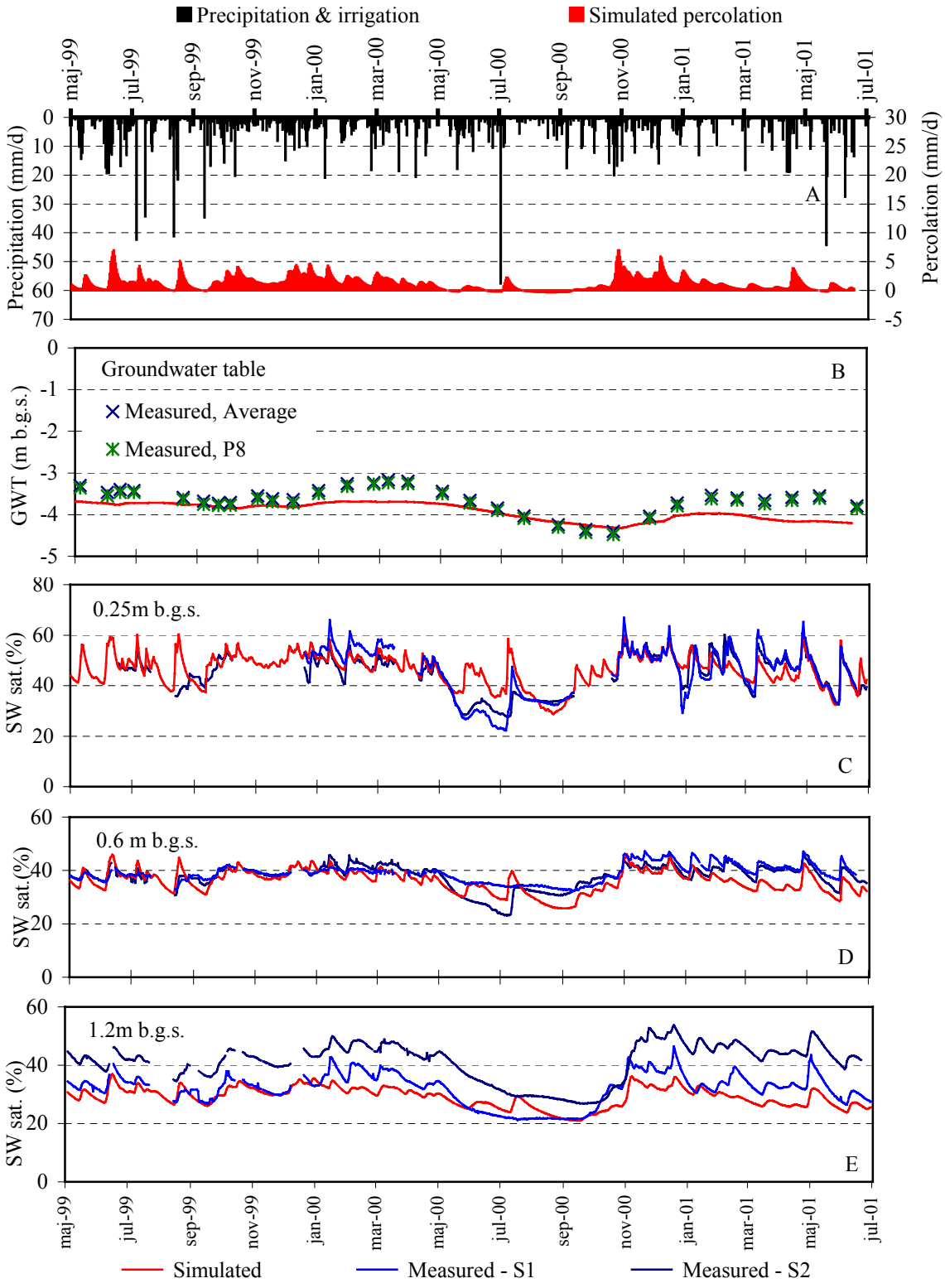

Figure 4. Soil water dynamics at Tylstrup: Locally measured precipitation and simulated percolation at 1 m b.g.s. (A), simulated and measured groundwater level (B), and simulated and measured soil water saturation (SW sat.) at 3 different soil depths (C, D and E). Measured data in B refer to piezometers located in the buffer zone. Measured data in C, D and E refer to TDR probes installed at locations S1 and S2 (see Figure 2).

The first monitoring period (May 1999–June 2000) was very wet at Tylstrup, with precipitation input exceeding the yearly normal by 33%. Precipitation was particularly high in June and August. Moreover, the summer period was characterized by percolation occurring in both June and July.

The second monitoring period (July 2000–June 2001) was also wet, with summed precipitation reaching 866 mm, which is 15% more than normal. Precipitation was particularly high in April and June, whereas August was very dry (Appendix 4). During the summer months the precipitation input was counterbalanced by the actual evapotranspiration and the summer period was characterized by an upward gradient (Figure **4**). Only the large precipitation and irrigation event at the beginning of July 2000 resulted in percolation to deeper than 1 m b.g.s. Percolation occurred continuously from September/October 2000 to April/May 2001.

2.2.2 Bromide leaching

In the unsaturated zone the breakthrough of bromide at 1 m b.g.s. started in August 1999, three months after application. The bromide concentration peaked in September, and the leaching continued throughout the whole winter period until March 2000 (Figure 5). As expected, the breakthrough of bromide at 2 m b.g.s. was delayed by a few months, and the concentration profile at this depth was somewhat wider due to hydrodynamic dispersion.

The model is generally able to satisfactorily simulate the bromide transport, and hence also the water flow. In terms of timing and concentration level of the breakthrough curves the bromide transport was well captured by the model. The results also exhibit some discrepancies, however. Thus although the simulated breakthrough matches the initial breakthrough, the concentration increases too fast when the transport of the main pulse is simulated. This is probably due to overestimation of percolation during the wet summer period in 1999. The tailing of the main pulse is well described at 2 m b.g.s. At 1 m b.g.s. , however, bromide is measured 2–3 months longer than simulated by the model. Improved modelling of the latter would necessitate thorough calibration of the dispersivity and mixing layer.

A mass balance for the applied bromide tracer based on daily, simulated values of water flux and bromide concentration revealed that 99% of the applied bromide had leached from the root zone (1 m b.g.s.) by the end of December 1999. Looking at the measured bromide concentrations (Figure 5), the tail of the main pulse continued throughout January and February 2000, and small amounts of bromide continued to leach as late as autumn 2000. These findings indicate that a minor part of the bromide had diffused into less accessible pore water which cannot be described by the MACRO model. The overall conclusion, though, is that the applied bromide leached out of the root zone (1 m b.g.s.) within a year of application.

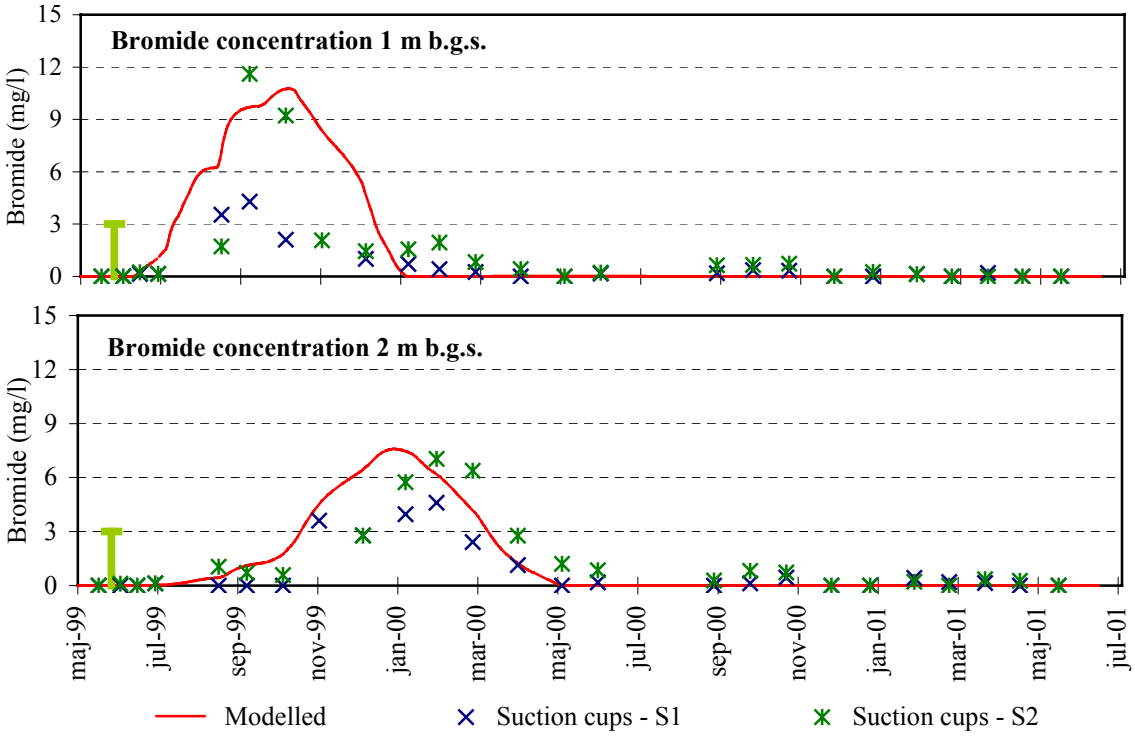

Figure 5. Simulated (solid lines) and measured (dots) bromide concentration in the unsaturated zone at Tylstrup. Measured data derive from suction cups installed 1 m b.g.s. and 2 m b.g.s. at locations S1 and S2 indicated in Figure 2. The green vertical line indicates the time of bromide application

In the saturated zone, marked breakthrough of bromide was detected in all downstream monitoring wells, although the temporal evolution varied markedly within the various monitoring wells. A rapid breakthrough of bromide occurred in monitoring well M4, where an elevated bromide concentration was detected as early as 6 months after application. The breakthrough in the other monitoring wells occurred much later, thus indicating much slower bromide transport, especially in the northern part of the field site. The bromide transport to M2 was thus delayed about a year compared to M4 (Figure 6).

The difference between the various monitoring wells demonstrates the marked heterogeneity within the test field. Silt lenses have also been identified in the northern part of the area that probably cause heterogeneous water flow (Lindhardt *et al*., 2001). Slightly elevated bromide concentrations were detected in monitoring well M1. As M1 is located about 3 m upstream of the treated area, the tracer bromide should not reach it. However, the presence of silt lenses might have deflected the vertical transport through the unsaturated zone, enabling bromide to be transported to this upstream monitoring well.

The applied bromide was not fully captured by the installed monitoring screens. Elevated bromide concentrations were thus detected in the lowest monitoring screen indicating that part of the bromide leaves the system beneath the lowest monitoring screen placed 5–6 m b.g.s. Three additional screens covering 6–7, 7–8 and 8–9 m b.g.s., respectively, were therefore installed near M4 and M5 during August 2001. It should be noted that based on the bromide concentration detected during the period 1 May 1999–1 November 1999, the background concentration of bromide at Tylstrup was 0.23 ± 0.06 mg/l.

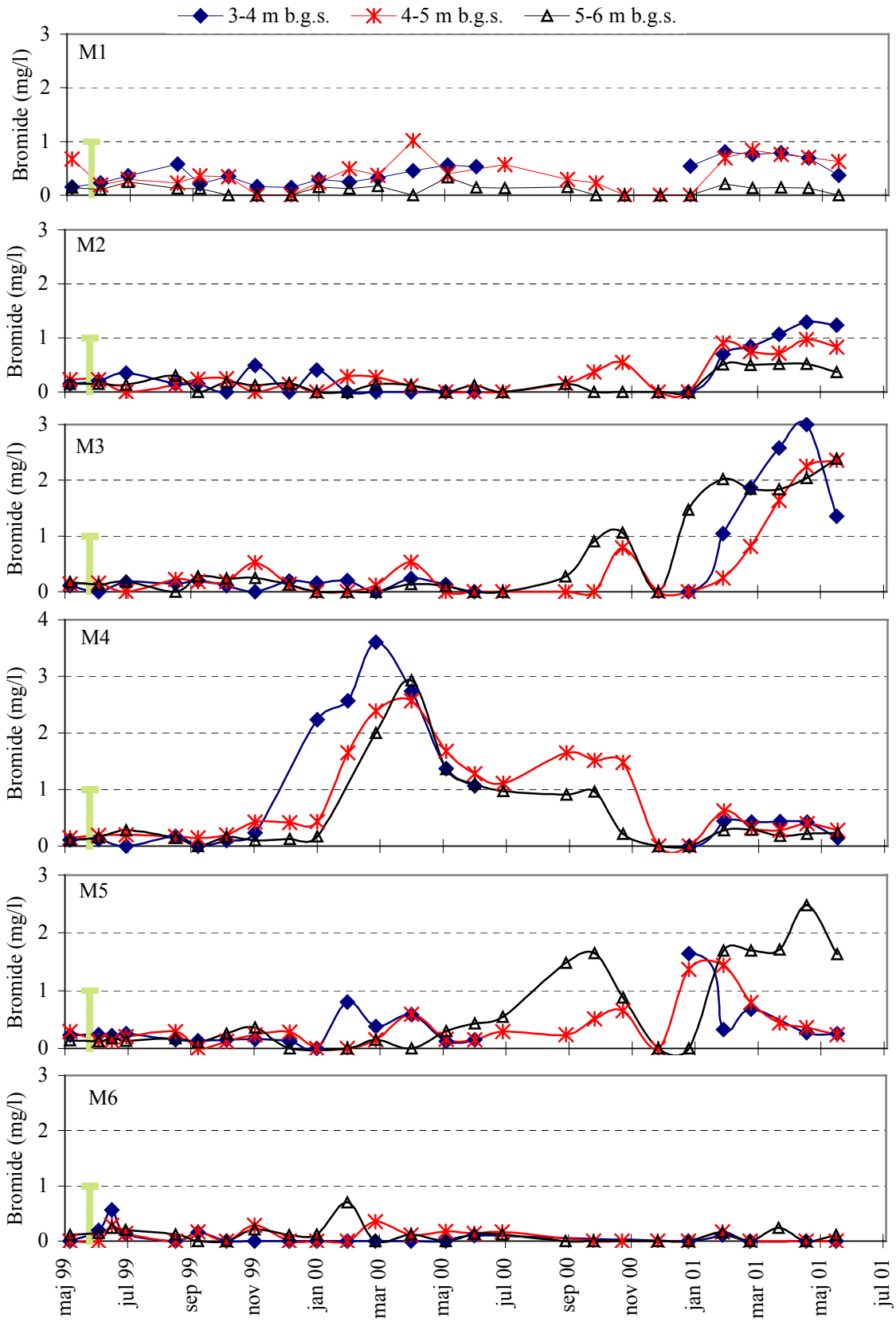

Figure 6. Bromide concentration in the groundwater at Tylstrup. The data derive from monitoring wells M1–M7. The screen depths are in m b.g.s. The green vertical line indicates the time of bromide application.

2.2.3 Pesticide leaching

At Tylstrup, the monitoring encompassed nine different pesticides and several metabolites (Table 4 and Figure 7). The leaching risk of triasulfuron, tribenuron-methyl, fenpropimorph, propiconazole and pirimicarb will not be evaluated until the 2002 monitoring results become available, i.e. when two years of monitoring data have been collated. However, it should be noted that none of these compounds nor the degradation products listed in Table 4 have yet been detected in any of the water samples analysed.

Table 4. Pesticides analysed at Tylstrup. Degradation products are indicated in italics. Percolation refers to the accumulated percolation (1 m b.g.s.) as estimated using the MACRO model.

Crop	Product	Pesticides analysed	Date of application	Precipitation[1)] (mm)	Percolation [1)] (mm)	1st month percolation [2)] (mm)
Potatoes						
	Afalon	Linuron	May 99	2115	990	62
	Sencor WG	Metribuzin - *metribuzin-diketo* - *metribuzin-desamino* - *metribuzin-desamino-diketo*	June 99	2050	983	53
	Dithane DG	- *ETU* (from mancozeb)	Jun–Sep 99	1564	824	54
Spring barley						
	Logran 20WG	Triasulfuron - *triazinamin*	May 00	1038	370	-5
	Pirimor G	Pirimicarb - *pirimicarb-desmethyl* - *pirimicarb-desmethyl-formamido*	June 00	928	374	11
	Tilt Top	Propiconazole	June 00	928	374	11
		Fenpropimorph - *fenpropimorphic acid*	Apr, May 01	91	6	6
Winter rye						
	Stomp SC	Pendimethalin	Nov 00	604	342	103
	Express	*Triazinamin-methyl (*from Tribenuron-methyl)	Nov 00	604	342	103

[1)] *Accumulated from date of application until 1 July 2001*
[2)] *Accumulated within the first month after application*

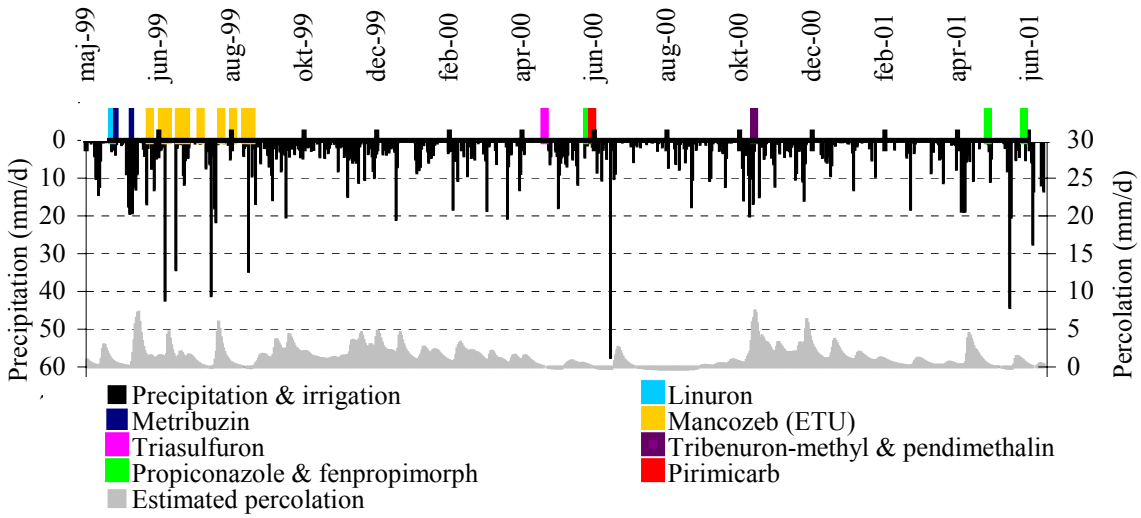

Figure 7. Pesticide application, precipitation and irrigation (primary axis) together with estimated percolation 1 m b.g.s. (secondary axis) at Tylstrup.

Linuron – the active ingredient in Afalon – was applied to the field in late May 1999 a few days before the application of bromide. Linuron has a high sorption capacity towards soil and groundwater sediments and a considerable delay is therefore to be expected relative to bromide transport. During the current monitoring period, linuron was not detected in any of the water samples. This finding should be viewed in relation to the rather wet monitoring period (Section 2.2.1.). Precipitation was particularly high during the first month following linuron application (155 mm), resulting in 62 mm of percolation (Figure 7).

Mancozeb – the active ingredient in Dithane DG – hydrolyses rapidly in the soil, and the leaching risk is therefore more associated with the degradation product ethylenethiourea (ETU). Mancozeb was applied 10 times during the summer of 1999. The last application occurred in mid September 1999 only shortly before the onset of a rather wet leaching period amounting to 449 mm during the period 1 September 1999–1 July 2000 (Figure 7). Despite of the large percolation only a limited amount of ETU leached from the root zone. ETU was only detected in few of the water samples in the unsaturated zone (Figure **8**) and in two samples from the saturated zone in concentrations of 0.02 µg/l. ETU is considered very mobile, and no retardation compared to the bromide transport is therefore expected. Consequently, the leaching risk of the applied Mancozeb and ETU is regarded inconsiderable at the Tylstrup site.

Metribuzin – the active ingredient in Sencor WG – was only detected in concentrations of 0.02 µg/l in two water samples collected from the unsaturated zone. However, two degradation products of metribuzin leached from the root zone (1 m b.g.s.) in average concentrations exceeding 0.1 µg/l. Both compounds leached throughout the entire monitoring period indicating that leaching continued to occur as much as two years following application (Figure 8). Leaching was most pronounced with metribuzin-desamino-diketo reaching an annual average concentration of 1.0 µg/l in suction cup S1. Metribuzin's other degradation product, metribuzin-diketo, also leached, in this case reaching an average concentration of 0.35 µg/l (Table 5 and Figure 8).

The average concentration of pesticides (Table 5) 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 from the MACRO model were assumed to be representative for both suction cups S1 and S2. It should also be noted that the average concentration for 1999/2000 is given as a range due to the high level of uncertainty that characterized the first analyses in 1999. The primary data and further information concerning the calculation methods are given in Appendix 6.

Table 5. Estimated average concentration (µg/l) of metribuzin-desamino-diketo and metribuzin-diketo 1 m b.g.s. at Tylstrup. The primary data are given in Appendix 6.

	Metribuzin-desamino-diketo		Metribuzin-diketo	
	Suction cup – S1	Suction cup – S2	Suction cup – S1	Suction cup – S2
1.7.99–30.6.00	0.91—1.0	0.14–0.27	0.25–0.35	0.05–0.11
1.7.00–30.6.01	0.28	0.34	0.11	0.20

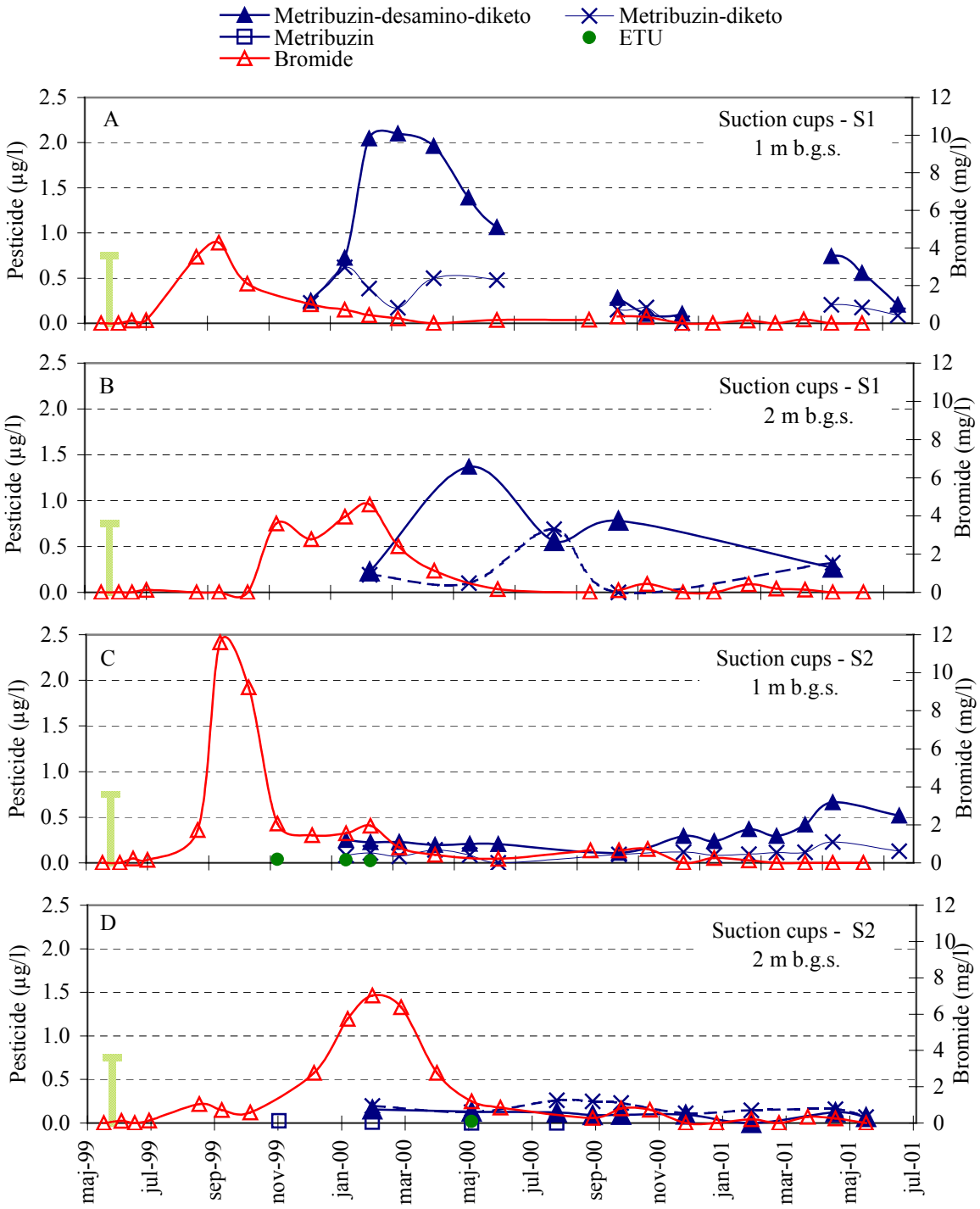

Figure 8. Bromide and pesticide concentrations in the unsaturated zone at Tylstrup. Measured data refer to suction cups installed 1 m b.g.s. and 2 m b.g.s. at locations S1 and S2 indicated in Figure 2. The green vertical line indicates the time of bromide application.

In the saturated zone a marked breakthrough of metribuzin-diketo was only seen in one screen in M4, while the pesticide concentration in the other screens could not be distinguished from the background level (Figure 9 - Figure 11). At Tylstrup, pesticide application prior to the monitoring period has thus resulted in marked groundwater contamination with the degradation products of metribuzin.

Evidence of previous contamination is provided by the initial screening analysis. The degradation products were present in the groundwater before the monitoring started in September 1999 (Appendix 7). In M3 and M5, both degradation products were detected long before the bromide had reached the monitoring wells. Bromide was not detected at M6 and the marked contamination was thus due to prior application of the pesticide on the neighbouring field located just south of the test site or on the fields located upstream of M6 (Appendix 8). The two degradation products of metribuzin were also detected in M1. In view of the slightly elevated bromide concentration detected in M1 (Section 2.2.2), part of the water infiltrating the test site might reach M1. Moreover, metribuzin was applied to the neighbouring field located upstream of the test site in 1999 concomitantly with application on the test site (Appendix 8). The degradation products detected in M1 may thus derive from the test site or the upstream neighbouring field. The origin of the breakthrough in M4 is also difficult to identify. In view of the bromide transport it may be due to application during the monitoring period. However, the concentration pattern at M4 was similar to that at M6, which was only affected by metribuzin applied prior to the monitoring period.

In conclusion, the high background concentration found in all monitoring wells makes it difficult to determine whether the observed groundwater contamination is due to the metribuzin applied during the PLAP programme or to metribuzin applied on the test site or on the "upstream" fields prior to the PLAP. It is thus still too early to fully verify the impact of the metribuzin applied during the PLAP on the quality of the groundwater. It should be noted, though, that the average concentration of metribuzin-diketo in the Tylstrup groundwater was 0.13 µg/l, and that the average concentration exceeded the maximum allowable concentration (0.1 µg/l) at 60% of the screens analysed (Appendix 7). Metribuzin-desamino-diketo was also detected in 60% of the analysed groundwater samples, although the concentration never exceeded 0.1 µg/l.

At Tylstrup, degradation of metribuzin takes place via both hydrolysis to metribuzin-diketo as well as via photodegradation to metribuzin-desamino (Figure 13). Metribuzin-desamino was not detected in any of the water samples, however, thus indicating that the compound is either strongly adsorbed to the soil, or is easily degraded to metribuzin-desamino-diketo. The further degradation of both metribuzin-diketo and metribuzin-desamino-diketo appears to be very slow in the groundwater. Evidence that these degradation products are still present in the groundwater at least four years after application is provided by the data from M6 (Figure 11). Metribuzin-diketo in particular appears to be relatively stable, degrading much slower than metribuzin-desamino-diketo. Previous applications of metribuzin have thus caused marked groundwater contamination in which metribuzin-diketo is present in much higher concentrations than metribuzin-desamino-diketo. It should be noted that the concentration of metribuzin-diketo in the unsaturated zone (i.e. deriving from the pesticide applied during the PLAP) was somewhat similar to that in the groundwater caused by prior application of metribuzin.

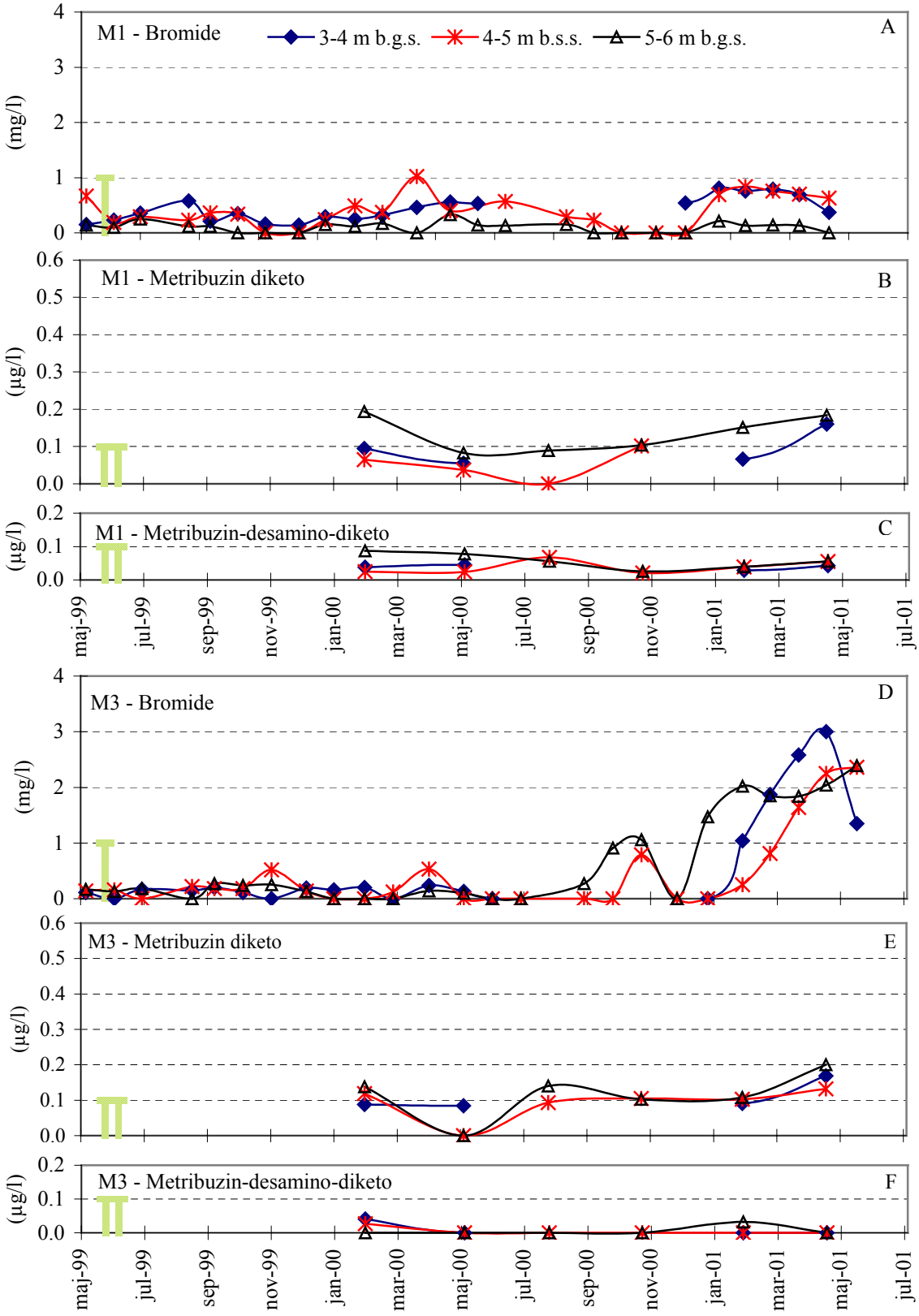

Figure 9. Bromide and pesticide concentrations in the groundwater at Tylstrup. The data derive from monitoring wells M1 (A,B,C) and M3 (D,E,F). Screen depth is indicated in m b.g.s. The green vertical line indicates the time of application.

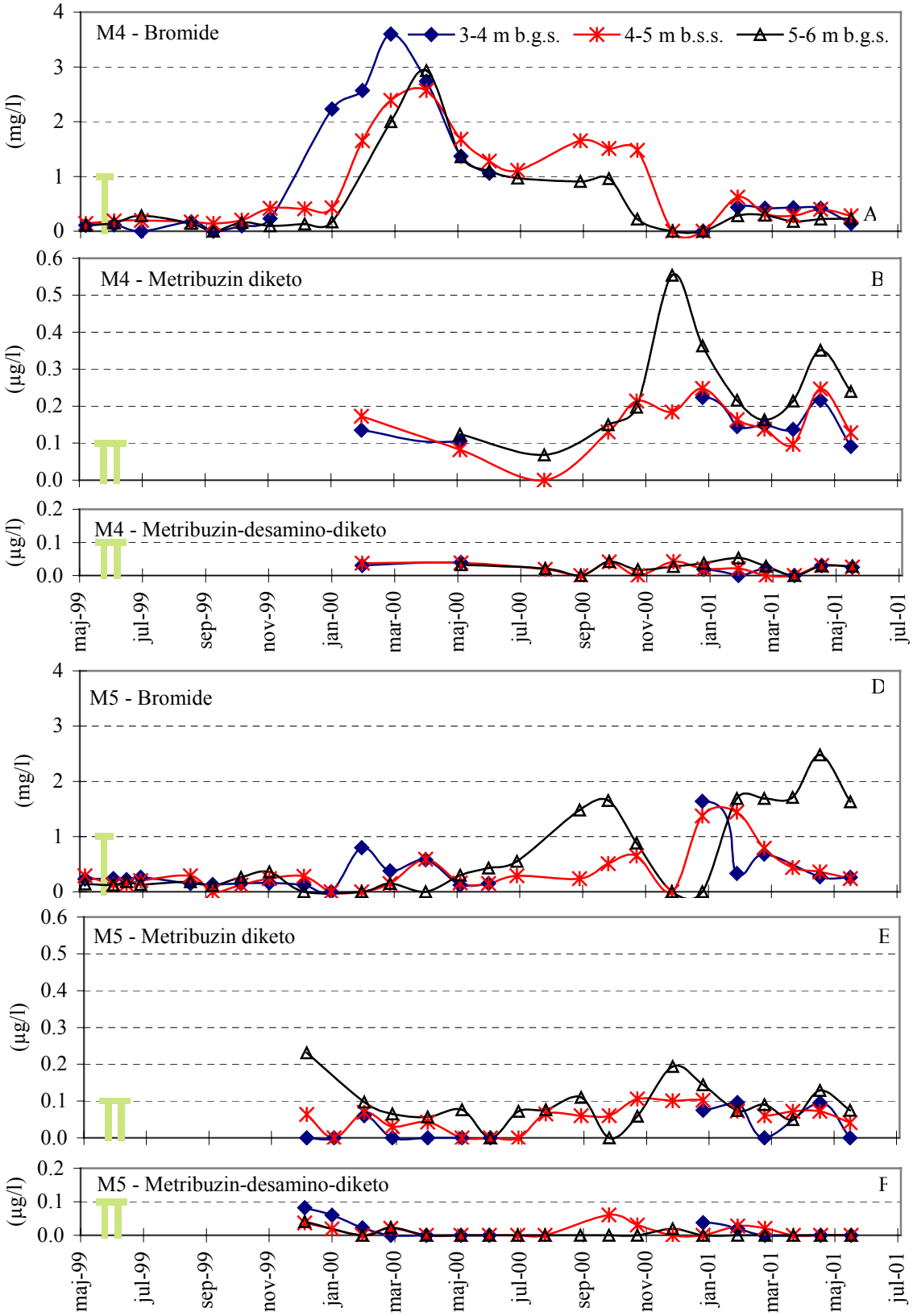

Figure 10. Bromide and pesticide concentration in the groundwater at Tylstrup. The data derive from monitoring well M4 (A,B,C) and M5 (D,E,F). Screen depth is indicated in m b.g.s. The green vertical line indicates the time of application.

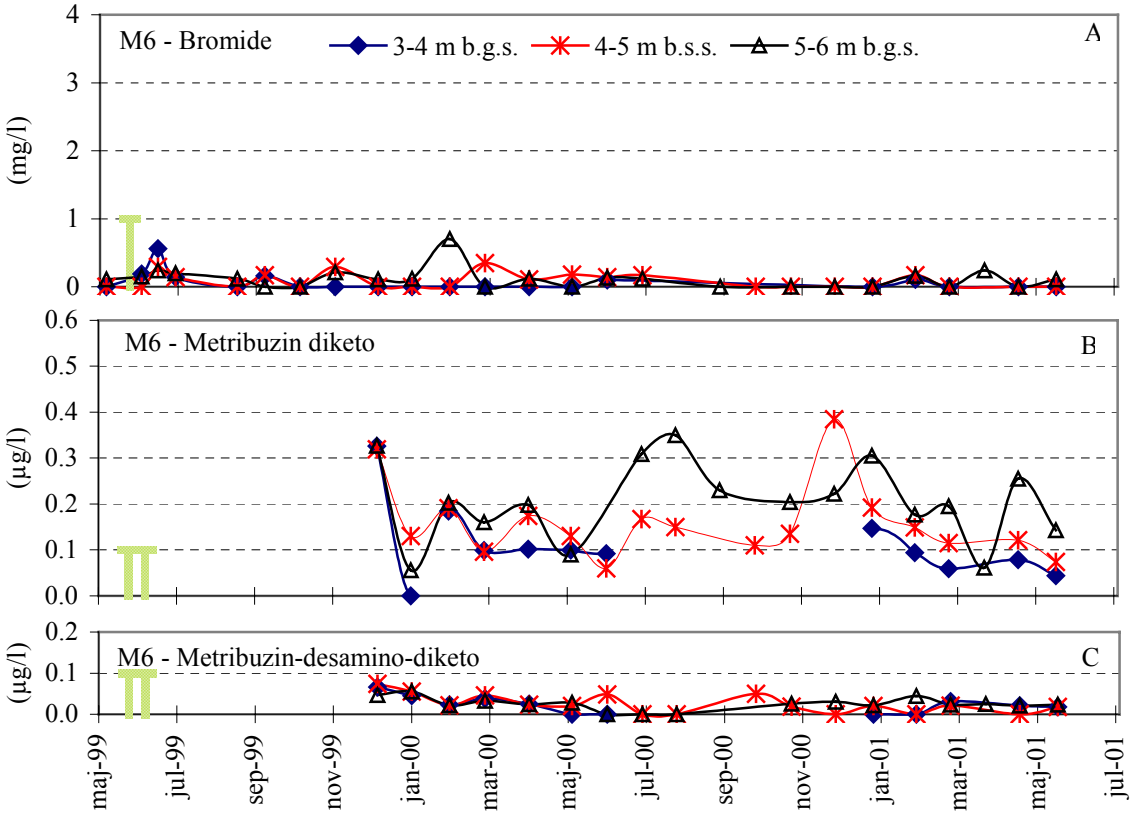

Figure 11. Bromide and pesticide concentration in the groundwater at Tylstrup. The data derive from monitoring well M6. Screen depth is indicated in m b.g.s. The green vertical line indicates the time of application.

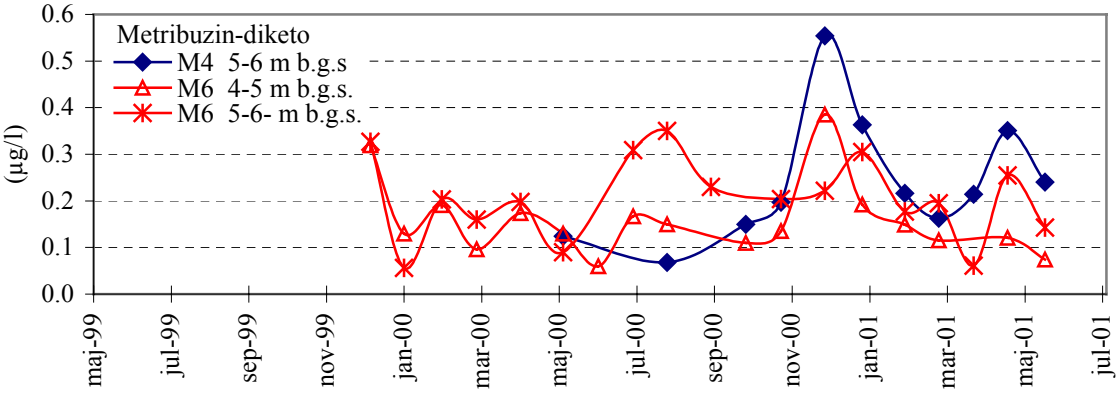

Figure 12. Concentration of metribuzin-diketo in selected screens in monitoring well M4 and M6.

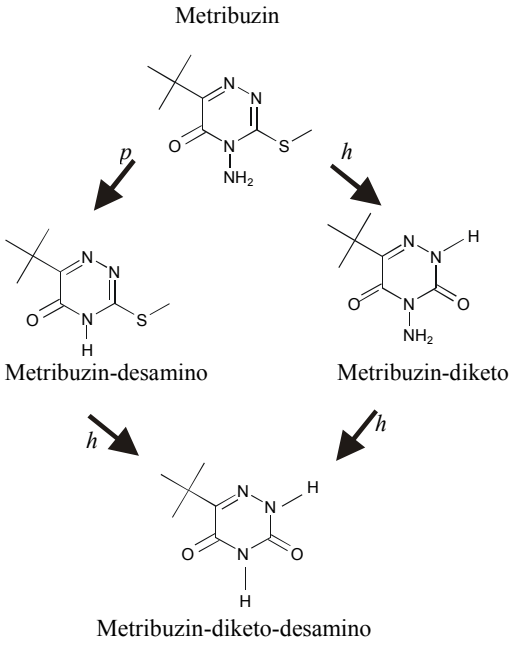

Figure 13. Metribuzin degradation pathways involving hydrolysis (*h*) and photodegradation (*p*).

2.3 Summary

The risk of pesticide leaching at Tylstrup can be summarized as follows:

- With triasulfuron, tribenuron-methyl, fenpropimorph, propiconazole, pendimethalin and pirimicarb the leaching risk will not be evaluated until the 2002 monitoring results become available, i.e. when a total of two years of monitoring data have been collated. It should be noted, though, that none of these pesticides or the degradation products fenpropimorphic acid, pirimicarb-desmethyl or pirimicarb-desmethyl-formamido have yet been detected in any of the water samples analysed.

- With metribuzin, ETU (degradation product of mancozeb) and linuron, the leaching risk was found to be negligible.

- Two degradation products of metribuzin (metribuzin-desamino-diketo and metribuzin-diketo) were found to leach from the root zone (1 m b.g.s.) in average concentrations exceeding 0.1 µg/l. The estimated leachate concentrations of metribuzin-desamino-diketo and diketo-metribuzin were 0.14–1.0 µg/l and 0.05–0.35 µg/l, respectively.

- The monitoring results indicate marked groundwater contamination with the degradation products of metribuzin. The average concentration of metribuzin-diketo was 0.13 µg/l, and the maximum allowable concentration of 0.1 µg/l was exceeded in 60% of the screens analysed. Metribuzin-desamino-diketo was also detected in 60% of the analysed groundwater samples, although the concentrations never exceeded 0.1 µg/l. Whether or not the observed groundwater contamination is due to the metribuzin applied during the PLAP or prior to the monitoring period cannot yet be determined.

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, with a terrain slope of only 0-12°. A windbreak borders the eastern side of the test side. The soil can be classified as Arenic Eutrudept and Humic Psammetic Dystrudept (Soil Survey Staff, 1999) with coarse sand as the dominant texture class and topsoil containing 5% clay and 1.8% organic carbon. The geological description points to a rather homogeneous aquifer of meltwater sand, with local occurrence of thin clay and silt beds (Figure 15). The area has a shallow groundwater table ranging from 1–2 m b.g.s. The overall direction of groundwater flow is towards northwest (Figure 14). A brief description of the sampling procedure and analysis methods is provided in Appendixes 1–2. The monitoring design and test site are described in detail in Lindhardt *et al.* (2001).

3.1.2 Agricultural management

The field was sprayed with glyphosate on 22 September 1999 prior to the sowing of winter rye (cv. Dominator) on 13 October. Weeds were sprayed on 12 November using tribenuron-methyl. At the same time, potassium bromide tracer was applied. Fungicide spraying was carried out twice on 5 May and 7 June, each time using propiconazole and fenpropimorph. On 6-7 May the site was irrigated with 29 mm/ha. The winter rye was harvested on 9 August, yielding 56.2 hkg/ha of grain (water content 15%), approximately 5 hkg/ha less than average for the location. On 24 April 2001, 49 tonnes/ha of cattle slurry was spread and incorporated. The field was ploughed two days later and sown with maize (cv. Loft) on 30 April. Herbicide spraying with terbuthylazine and pyridate was carried out on 14 May and on 30 May. The site was irrigated twice with 31 mm/ha on 4–5 July and 30 mm/ha on 23–24 July. The maize was harvested on 1 October yielding 151.4 hkg/ha (100% dry matter) cobs and stalks. Management practice at the site is detailed in Appendix 3, Table A3.2.

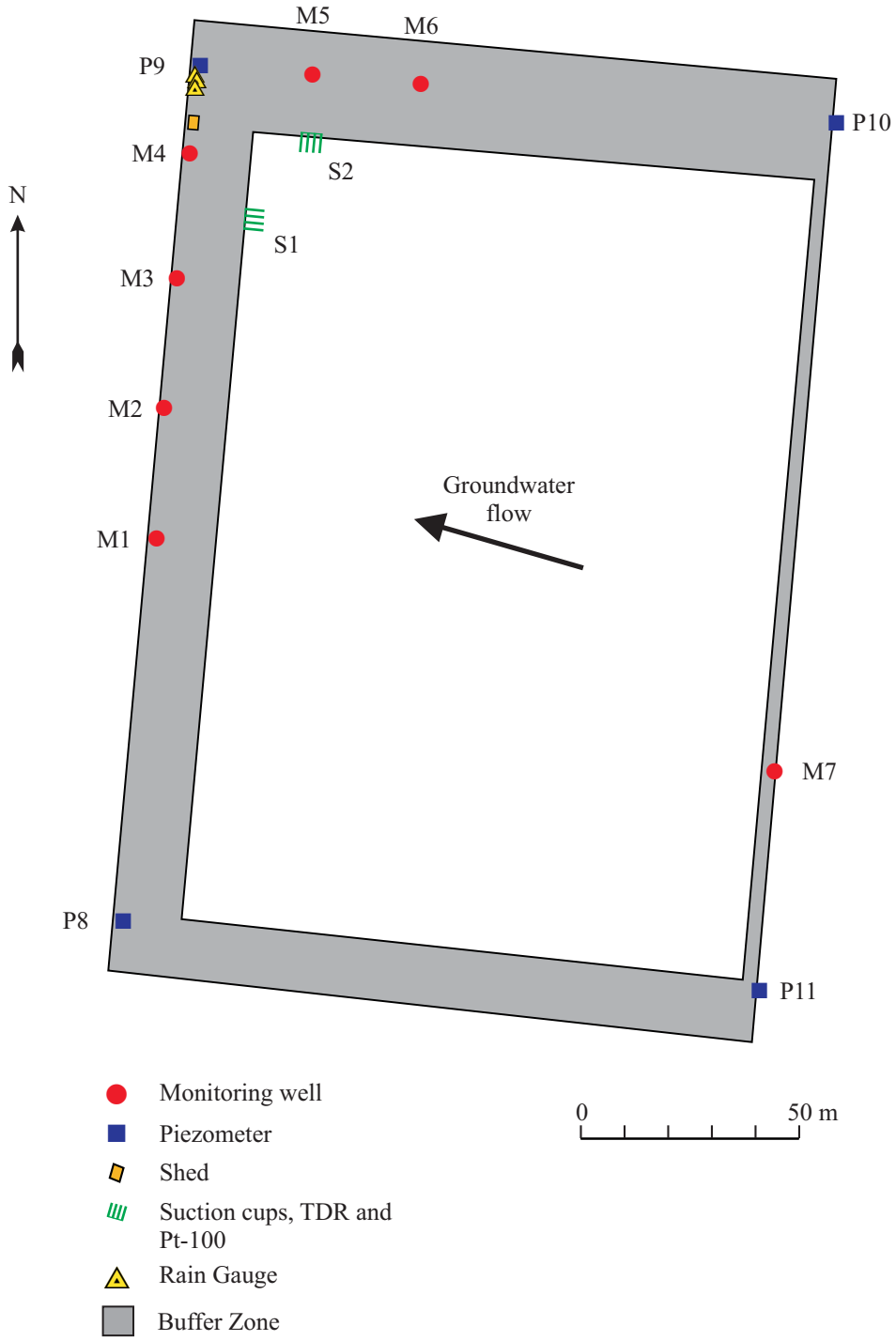

Figure 14. Overview of the Jyndevad test site. The innermost white area indicates the cultivated land, while the grey area indicates the surrounding buffer zone. The positions of the various installations are indicated, as is the direction of groundwater flow.

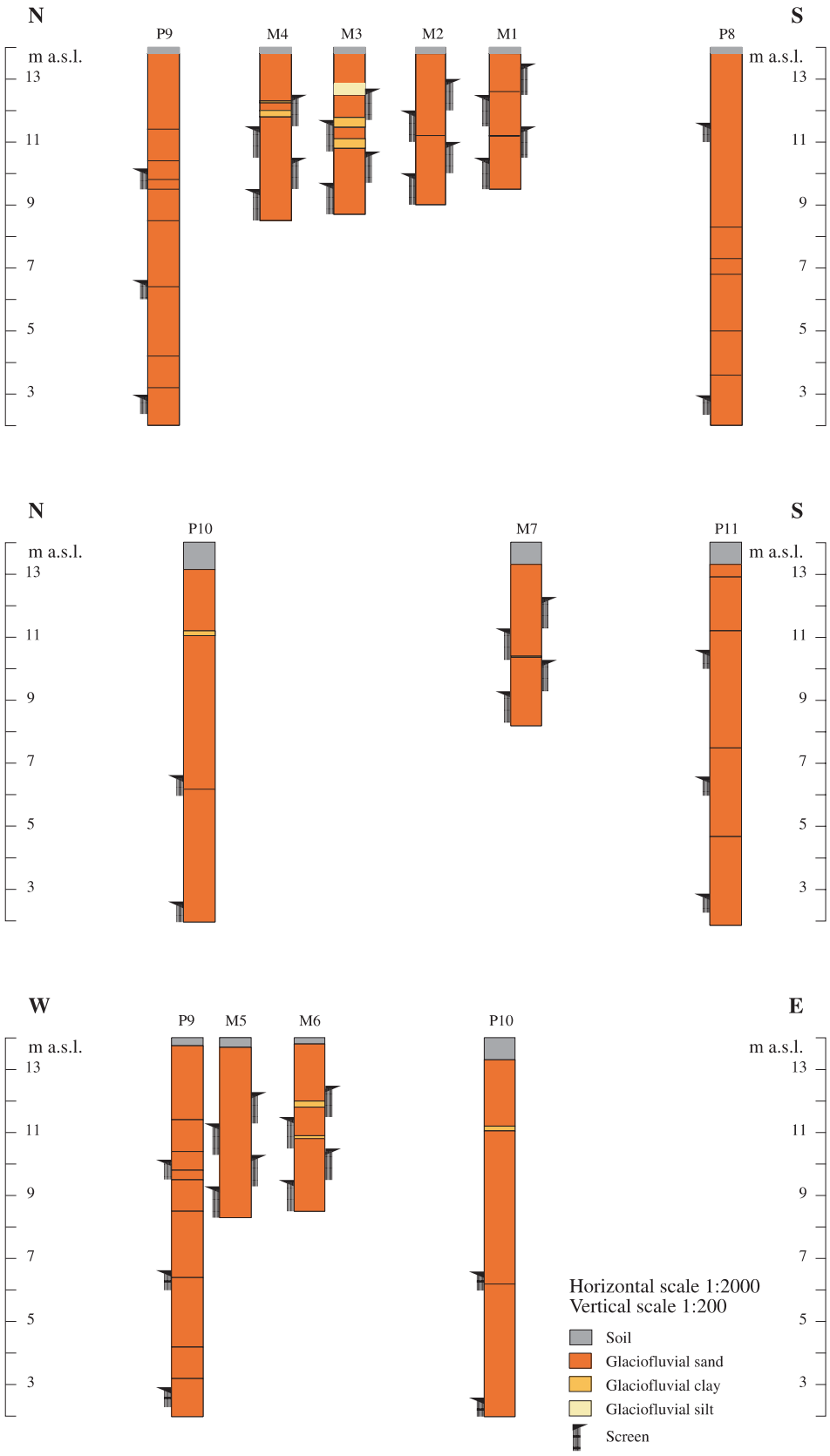

Figure 15. Geological description of the Jyndevad site (Lindhardt *et al.*, 2001).

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 the water flow in the unsaturated zone and to establish an annual water balance during the full monitoring period July 1999–June 2001.

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 14). The calibration procedure only involved adjustment of the empirical BGRAD parameter regulating the boundary flow. Data acquisition and model set-up are described in Appendix 5.

3.2 Results and discussion

3.2.1 Soil water dynamics and water balances

The model simulations were generally consistent with the observed data, thus indicating a good model description of the overall soil water dynamics in the unsaturated zone. The model was able to match the small fluctuations in the measured groundwater table well. The overall dynamics of the measured soil water saturation was successfully modelled, although the model had some difficulty in capturing the degree of the soil water saturation (Figure 16D and E). The overestimation of water saturation at 60 cm b.g.s. is probably due to a poorly fitted retention curve for saturation ranging from 15 to 45% (7–20% vol./vol.) (see Appendix 5, Figure A5.3).

The measured soil water saturation in the C horizon in which the TDR probes are installed 110 cm b.g.s. differed markedly by 16% between the two groups of probes. The model simulated an even lower saturation. Because the pore size distribution factor (λ) of the soil in the C horizon is large, small changes in the soil water tension cause large differences in the soil water saturation in the intermediate saturation range. This characteristic behaviour of well-sorted sand could explain the described differences between the probes in the two profiles.

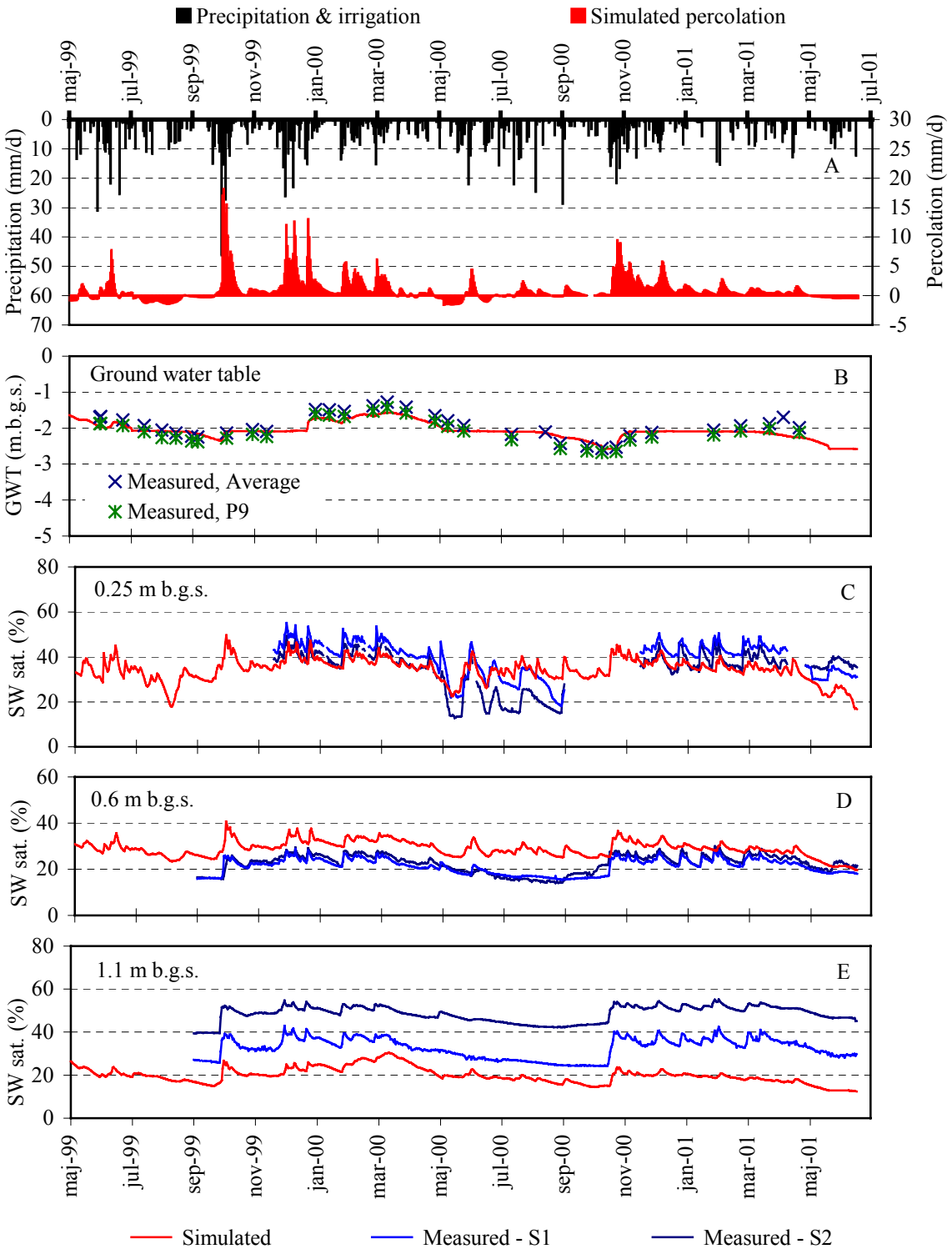

Figure 16. Soil water dynamics at Jyndevad: Locally measured precipitation and simulated percolation (1 m b.g.s.) (A), simulated and measured groundwater level (B), and simulated and measured soil water saturation (SW sat.) at 3 different soil depths (C, D and E). Measured data in B refer to piezometers located in the buffer zone. Measured data in C, D and E refer to TDR probes installed at location S1 and S2 (see Figure 14).

Table 6. 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	964	966	29	560	437
1.7.00–30.6.01	964	723	0	474	277

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

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

During the first monitoring period (July 1999–June 2000), precipitation was close to a normal year at Jyndevad (Table 6). Precipitation was particularly high in December at 95 mm above normal, whereas July and August and especially November were dry months. Percolation occurred continuously during the winter months from October to March.

The second monitoring period (July 2000–June 2001) was dry, summed precipitation amounting to only 752 mm, which is 22% less than normal. Precipitation was low in September and January, and particularly in May, when precipitation amounted to only 25% of normal for the month of May (see Appendix 4). During the late spring/early summer months the precipitation input was counterbalanced by evapotranspiration. Only a short wet period in June resulted in percolation to deeper than 1 m b.g.s. (Figure 16). The late summer period (August to October) was characterized by low or no percolation, whereas the higher winter percolation was initiated in late October and continued until May.

3.2.2 Bromide leaching

The autumn application of bromide was followed by high autumn precipitation with a resultant high level of infiltration and rapid leaching of bromide. The bromide concentration thus increased rapidly at 1 m b.g.s. as early as one month after application. All of the bromide had leached from the uppermost metre of the soil about four months after application (Figure 17). At 2 m b.g.s. the concentration profiles varied considerably within the two suction cups. The breakthrough of bromide occurred two months after application in both suction cups, but the bromide concentration in S2 subsequently remained elevated for a much longer period than in S1. As the groundwater table was located 2 m b.g.s., the difference in duration of the bromide peak was probably due to the different saturation index at the two sets of suction cups. Thus S2 was saturated throughout the whole monitoring period, whereas S1 was only saturated during the winter period (Figure 18). The elevated bromide concentration, which was maintained in S2, indicates that a continuous groundwater transport of bromide occurred throughout the monitoring period.

In the saturated zone, marked breakthrough of bromide was detected in all downstream monitoring wells, with the results indicating rather homogeneous groundwater flow. Elevated bromide concentrations were thus detected in all downstream monitoring wells around July, with the temporal evolution being somewhat similar (Figure 19). The area around M3 was characterized by a more heterogeneous flow pattern, however. The bromide concentration in the upper screen (located 2–3 m b.g.s.) of M3 was thus only slightly elevated, while transport of the majority of the bromide took place at lower depths. The flow pattern may be governed by silt and clay lenses located in the upper three meters of M3 (see Figure 13).

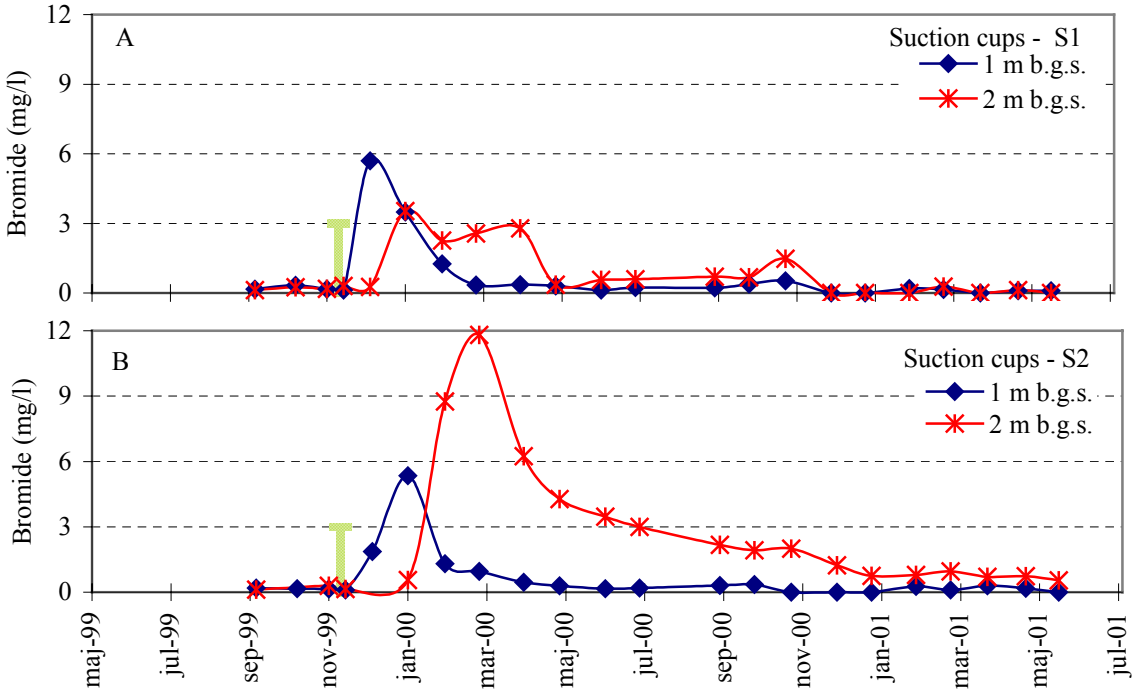

Figure 17. Bromide concentration at Jyndevad. The data derive from suction cups installed 1 m b.g.s. and 2 m b.g.s. at locations S1 and S2 (see Figure 14). The green vertical line indicates the time of bromide application.

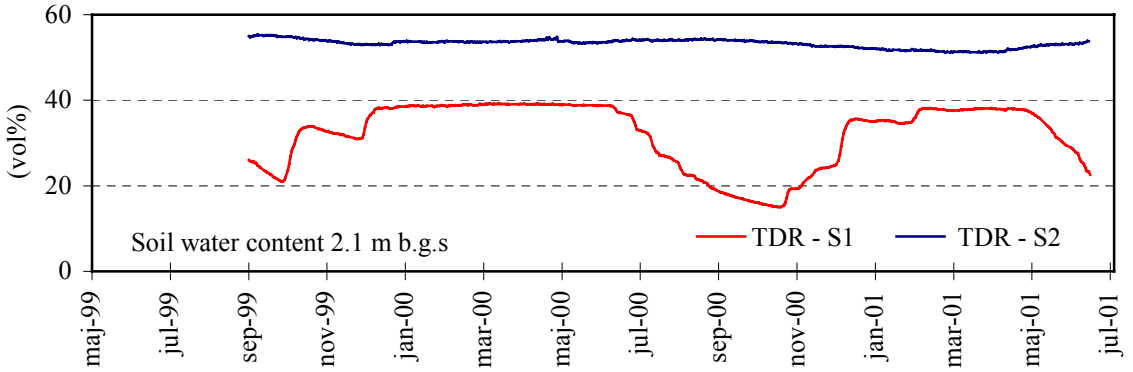

Figure 18. Measured soil water content at Jyndevad. The data derive from TDR probes installed at locations S1 and S2 (see Figure 14).

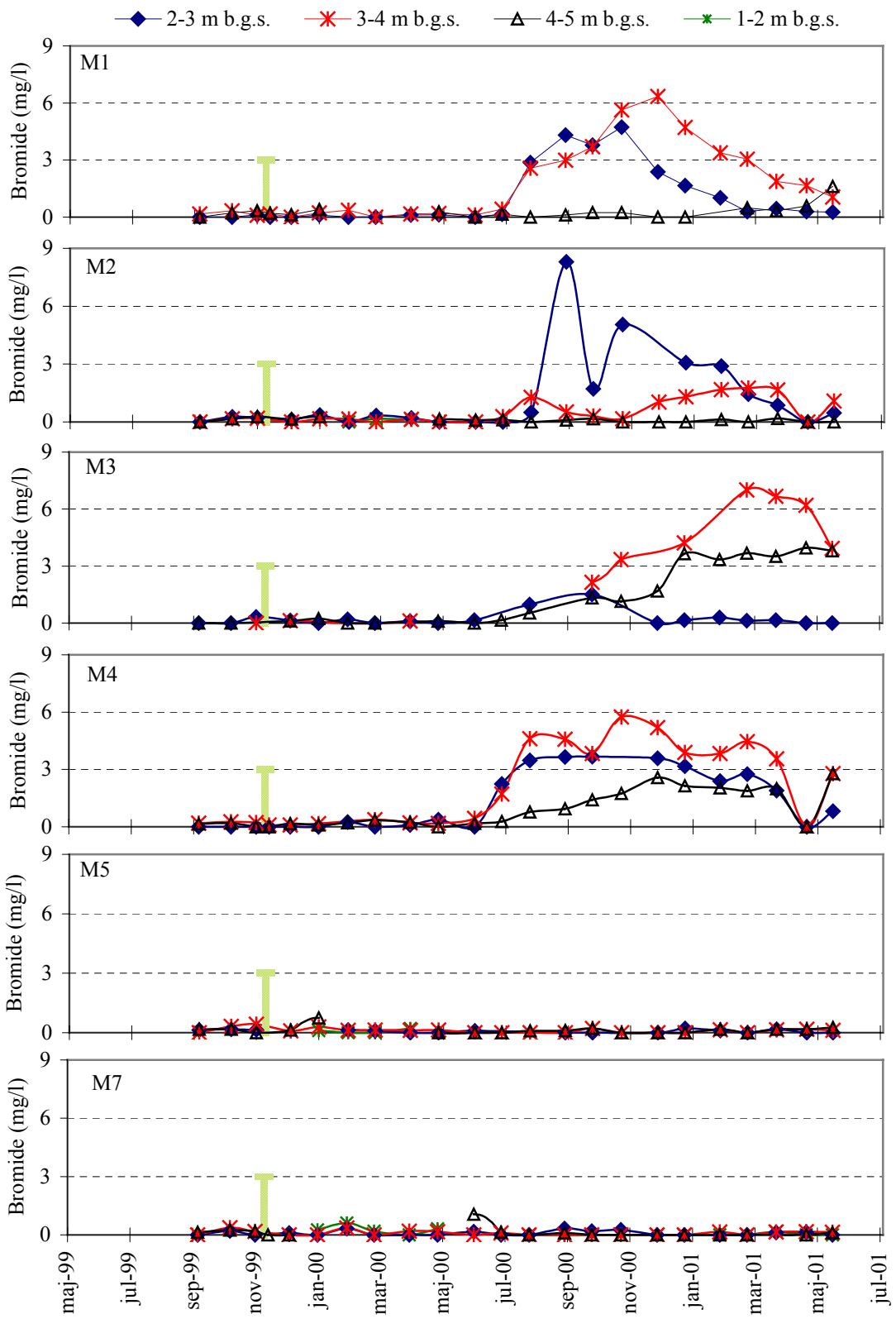

Figure 19. Bromide concentration in the groundwater at Jyndevad. The data derive from monitoring wells M1–M7. The screen depths are in m b.g.s. The green vertical line indicates the time of bromide application.

3.2.3 Pesticide leaching

At Jyndevad, the monitoring encompassed six different pesticides and several metabolites (Figure 20 and Table 7). The leaching risk of fenpropimorph, propiconazole, terbuthylazine and pyridate will not be evaluated until the 2002 monitoring results become available, i.e. when two years of monitoring data have been collated. It should be noted, though, that apart from one sample containing 0.04 µg/l of fenpropimorph, none of these compounds or the degradation products listed in Table 7 have yet been detected in any of the water samples analysed.

Table 7. Pesticides analysed at Jyndevad. Degradation products are indicated in italics.

Crop	Product	Pesticides analysed	Date of application	Accumulated precipitation [1)] (mm)
Winter rye				
	Roundup 2000	Glyphosate - *AMPA*	Sep 99	1603
	Express	*Triazinamin-methyl* *(*from tribenuron-methyl)	Nov 99	1391
	Tilt Top	Propiconazole Fenpropimorph - *fenpropimorphic acid*	Apr 00, May 00	926, 809
Maize				
	Lido	Terbuthylazine - *desethylterbuthylazine* Pyridate - *PHPC*	May 01	80

[1)] *Accumulated from date of application until 1 July 2001.*

Glyphosate – the active ingredient of Roundup – and the degradation product AMPA did not leach from the root zone during the monitoring period. Apart from three samples exhibiting AMPA concentration of 0.01–0.02 µg/l, neither of the substances has been detected in any of the water samples.

Tribenuron-methyl – the active ingredient of Express – degrades rapidly in the soil, and the risk of leaching is therefore more associated with the degradation product metabolite triazinamin-methyl. Triazinamin-methyl has not yet been detected in any of the water samples analysed, however.

These results should be viewed in relation to a rather wet monitoring period, with percolation occurring shortly after pesticide application in both years. Tribenuron-methyl was applied in mid November concomitantly with the bromide tracer. The tracer results indicate high infiltration and a rapid leaching of the applied bromide (Figure 17). Glyphosate was applied on stubble in mid September. A storm event (43 mm/d) occurred just 8 days after application. The following October there was 115 mm of precipitation, 17% more than normal (Appendix 4, Figure A4.2). Percolation, as estimated using MACRO, also started at the beginning of October just 8 days after application. The groundwater recharge during the 1999–2000 monitoring period amounted to 437 mm (Table 6).

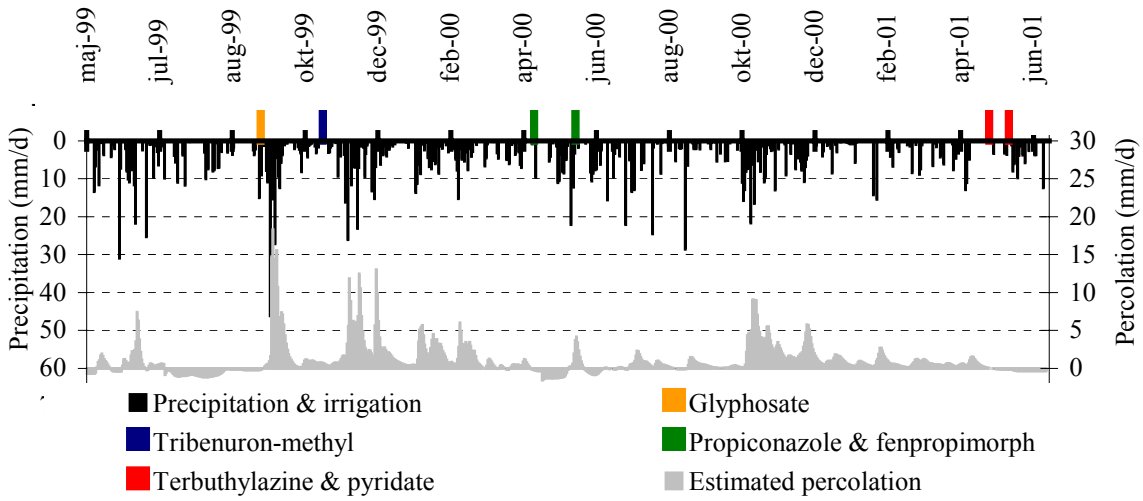

Figure 20. Pesticide application, precipitation and irrigation (primary axis) together with estimated percolation 1 m b.g.s. (secondary axis) at Jyndevad.

However, the short time lag between pesticide application and onset of the leaching appeared to be sufficient for degradation and sorption processes to prevent the leaching of both glyphosate and tribenuron-methyl. The sorption capacity at Jyndevad was also expected to be high due to the high content of Fe and Al present in the Bhs horizons just beneath the plough layer (Lindhardt *et al.*, 2001). Moreover, the infiltration of water primarily takes place in the soil matrix as macropore transport is limited in the unstructured coarse sandy soil. The absence of macropores thus provides much better conditions for sorption and degradation processes in terms of a longer residence time in the root zone, as well as better contact between the infiltrating water and the surrounding soil matrix. Finally, it should be noted that the monitoring of glyphosate and triazinamin-methyl will continue throughout the coming monitoring period.

Previous application of pesticides has caused marked groundwater contamination with the degradation products of metribuzin. Metribuzin-diketo was detected in concentrations as high as 1.37 µg/l (monitoring well M2) and exceeded 0.1µg/l in 73% of the water samples analysed. Metribuzin-desamino-diketo was detected in all the downstream monitoring wells, with the concentration again being highest in M2 (1.83 µg/l) (Table 8) and exceeding 0.1µg/l in 50% of the water samples analysed. The marked groundwater contamination was due to prior application either on the Jyndevad site or on fields located upstream of the site. It should be noted that the previous application of metribuzin at Jyndevad and the neighbouring upstream fields had been carried out in accordance with current regulations, which permit a maximum dosage of 0.35 kg/ha/yr (Appendix 9).

Table 8. Groundwater concentration of metribuzin-diketo, metribuzin-desamino-diketo at Jyndevad (µg/l). Monitoring well M7 is located upstream of the test site, whereas the others are all located downstream. The data derive from supplementary analyses carried out in spring 2001.

Monitoring well		M2			M4			M1	M5	M7		
Screen depth (m b.g.s.)		2–3	3–4	4–5	2–3	3–4	4–5	2– 3	4 – 5	3–4	4–5	5–6
Metribuzin-diketo												
	02.01.01	0.07	0.54	0.53				0.10	0.28	0.06	0.05	0.05
	05.03.01	0.05	0.47	1.37	0.35	0.50	0.72					
	03.04.01	0.04	0.45	0.96	0.44	0.55	0.58					
	03.05.01	0.06	0.37	0.77	0.44	0.72	0.53					
Metribuzin-desamino-diketo												
	02.01.01	0.02	0.65	1.10				0.03	0.07	<	<	<
	05.03.01	<	0.35	1.31	0.09	0.13	0.23					
	03.04.01	<	0.24	1.83	0.04	0.11	0.32					
	03.05.01	<	0.40	1.76	0.03	0.09	0.40					

< Below the detection limit of 0.02 µg/l; The concentrations of metribuzin and metribuzin-desamino were below the detection limit in all samples

3.3 Summary

The risk of pesticide leaching at Jyndevad can be summarized as follows:

- With fenpropimorph, propiconazole, terbuthylazine and pyridate the leaching risk will be evaluated when the 2002 monitoring results become available, i.e. when two years of monitoring data have been collated. It should be noted, though, that there were no evidence of leaching of either of these compounds or their degradation products fenpropimorphic acid, desethylterbuthylazine and PHPC.

- With glyphosate and triazinamin-methyl (from tribenuron-methyl), the leaching risk was found to be negligible.

- Previous applications of pesticides have resulted in marked groundwater contamination with metabolites of metribuzin. Metribuzin-diketo was detected in concentrations as high as 1.37 µg/l, and exceeded 0.1µg/l in 73% of the water samples analysed. Metribuzin-desamino-diketo was detected in concentrations as high as 1.83 µg/l and exceeded 0.1 µg/l in 50% of the water samples analysed.

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. 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 and contained 20–35% clay, 20–40% silt and 20–40% sand (Figure 22). 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 and analysis methods is provided in Appendixes 1–2. The monitoring design and test site are described in detail in Lindhardt *et al.* (2001).

4.1.2 Agricultural management

Cattle slurry (36.5 tonnes/ha) was spread on 19 April 2000, whereafter the field was ploughed. Fodder beet (cv. Kyros) was sown on 5 May and emerged unevenly across the field within 1 to 3 weeks. The herbicides metamitron, phenmedipham, desmedipham and ethofumesate were applied on 22 May, 15 June and 12 July. Potassium bromide tracer was applied on May 22. The field was sprayed with fluazifop-p-butyl on 28 June to combat wild oats and with pirimicarb on 5 July to combat aphids. The crop was harvested on 15 November yielding 134.5 hkg/ha of beet roots (100% dry matter) and 26.3 hkg/ha of beet tops. Taken together, the dry matter yield was at the same level as the normal yield recorded in the area that year. The field was ploughed in spring 2001. Due to ample precipitation, sowing of the spring barley (cv. Otira) was delayed until 9 May. Crop emergence was recorded 11 days later. The herbicides tribenuron-methyl and flamprop-M-isopropyl were sprayed on 9 and 21 June, respectively. The fungicides propiconazole and fenpropimorph were spread on 21 June and 4 July. The insecticide dimethoat was sprayed on 6 July. Despite the very late sowing, grain yield at harvest on 5 September was as high as 88.0 hkg/ha with 15% water content. Precipitation prevented the straw being pressed until late October, resulting in a low straw yield of 28.6 hkg/ha (dry matter). Management practice at the site is detailed in Appendix 3 (Table A3.3).

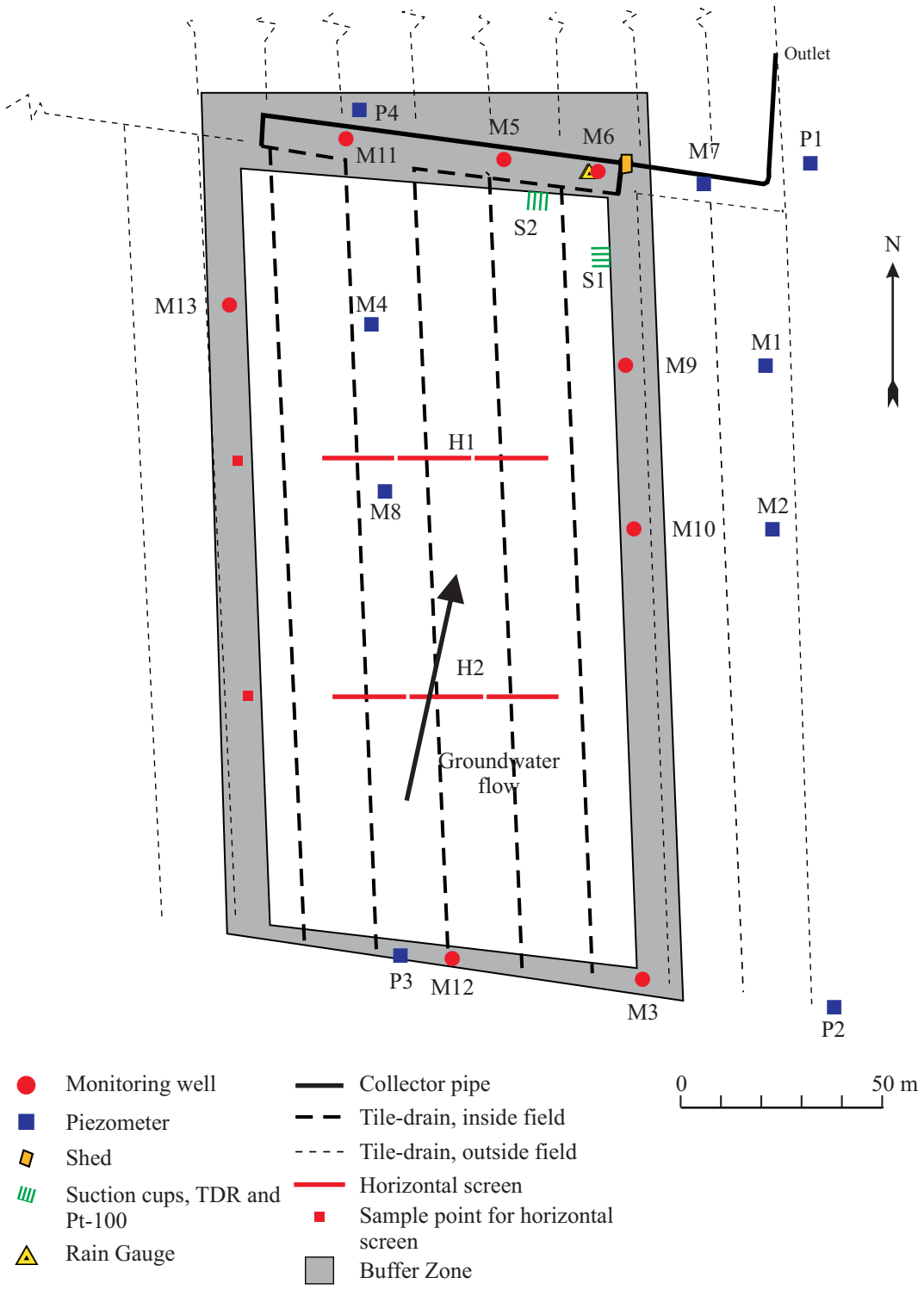

Figure 21. Overview of the Silstrup site. The innermost white area indicates the cultivated land, while the grey area indicates the surrounding buffer zone. The positions of the various installations are indicated, as is the direction of groundwater flow (by an arrow).

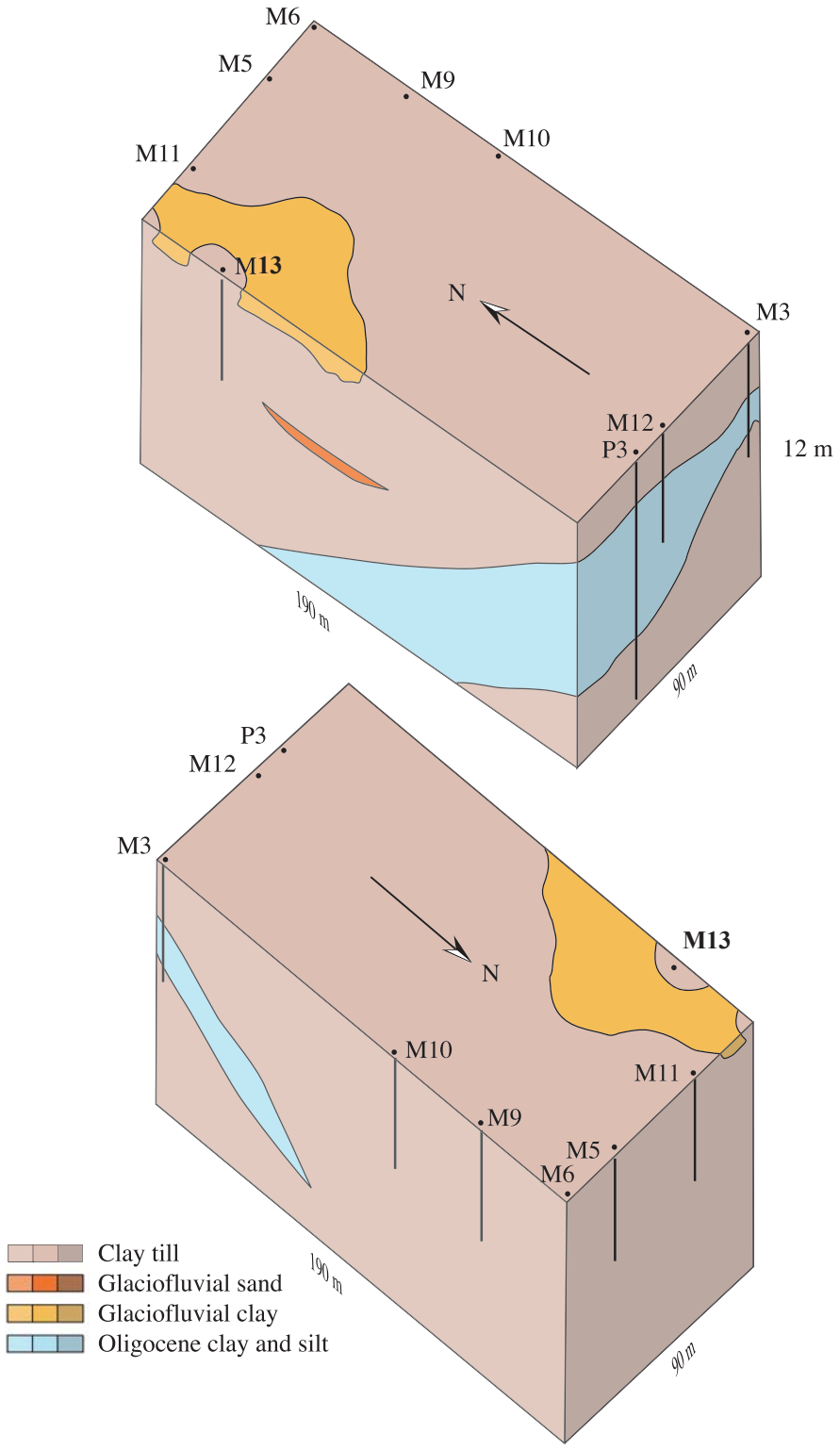

Figure 22. Geological description of the Silstrup site (Lindhardt *et al.,* 2001).

4.1.3 Model set-up and calibration

The MACRO model was 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 was used to simulate the water flow in the unsaturated zone during the full monitoring period April 2000–June 2001 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 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 (see Figure 21). 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. Data acquisition and model set-up are described in Appendix 5.

4.2 Results and discussion

4.2.1 Soil water dynamics and water balances

The model simulations were generally consistent with the observed data, thus indicating a good model description of the overall soil water dynamics in the unsaturated zone. The dynamics and level of the groundwater table were captured well by the model except for the initial rise in the autumn 2001, where percolation and drainage flow were initiated. The delayed rise in the groundwater table resulted in a delayed response in the drainage flow (Figure 23B).

Even though the model has not yet been calibrated, the drainage flow pattern was captured well, although the onset of drainage flow was delayed by a few days and the flow rise was less dynamic, as reflected by the height and width of the simulated versus measured flow events (Figure 23C).

The overall trends in soil water content could be modelled reasonably well, especially in the A horizon. The model tended to describe dryer soil during the summer periods than measured by the TDR probes (Figure 23D, E and F). Unexpectedly, the measured time series at 60 and 110 cm b.g.s. were not affected by the lower groundwater table during the summer 2000. Measured water saturation ranged from 90 to 110%, with the highest values during the driest period. The quality of the measured time series needs to be thoroughly analysed. The unexpected pattern may be attributable to the use of a general relationship between measured primary TDR data and the calculated soil water content. The use of a calibrated, soil-specific relationship would improve the finding. Another explanation may be the limited applicability of TDR in near-saturated soils.

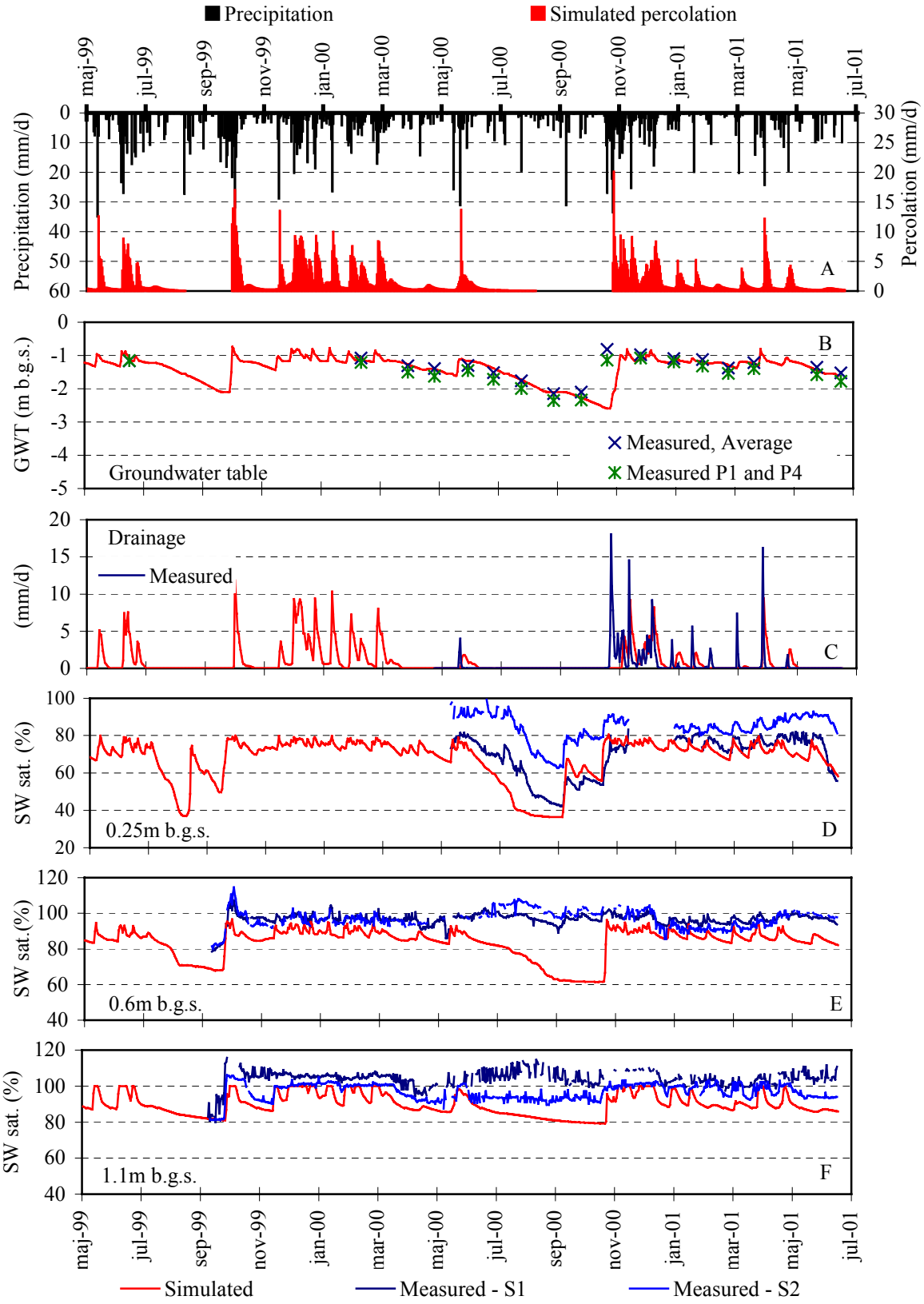

Figure 23. Soil water dynamics at Silstrup: Locally measured precipitation and simulated percolation (1 m b.g.s.) (A), simulated and measured groundwater level (B), simulated and measured drainage flow (C), and simulated and measured soil water saturation (SW sat.) at 3 different soil depths (D, E and F). Measured data in B refer to piezometers located in the buffer zone. Measured data in D, E and F refer to TDR probes installed at location S1 and S2 (see Figure 21).

The monitoring period (April 2000–June 2001) was dry at Silstrup, with precipitation input reaching only 86% of the yearly normal. In contrast, the previous year was wet, with precipitation exceeding the yearly normal by 11% (Table 9). Precipitation was particularly sparse from June to September 2000, whereas October and November 2000 and especially April 2001 were wet months (Appendix 4, Figure A4.3). The calculated groundwater recharge was 223 mm for both monitoring years (Table 9). Thus the elevated precipitation input in the first monitoring year (240 mm more than in the second year) was mainly discharged through the drainage system, simulated drainage being 412 mm as compared to 211 mm in the second monitoring year.

Table 9. 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)]
1.7.99–1.7.00 [1)]	976	1079	444	–	412	223 [4)]
1.7.00–1.7.01	976	839	399	217	211	223

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 24C). A week later on 7 June, elevated bromide concentrations were detected in the soil water in the suction cups located 1 m b.g.s. On the same day, bromide was also detected in the groundwater in suction cup S1 located 2 m b.g.s. and in the horizontal well of H1 located 3.5 m b.g.s. Moreover, elevated bromide concentrations were also detected in all of the uppermost screens of the vertical monitoring wells downstream of the test field except for M6 (Figure 25). The very rapid movement of bromide was presumably due to numerous biopores, desiccation cracks and fractures, as described by Lindhardt *et al.* (2001). The orientation and magnitude of the fractures may also explain why the lower screen of M12, which is located upstream of the test field, was also affected by bromide.

During the monitoring period a total of 1.6 kg/ha of bromide leached to the drains, equivalent to 7.7% of the amount applied. Based on the bromide concentration measured in April and May 2000, the background concentration of bromide at Silstrup was 0.13 ±0.09 mg/l.

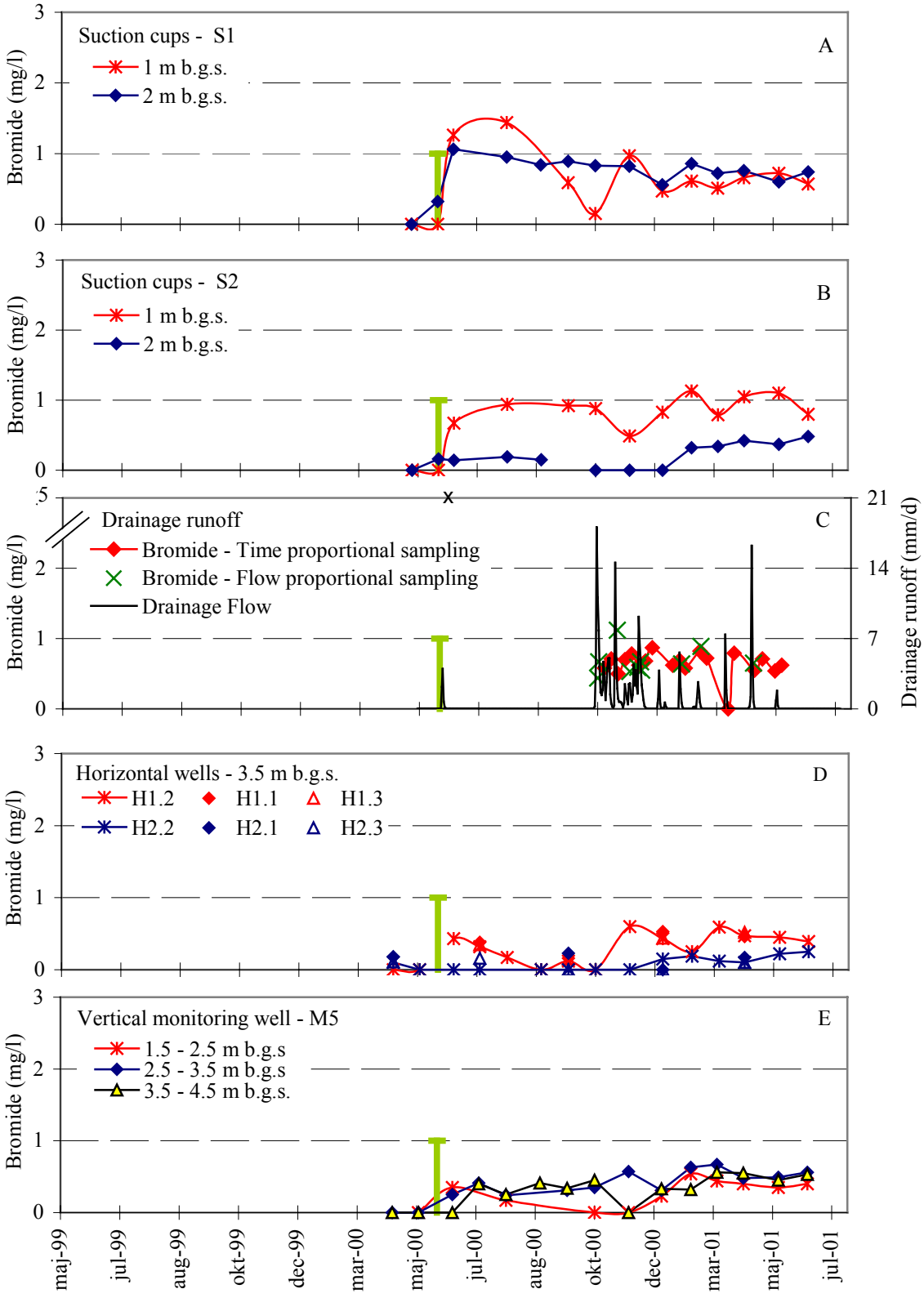

Figure 24. Bromide concentration at Silstrup. A and B refer to suction cups S1 and S2. The bromide concentration is also shown for drainage runoff (C), the horizontal monitoring wells (D) and vertical monitoring well M5 (E). The green vertical line indicates the time of bromide application.

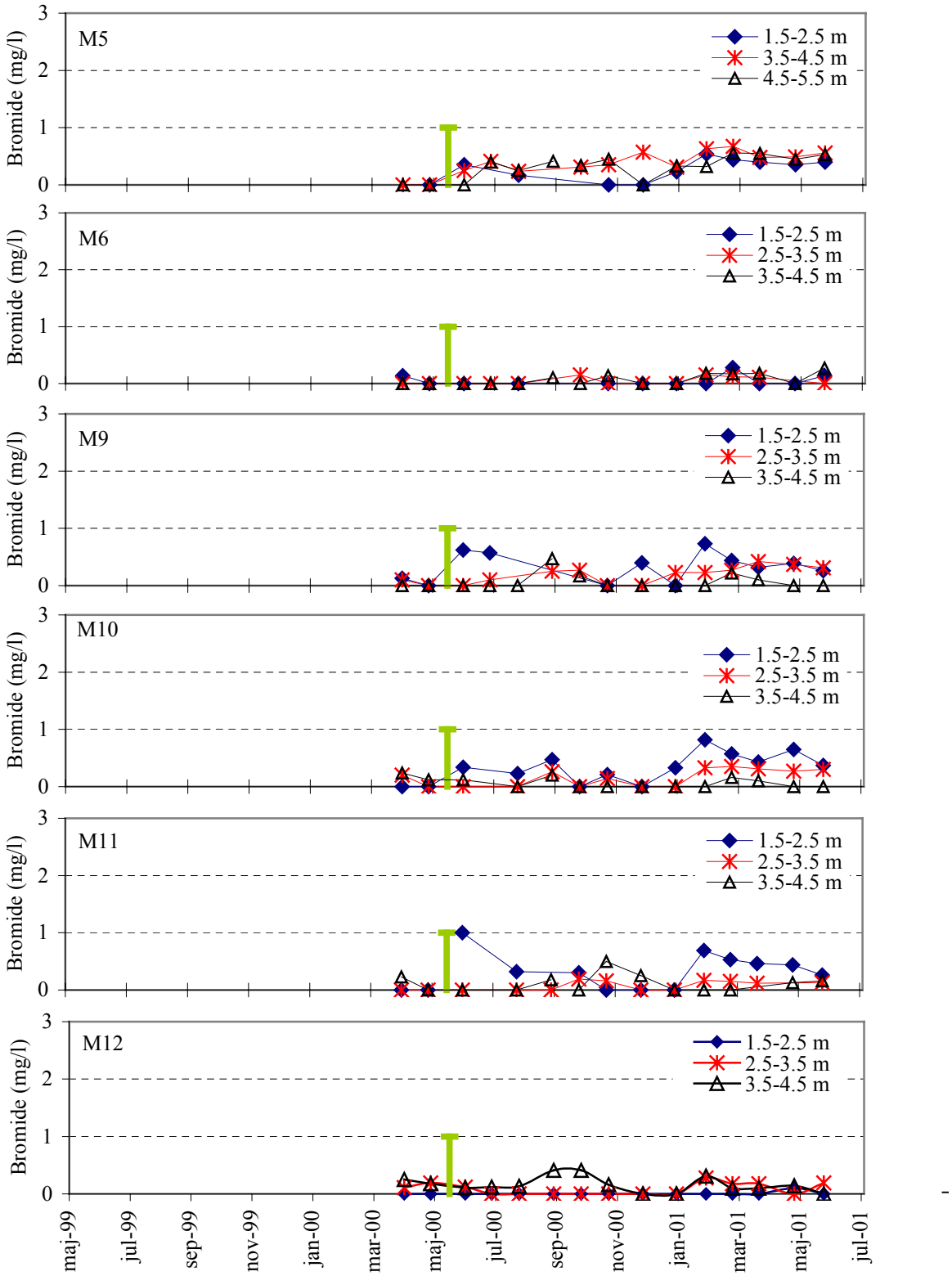

Figure 25. Bromide concentration in the groundwater at Silstrup. The data derive from the vertical monitoring wells (M5–M12). The screen depths are indicated in m b.g.s. The green vertical line indicates the date of bromide application.

4.2.3 Pesticide leaching

Monitoring began at Silstrup in April 2000 and presently encompasses 10 pesticides and 10 degradation products (Table 10). Only preliminary evaluation of their leaching risk is possible at present as the potential leaching period extends beyond the current monitoring period. The monitoring results nevertheless indicate that metamitron, metamitron-desamino, ethofumesate and pirimicarb leached from the root zone during the current monitoring period. The remaining substances listed in Table 10 were not detected in any of the water samples analysed.

Table 10. Pesticides analysed at Silstrup. Degradation product are indicated in italic.

Crop	Product	Pesticides analysed	Date of application	Accumulated precipitation[1)] (mm)
Fodder beet				
	Goltix WG	Metamitron - *metamitron-desamino*	May, June, July 00	937, 869, 862
	Betanal Optima	Ethofumesate Desmedipham - *EHPC* - *3-aminophenol* Phenmedipham - *MHPC* - *3-aminophenol*	May, June, July 00	937, 869, 862
	Fusilade X-tra	Fluazifop-P-butyl - *fluazifop (free acid)*	June 00	848
	Pirimor	Pirimicarb - *pirimicarb-desmethyl* - *pirimicarb-desmethyl-formamido*	July 00	839
Spring barley				
	Express	*triazinamin-methyl* (from tribenuron-methyl)	May 01	26
	Barnon Plus	Flamprop-M-isopropyl - *flamprop (free acid)*	June 01	14
	Tilt Top	Propiconazole Fenpropimorph - *fenpropimorphic acid*	June 01	14

1) Accumulated from date of application until 1 July 2001.

Shortly after Goltix WG and Betanal Optima had been applied to the field, a large storm event caused rapid leaching of both metamitron and ethofumesate (Figure 26). As with bromide (applied on 22 May concomitantly with the first pesticide application), these pesticides were transported rapidly through the unsaturated zone. On 29 May, only seven days after application, metamitron, metamitron-desamino and ethofumesate were detected in the drainage water in concentrations reaching 0.3 µg/l, 0.4 µg/l and 0.05 µg/l, respectively (Figure 28B, C and D).

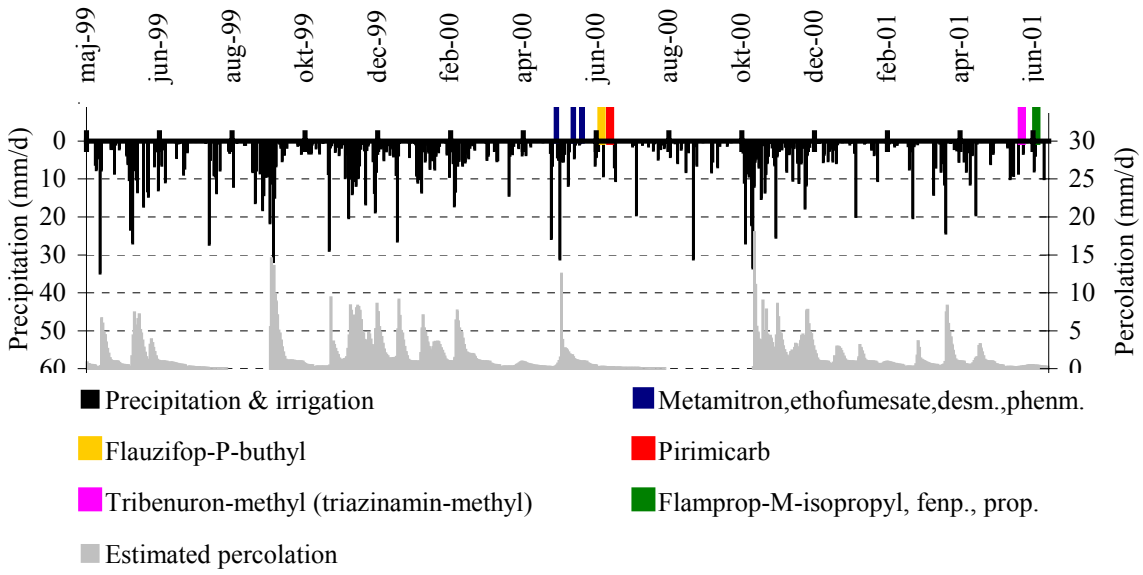

Figure 26. Pesticide application and precipitation (primary axis) and estimated percolation 1 m b.g.s. (secondary axis) at Silstrup. Desm.: desmedipham. Phenm.: phenmedipham. Fenp.: fenpropimorph. Prop.: propiconazole.

One week later, on 7 June, all the three compounds were also detected in water samples from the suction cups located 1 m b.g.s. (Figure 27A and C). In addition, metamitron and metamitron-desamino were detected in the horizontal well H1 and the downstream monitoring wells M5 and M6 (Appendix 10).

Throughout the 2000/2001 leaching period, metamitron and metamitron-desamino leached to the drainage system in average concentrations reaching 0.05 µg/l and 0.05 µg/l, respectively. In addition, both compounds were detected in several groundwater samples from monitoring wells M5, M6 and H1 (Appendix 10) as well as from the suction cups located 2 m b.g.s. In total, only four groundwater samples contained concentrations exceeding 0.1 µg/l. The maximum concentrations detected were 0.17 µg/l for metamitron and 0.13 µg/l for metamitron-desamino (Appendix 10).

When evaluating the leaching risk, it should be noted that metamitron is unstable. Results from the field-spiked samples indicated that metamitron may even have degraded to metamitron-desamino during storage and transport (Section 9). From the monitoring data it is thus not possible to know whether the observed metamitron-desamino was due to degradation in the soil or degradation in the sample during subsequent storage and transport. An example of metamitron being transformed into metamitron-desamino during the subsequent storage and transport could be the time-proportional sample taken on 12 December. Here, the content of metamitron-desamino was very high, whereas that of metamitron was almost nil (Figure 28B and C). This may explain why the time-proportional sample contains so much more metamitron-desamino than the flow-proportional sample, where the opposite would normally be the case.

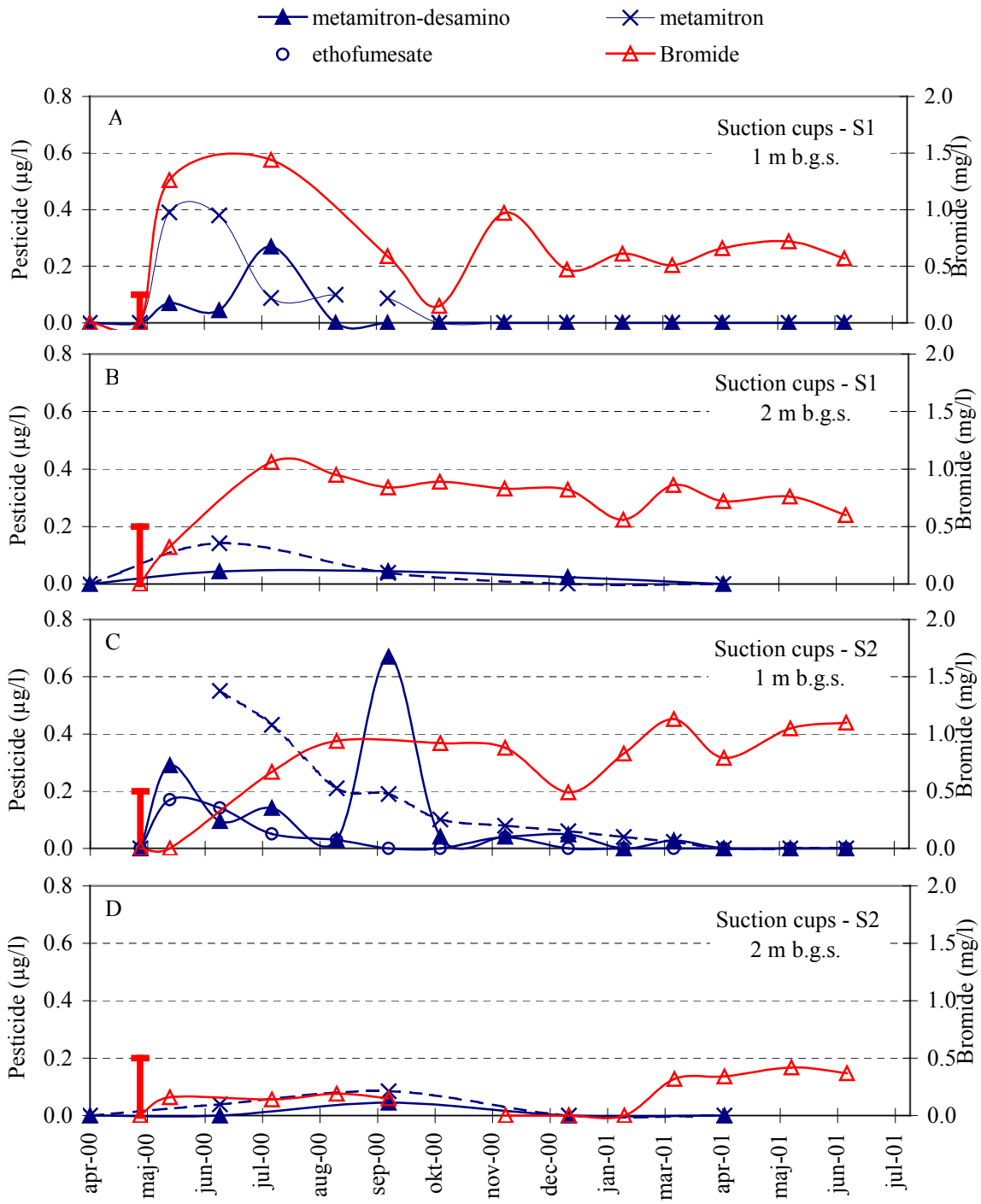

Figure 27. Bromide and pesticide concentrations at Silstrup. Measured data refer to suction cups installed 1 m b.g.s. and 2 m b.g.s. at S1 and S2 in Figure 21. The red vertical line indicates the time of bromide application.

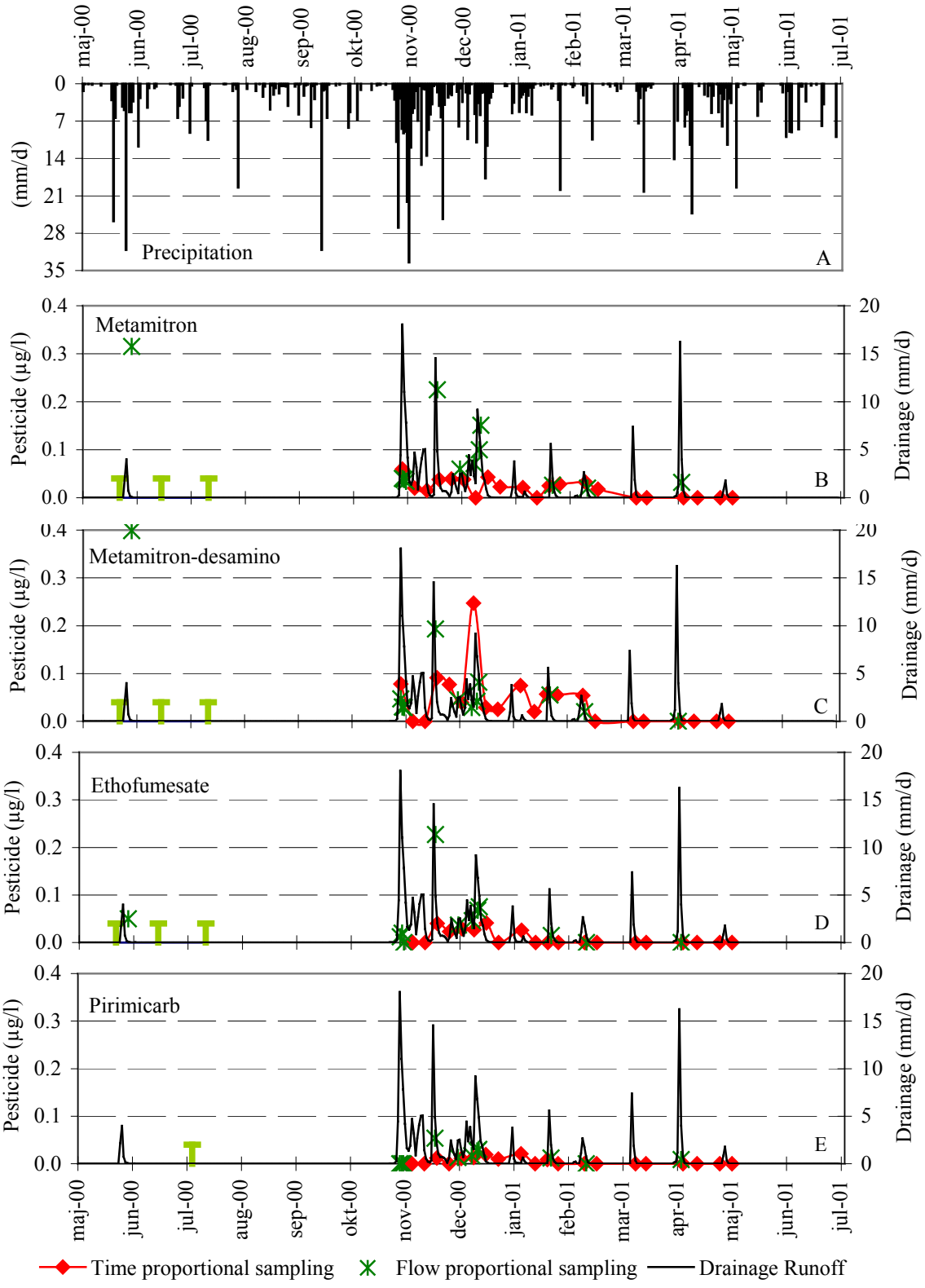

Figure 28. Precipitation (A) together with concentration of metamitron (B), metamitron-desamino (C) and ethofumesate (D) in the drainage runoff. The green vertical lines indicate the time of application.

Evidence of ethofumesate leaching was seen in suction cup S2 located 1 m b.g.s. as well as in the drainage water. Throughout the 2000/2001 leaching period, ethofumesate leached to the drainage system in average concentrations reaching 0.03 µg/l. The concentration only exceeded 0.1 µg/l in one sample. In groundwater ethofumesate was detected in concentrations ranging from 0.01 to 0.02 µg/l in four samples (Appendix 10, Table A10.3).

Although pirimicarb was detected in the drainage water samples, the concentration was always below 0.1 µg/l. The average concentration was 0.01 µg/l. Pirimicarb was not detected in the suction cups, but was detected in a concentration of 0.01 µg/l in three groundwater samples (Appendix 10, Table A10.3).

With regard to Figure 28, it should be noted that time-proportional sampling refers to continuous drainage runoff occurring throughout the whole drainage season, whereas the flow-proportional sampling refers to the drainage runoff induced by the sudden storm events occurring several times during the drainage season. The leaching of pesticides to the drains was completely governed by the individual storm/flow events. Of the total amount of pesticide leached, sudden storm events accounted for 92% of the metamitron, 89% of the metamitron-desamino and 97% of the ethofumesate.

4.3 Summary

The risk of pesticide leaching at Silstrup cannot be fully evaluated at present as the potential leaching period extends beyond the present monitoring period. The results hitherto obtained nevertheless suggest that:

- Metamitron, metamitron-desamino, ethofumesate and pirimicarb did leach from the root zone during the current monitoring period, but not in unacceptable levels. Although the concentration exceeded 0.1 µg/l in several samples, the average concentration did not. The observed leaching appeared to be associated with pronounced macropore transport resulting in very rapid movement of pesticide through the unsaturated zone.

- No evidence was found to indicate leaching of fluazifop-P-butyl, triazinamin-methyl, flamprop-M-isopropyl, fenpropimorph and propiconazole, or of their degradation products fluazifop (free acid), flamprop (free acid) or fenpropimorphic acid.

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 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 30). A brief description of the sampling procedure and analysis methods is provided in Appendixes 1–2. The monitoring design and the test site are described in detail in Lindhardt *et al.* (2001). 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

The field was ploughed on 11 April 2000 whereafter spring barley (cv. Barke) was sown. The barley emerged on 25 April. On 15 May the herbicide metsulfuron-methyl and potassium bromide tracer were applied. The herbicide flamprop-M-isopropyl was applied on 31 May. Combined fungicide and insecticide spraying with propiconazole, fenpropimorph and dimethoat was carried out on 15 June and 5 July. The barley was harvested on 28 August yielding 52.6 hkg/ha of grain (85% dry matter). The low yield is attributable to at least two factors. Firstly, the soil in parts of the field had been compacted in autumn and winter 1999 during installation of the measuring equipment. Secondly, due to the instrumentation work the field had to be ploughed in the spring rather than in the autumn as would normally be the case on this soil. As a consequence a proper seedbed could not be established, and crop establishment was therefore poor. On 13 October 2000, glyphosate was sprayed to combat couch grass. The field was ploughed on 23 October and sown with field pea (cv. Julia) on 2 May. The peas emerged on 13 May. Weeds were sprayed only once using bentazone and pendimethalin on 22 May. The insecticide pirimicarb was sprayed on 26 June. The crop was harvested on 22 August yielding 43.2 hkg/ha of peas (86% dry matter). As the stems were incorporated, the stem yield was not determined. Management practice at the site is detailed in Appendix 3 (Table A3.4).

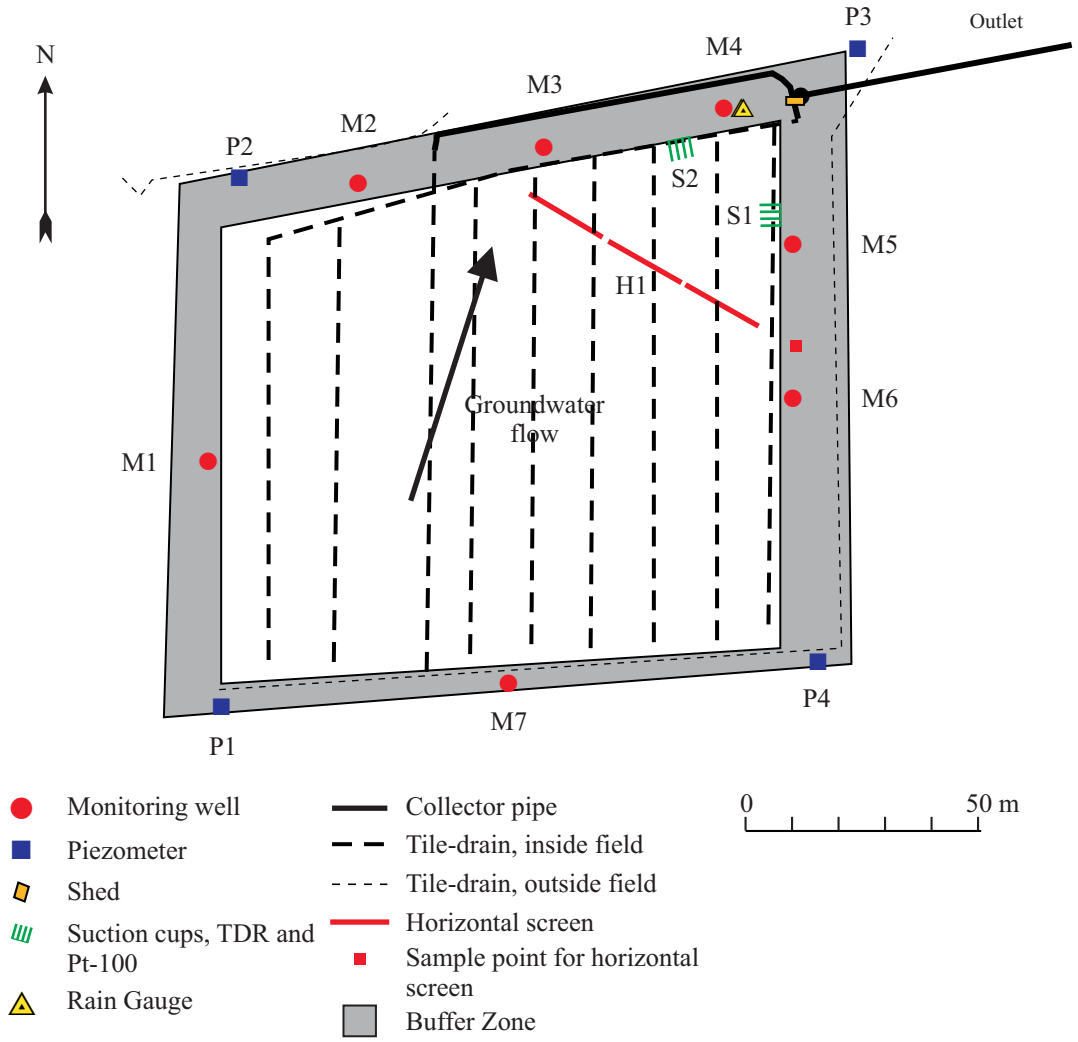

Figure 29. Overview of the Estrup site. The innermost white area indicates the cultivated land, while the grey area indicates the surrounding buffer zone. The positions of the various installations are indicated, as is the direction of groundwater flow (by an arrow).

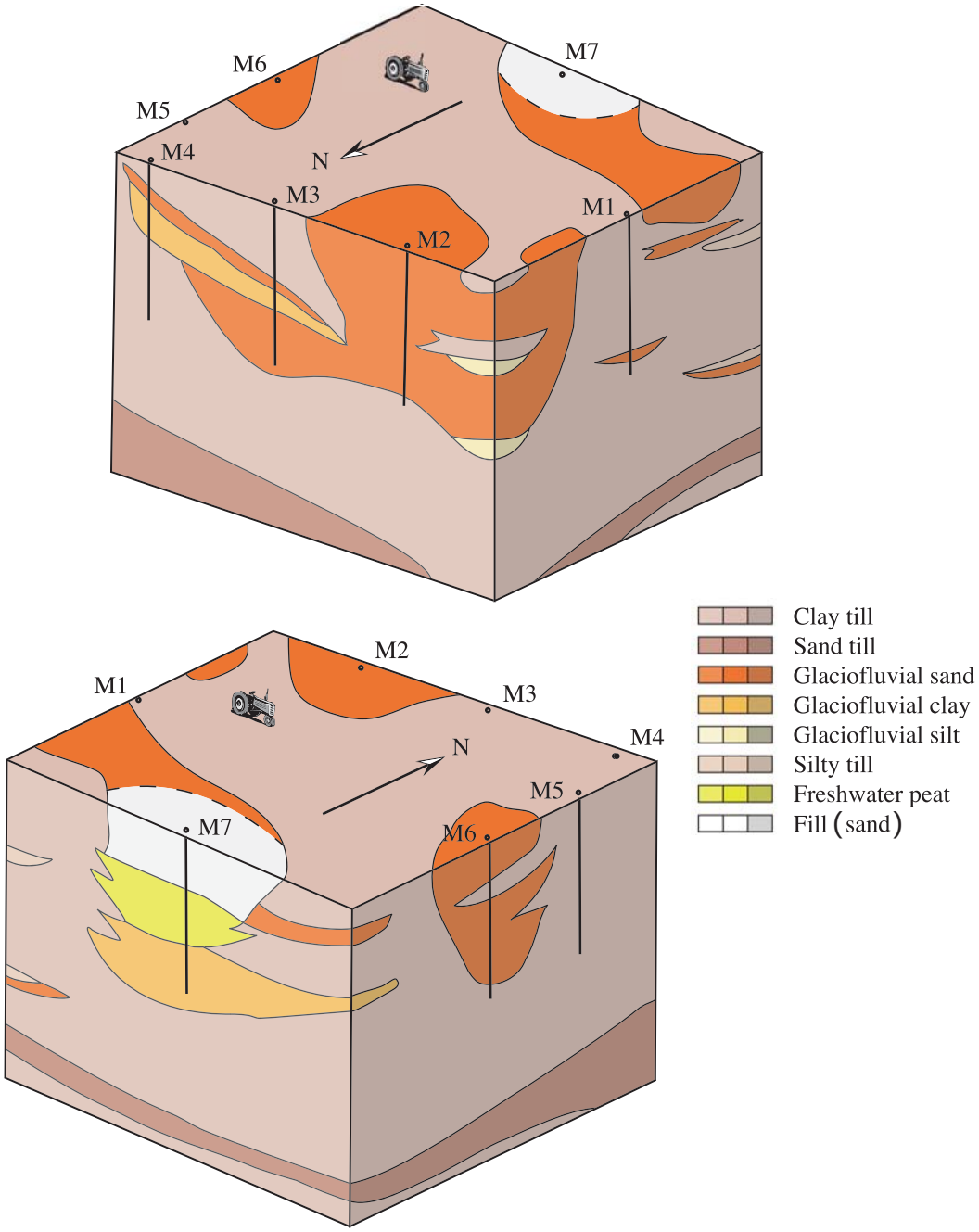

Figure 30. Geological description of the Estrup site (Lindhardt *et al.,* 2001).

5.1.3 Model set-up and calibration

The MACRO model was 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 was used to simulate the water flow in the unsaturated zone during the monitoring period from July 2000–June 2001 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 three different depths (25, 60 and 110 cm b.g.s.) from the two profiles S1 and S2 (see Figure 29). 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. Data acquisition and model set-up are described in Appendix 5.

5.2 Results and discussion

5.2.1 Soil water dynamics and water balances

The model simulations were largely consistent with the observed data, thus indicating a reasonably model description of the overall soil water dynamics in the unsaturated zone (Figure 31).

The model was able to match the trends in the measured groundwater table, but had difficulty in simulating the quick rise of the groundwater table at the end of October 2000. A 2 m rise was followed by a 1.5 m fall within a few days during a period of high precipitation flow (Figure 31A and B). This unexpected fall was probably due to numerical problems caused by the quick rise of the groundwater table. A better and constant discretization of the soil profile could not solve the problem. The simulated groundwater table often fluctuated slightly during periods where drain flow occurred. The peaks corresponded to larger storm events and resulted in an almost fully saturated soil profile. The groundwater table was located as high as 0.5 m b.g.s.

The simulated accumulated drainage flow amounted to only 43% of the measured drainage flow. However, the drainage flow pattern and the onset of the drainage flow were well captured by the model, but with a less dynamic flow rise. The drainage flow was generally underestimated, especially at the onset of flow, because of the above-mentioned simulated fall in the groundwater table. The measured drainage flow amounted to as much as 80% of the percolation. The high drainage runoff was due to the significantly lower permeability of the C horizon than of the overlaying A and B horizons. The percolation rate presumably exceeded the infiltration capacity of the C horizon during long periods leaving the groundwater table to rise above the drain depth into the B horizon. This process was not fully captured by the model, and further calibration of the hydraulic properties of the C horizon and of drainage efficiency are thus needed if model performance is to be improved.

Measured time series of soil water content were available from 1 July 2000. Overall trends in simulated soil water content was successfully modelled in the A horizon. In the measured time series for 60 and 110 cm b.g.s. (Figure 23E and F) the water saturation is unrealistically high ranging from 100 to 180%. Thus these two time series are of no value for the present purpose. Thorough analysis of all these soil water content time series is needed, especially to determine how the TDR calibration reacts when extrapolated into the wet range of soil water content.

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. was saturated for long periods (Figure 31). Percolation occurred continuously in both years from September to May/June. The first year was characterized by a large initial peak at the onset (30 mm/d), followed by a more stable period with minor peaks, all below 7 mm/d. A similar pattern occurred the following year, except that the percolation started with a one-month low flow period (~0.2 mm/d) before the flow peaked at 20 mm/d.

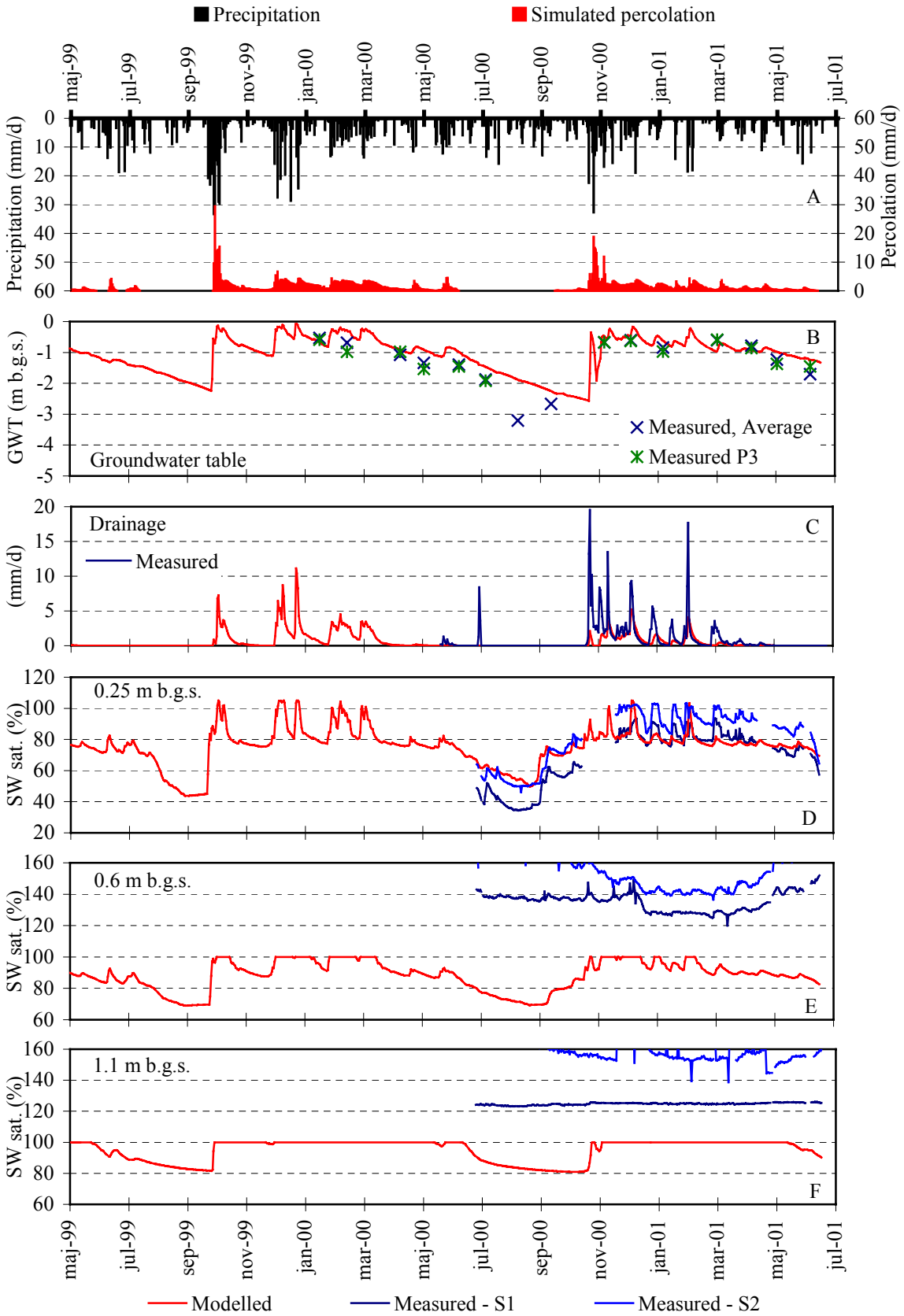

Figure 31. Soil water dynamics at Estrup: Locally measured precipitation and simulated percolation at 0.6 m b.g.s. (A), simulated and measured groundwater level (B), simulated and measured drainage flow (C), and simulated and measured soil saturation (SW sat.) at 3 different soil depths (D, E and F). Measured data in B refer to piezometers located in the buffer zone. Measured data in D, E and F refer to TDR probes installed at locations S1 and S2 (see Figure 29).

Table 11. 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 evapotrans-piration	Measured drainage	Simulated drainage	Groundwater recharge [3]
1.7.99–30.6.00[1]	968	1079	432	–	331	315 [4]
1.7.00–30.6.01	968	820	376	356	153	88

1) The monitoring was 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

The monitoring period (April 2000–June 2001) was dry compared to a normal year, with precipitation input reaching only 85% of the yearly normal. In contrast, the previous year was wet, with precipitation exceeding the yearly normal by 11% (Table 11). Precipitation was particularly sparse from June to September 2000 and in May 2001, whereas October and November 2000 were wet months (Appendix 4, Figure A4.4).

The groundwater recharge for the year July 1999–June 2000 was 315 mm based on the simulated drainage (Table 11). This is probably an overestimate as the simulated drainage was probably underestimated. The same also applies to the subsequent monitoring year, when groundwater recharge was only 88 mm based on measured drainage flow. Due to poor simulation of drainage flow, the water balance for Estrup was less reliable than that for the other test sites, where the model generally performed better.

5.2.2 Bromide leaching

The bromide concentration profiles in the unsaturated zone clearly illustrated the marked heterogeneity characterizing the Estrup site. Rapid breakthrough of bromide occurred at S1, where elevated bromide concentrations were detected less than one month after application (Figure 32.A). In contrast, the breakthrough at S2 occurred much later, thus indicating that water transport in this part of the field is much slower (Figure 32.B).

When evaluating the bromide concentration profiles from the suction cups located 1 m b.g.s. it should be kept in mind that they were beneath the groundwater table from November 2000 to July 2001(Figure 31B). The enhanced bromide concentration thus indicates that the tracer had leached from the unsaturated zone during the current monitoring period. The majority of the leached bromide probably left the system through drainage runoff as the modelled water balance suggested that 80% of the percolating water left through the drainage system (Table 11). Total recovery of bromide tracer in drainage water during the monitoring period amounted to 18%, thus indicating that only a small part of the applied bromide was leached from the unsaturated zone during the monitoring period.

The results also indicate subsequent transport of bromide down to a depth of both 2 and 3.5 m b.g.s. Slightly elevated bromide concentrations were detected 2 m b.g.s. in both S1 and S2 and 3.5 m b.g.s. in the horizontal wells (Figure 32.C). Bromide has not yet been detected in the downstream monitoring wells, thus indicating that the lateral groundwater transport is of less importance at the Estrup site (Figure 32).

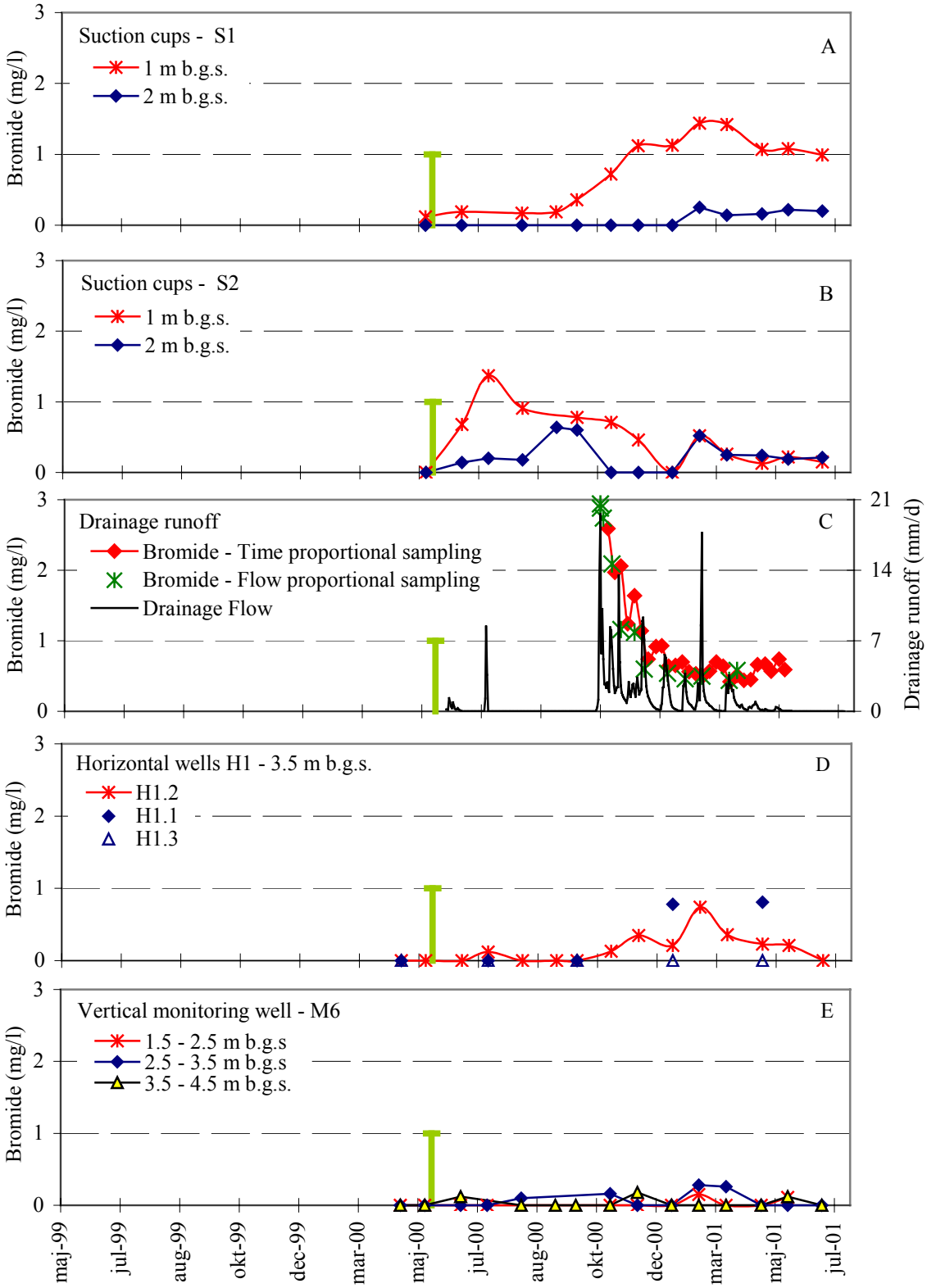

Figure 32. Bromide concentration at Estrup. A and B refer to suction cups S1 and S2. The bromide concentration is also shown for drainage runoff (C), the horizontal monitoring well H1 (D) and horizontal monitoring well M6 (E). The green vertical line indicates the date of bromide application.

5.2.3 Pesticide leaching

Monitoring at Estrup began in April 2000 and encompasses 10 pesticides and 10 degradation products (Table 10). Only preliminary evaluation of their leaching risk is possible at present as the potential leaching period extends beyond the current monitoring period. It should be noted, though, that neither metsulfuron-methyl, fenpropimorph, dimethoat, bentazone and pendimethalin nor their degradation products listed in Table 12 have yet been detected in any of the water samples analysed.

Table 12. Pesticides analysed at Estrup. Degradation products are indicated in italics.

Crop	Product	Pesticides analysed	Date of application	Accumulated precipitation[1)] (mm)
Spring barley				
	Ally	Metsulfuron-methyl - *triazinamin*	May 00	945
	Barnon Plus 3	Flamprop-M-isopropyl - *flamprop (free acid)*	May 00	865
	Tilt top	Propiconazole Fenpropimorph - *fenpropimorphic acid*	June, July 00	851, 819
	Perfection 500 S	Dimethoat	June, July 00	851, 819
	Roundup Bio	Glyphosate - *AMPA*	Oct 00	613
Pea				
	Basagran 480	Bentazone - *2-amino-N-isopropyl-benzamid*	May 01	68
	Stomp	Phendimenthalin	May 01	68
	Pirimor	Pirimicarb - *pirimicarb-desmethyl* - *pirimicarb-desmethyl-formamido*	June 01	6

[1)] *Accumulated from date of application until 1 July 2001*

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 2000/2001 leaching period was 0.54 µg/l, while that of AMPA was 0.17 µg/l. The leaching appeared to be governed by a combination of pronounced macropore flow occurring shortly after application and a limited sorption and degradation capacity. Both compounds leached from the root zone continuously throughout the whole six-month runoff period (Figure 34).

Glyphosate (1.44 kg/ha) was applied on stubble in mid October 2000 in accordance with current regulations. No precipitation occurred in the subsequent 10-day period prior to ploughing on 23 October. Thereafter the drainage runoff responded rapidly to the first storm events. The heavy storm events in October/November 2000 induced marked, rapid leaching of glyphosate and AMPA in concentrations reaching 2.1 µg/l and 0.73 µg/l, respectively.

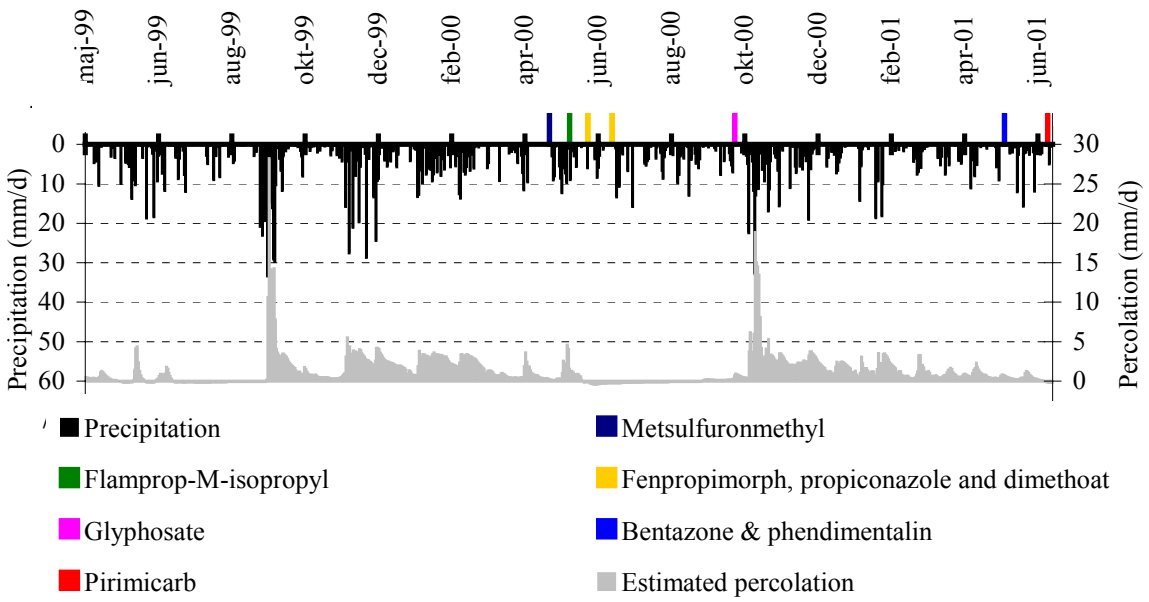

Figure 33. Pesticide application and precipitation (primary axis) together with estimated percolation 0.6 m b.g.s. (secondary axis) at Estrup.

The concentrations reached during these storm events was considerably higher than the concentrations in the continuous drainage runoff. The 11 storm events that activated the flow-proportional sampler thus accounted for 97% of the leached glyphosate (Figure 34B). This indicates fast water and pesticide transport, presumably through macropores.

The bromide leaching pattern was somewhat different. The concentrations reached during storm events were the same as those during continuous drainage runoff. The 11 storm events accounted for only 58% of the leached bromide. Compared with glyphosate, macropore transport thus had a minor impact on bromide leaching, much more of which took place through the soil matrix.

A likely explanation for these differences is that the residence time of bromide in the root zone was much longer prior to the autumn storm event. The longer residence time and the higher diffusion coefficient of bromide (Mortensen, 2001) thus allowed a larger part of the bromide to diffuse into the soil matrix, where it would be unaffected by the bypass flow in the macropores. If a significant proportion of the precipitation flows into the macropores at the soil surface, it would have little contact with the soil matrix. With the majority of the bromide present in the soil matrix, it would thus be “protected” from the bypass flow, as also suggested by Larsson *et al.* (1999). Moreover, bromide will not be retained by sorption. Although located in the soil matrix "protected" from the bypass flow, bromide is still prone to leaching with water infiltrating through the soil matrix.

With regard to Figure 34 it should be noted that time-proportional sampling refers to continuous drainage runoff occurring throughout the whole drainage season, whereas the flow-proportional sampling refers to the drainage runoff induced by the sudden storm events oc

curring several times within the drainage season. The sampling procedures and calculation methods are described in Appendix 2, and the primary data are given in Appendix 11.

When evaluating the observed leaching it should be noted that the climatic conditions at Estrup during the monitoring period were not abnormal. October and November were characterized by high precipitation input exceeding the monthly normal by 20% (Appendix 4) and several heavy storm events reaching 30 mm/day. This precipitation pattern – in terms of daily and monthly precipitation – is not unusual for the Estrup region, however. A similar pattern has occurred several times in the preceding 10 years (Appendix 12).

Evidence of glyphosate and AMPA leaching was only seen in drainage water, neither of these compounds being detected in any of the suction cup and monitoring well samples.

The majority of the leached glyphosate probably left the system through drainage runoff as the water balance suggested that 80% of the percolation left the system through drainage runoff (Section 5.2.1). In the hydrological year of 2000/2001 the groundwater recharge was 88 mm, corresponding to 20% of the percolation. Moreover, elevated bromide concentrations in the horizontal screens also indicated the occurrence of groundwater recharge at the Estrup site. Water and solute transport at Estrup were much slower beneath than above the drainage system due to decreased hydraulic conductivity (Lindhardt *et al.* 2001). The fact that neither AMPA nor glyphosate have yet been detected in the horizontal screens might be due to sorption or degradation in the deeper soil layers or because the horizontal flow component was minor at Estrup.

The fact that neither AMPA nor glyphosate have yet been detected in the suction cups might be due to the differences in the sampling method. The suction cups primarily extract water from the soil matrix. Moreover, the water sampled represent a relatively small part of the test site. In contrast, the drainage system provides integrated samples, capturing water infiltrating through both the soil matrix and the macropores. The high proportion of leaching mediated by macropore flow is therefore more likely to be detected in water samples from the drainage system.

Minor leaching of flamprop-M-isopropyl, flamprop (free acid) and propiconazole was also observed. All three substances were detected in several drainwater samples, although in concentrations below 0.1 µg/l (Figure 35).

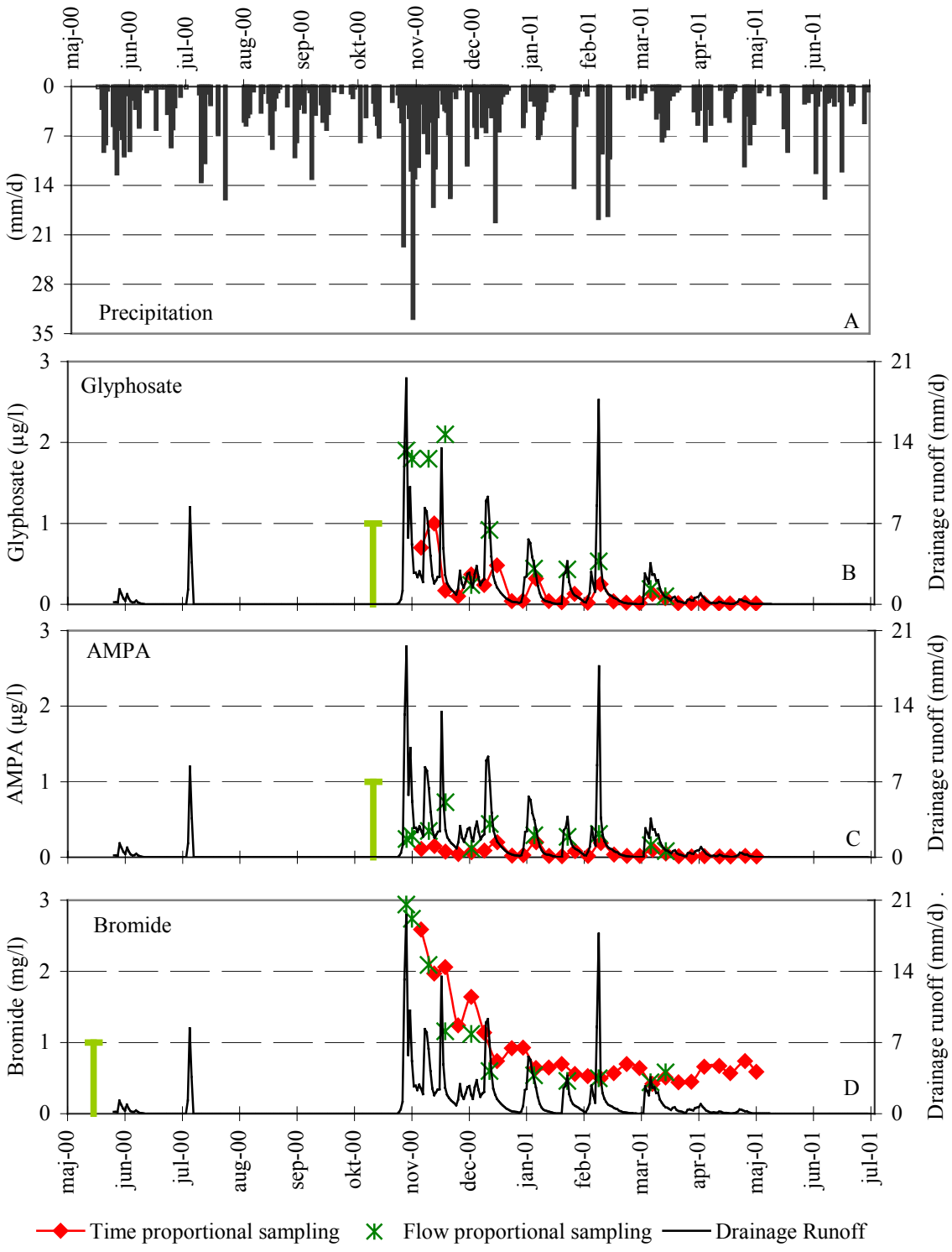

Figure 34. Precipitation (A) together with concentration of glyphosate (B), AMPA (C) and bromide (D) in the drainage runoff. The green vertical lines indicate the time of application.

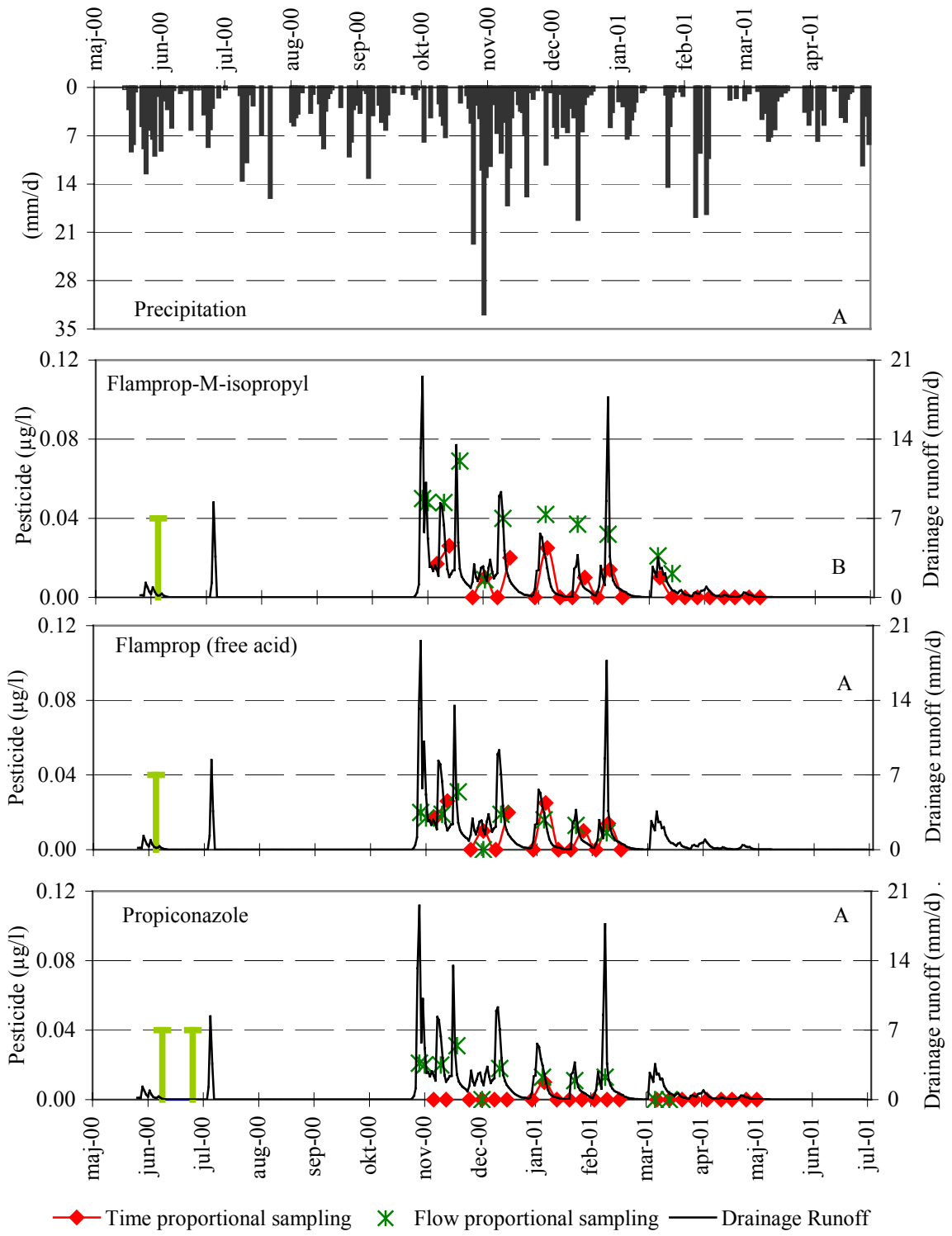

Figure 35. Precipitation (A) together with concentration of flamprop-M-isopropyl (B), flamprop (free acid) (C) and propiconazole (D) in the drainage runoff. The green vertical lines indicate the time of application.

5.3 Summary

The risk of pesticide leaching at Estrup cannot be fully evaluated at present as the potential leaching period extends beyond the current monitoring period. The results hitherto obtained nevertheless suggest that:

- Neither metsulfuron-methyl, fenpropimorph, dimethoat, bentazone, and pendimethalin nor their degradation products triazinamin, fenpropimorphic acid or 2-amino-N-isopropyl-benzamid have been detected in any of the water samples analysed.

- Glyphosate and its metabolite AMPA leached from the root zone in average concentrations considerably exceeding 0.1 µg/l. Thus the average concentration of glyphosate in the drainage water during the 2000/2001 leaching period was 0.54 µg/l, while that of AMPA was 0.17 µg/l. Flamprop-M-isopropyl, flamprop (free acid) and propiconazole were also detected in several drain water samples, but only in concentrations below 0.1 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°. Based on three profiles excavated in the buffer zone bordering the field the soil was classified as Haplic Vermudoll, Oxyquic Hapludoll and Oxyaquic Argiudoll (Soil Survey Staff, 1999). The topsoil is characterized as sandy loam with 15% clay and 1.4% organic carbon (Table 1). Within the upper 1.5 m, numerous desiccation cracks coated with clay skins are present. The aquifer material contains glacial deposits dominated by sandy till to a depth of approx. 1.5 m, whereafter the till is clayey. The geological description suggests that small channels or basins consisting of meltwater clay and sand occur in the clay till body (Figure 37). The calcareous matrix and reduced matrix begin at 1.5 m b.g.s. and 4.2 m b.g.s., respectively (Table 1). The overall direction of groundwater flow is towards the west in the upper part of the aquifer (Figure 36). During the monitoring period the groundwater table ranged from 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 at a depth of 4.0–4.3 m. This fractured zone probably acts as a drainage system and may be present under large parts of the test site. A brief description of the sampling procedure and analysis methods is provided in Appendixes 1–2. The monitoring design and test site are described in detail in Lindhardt *et al.* (2001).

6.1.2 Agricultural management

The field was sprayed with glyphosate on 11 August 1999 and sown with winter wheat (cv. Stakado) on 20 August. Potassium bromide tracer was applied on 5 October. Weeds were sprayed on 14 October using ioxynil and bromoxynil and again on 4 April using fluroxypyr. Fungicide spaying was carried out on 5 May and 31 May using propiconazole and fenpropimorph. The insecticide pirimicarb was applied on 19 June. The crop was harvested on 28 August yielding 92.7 hkg/ha of grain and 76.2 hkg/ha of straw (85% and 100% dry mater, respectively). On 4 October 2000 the field was sprayed with glyphosate and ploughed 12 days later on 16 October. Sugar beet was sown on 2 May 2001. The herbicides metamitron, phenmedipham, desmedipham and ethofumesate were sprayed on 21 May, 30 May and 15 June. Fluazifop-P-butyl was sprayed on 21 June to combat wild oats and pirimicarb on 17 July to combat pests. The crop was harvested on October 24 yielding 147.9 hkg/ha of roots and 38.0 hkg/ha of tops (both 100% dry matter). Management practice at the site is detailed in Appendix 3 (Table A3.5).

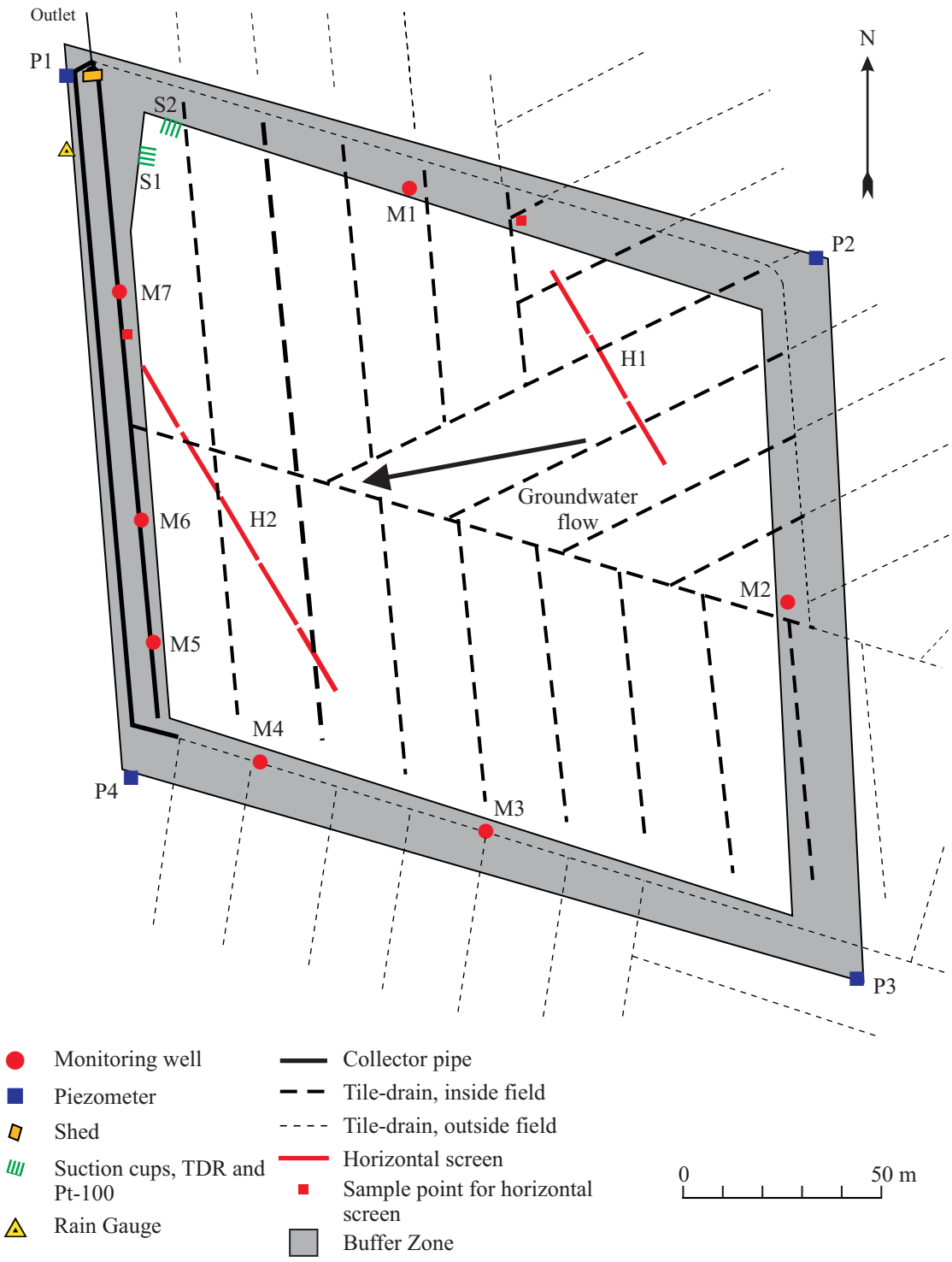

Figure 36. Overview of the Faardrup site. The innermost white area indicates the cultivated land, while the grey area indicates the surrounding buffer zone. The positions of the various installations are indicated, as is the direction of groundwater flow (by an arrow).

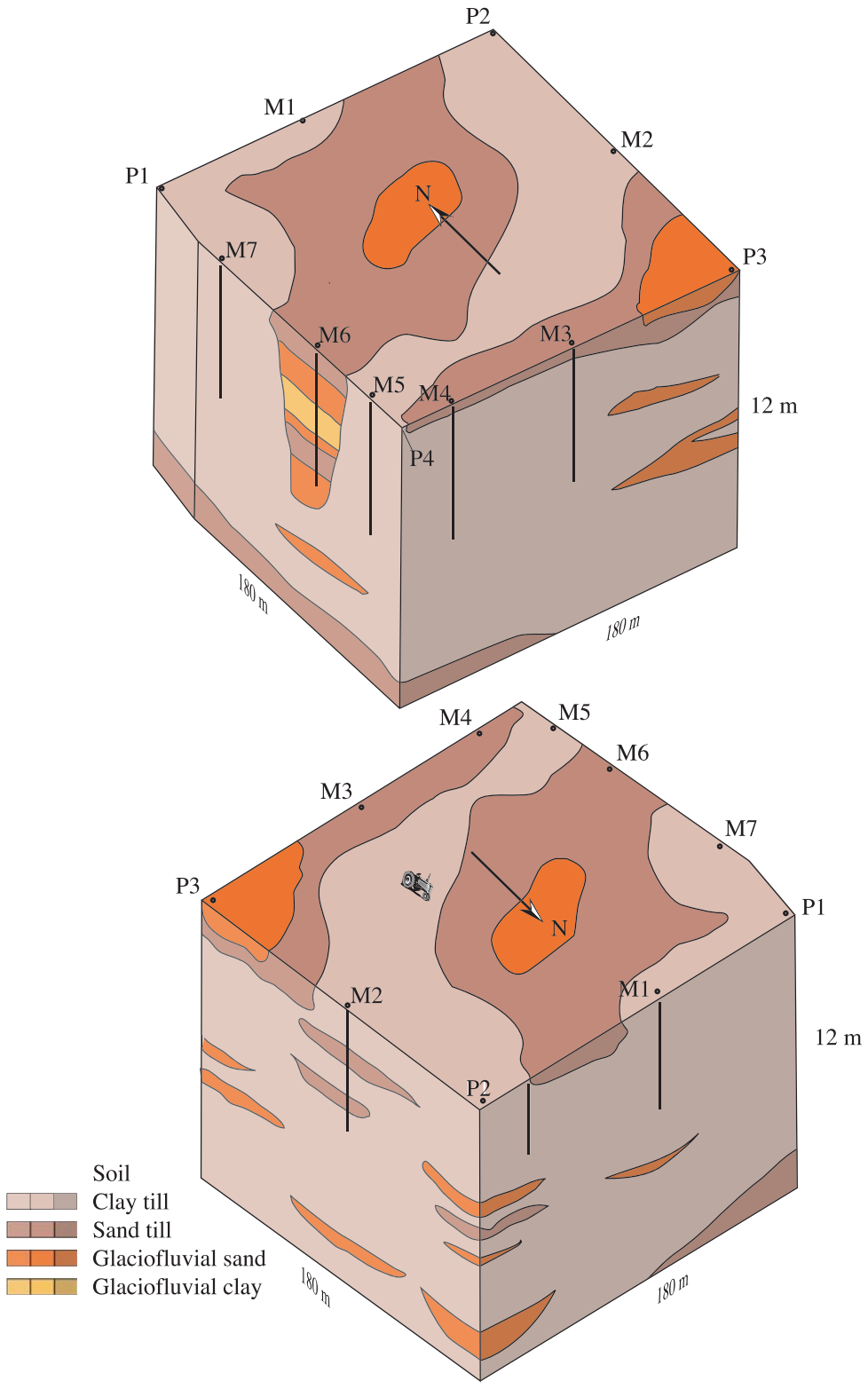

Figure 37. Geological description of the Faardrup site (Lindhardt *et al.,* 2001).

6.1.3 Model set-up and calibration

The MACRO model was 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 was used to simulate the water flow in the unsaturated zone during the full monitoring period September 1999–June 2001 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 (see Figure 36). 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. Data acquisition and model set-up are described in Appendix 5.

6.2 Result and discussion

6.2.1 Soil water dynamics and water balances

The model simulations were generally consistent with the observed data, thus indicating a good model description of the overall soil water dynamics in the unsaturated zone. The dynamics and level of the measured groundwater table were captured well by the model. Overall trends in soil water content could also be modelled successfully (Figure 38D, E and F). The soil water dynamics in the A and B horizons was captured particularly well by the model, whereas the simulated level in the C horizon was somewhat lower than the measured level.

The simulated accumulated drainage flow corresponded well to the measured drainage flow for both monitoring years (Table 13). The dynamics of the measured drain flow was also well described by the model, although the duration of the drainage period was not fully captured by the model. In the second monitoring year (2000–2001), measured drainage flow during the winter period was only 47 mm. This was generated during a long period with very low flow (December 2000–June 2001) with the drainage water probably deriving from a limited area of the field. In contrast, the simulated drain flow was generated through a 6-week period January–February 2001 during which the groundwater level was above the drain depth.

The first monitoring period (July 1999–June 2000) was rather wet at Faardrup with precipitation input exceeding the yearly normal by 28% (Table 13). Precipitation was particularly high in August and December 1999, whereas November 1999 and May 2000 were dry months (Appendix 4, Figure A4.5). The model simulation showed that percolation 1 m b.g.s. occurred continuously from September to mid May with an initial low flow period in September. The groundwater recharge was low (84 mm). As much as 70% of the infiltrating water was discharged through the drainage system. This was due to a long period (October to May) with a high groundwater table.

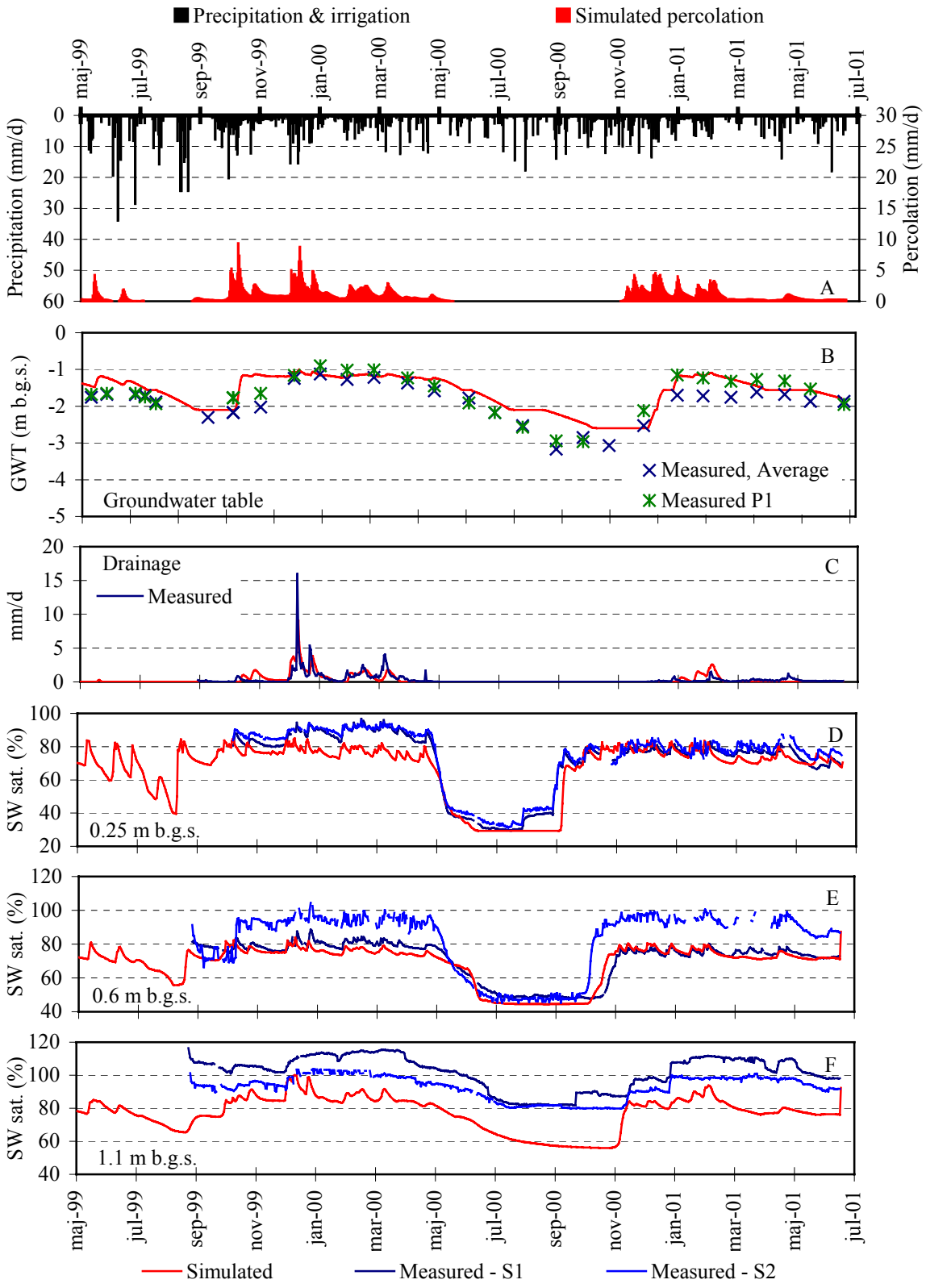

Figure 38. Soil water dynamics at Faardrup: Locally measured precipitation and simulated percolation 1 m b.g.s. (A), simulated and measured groundwater level (B), simulated and measured drainage flow (C), and simulated and measured soil water content at 3 different soil depths (D, E and F). Measured data in B refer to piezometers located in the buffer zone. Measured data in D, E and F refer to TDR probes installed at S1 and S2 (see Figure 36).

Thus, the combination of a high actual evapotranspiration (due to a winter crop type having higher transpiration during winter and spring) and a high drainage flow (due to a high groundwater level) resulted in low groundwater recharge despite the high precipitation input.

The second monitoring period (July 2000–June 2001) was close to normal at Faardrup with precipitation input being 3% above the yearly normal. The autumn was fairly wet and the spring more dry than normal. Percolation was initiated in mid November and continued until June 2001, with low flow from March to June 2001. The simulated groundwater recharge differed significantly between the two years (84 mm in 1999–2000 versus 286 mm in 2000–2001), reflecting the low evapotranspiration and high drainage flow during the first period.

Table 13. 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	Actual evapotranspiration	Measured drainage	Simulated drainage	Groundwater recharge [2)]
1.7.99–30.6.00	626	802	536	182	187	84
1.7.00–30.6.01	626	647	314	47	45	286

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

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

6.2.2 Bromide leaching

The bromide tracer was not detected 1 m b.g.s. until late December, about three months after application (Figure 39A and B). When evaluating the bromide concentration profiles of suction cups located 1 m b.g.s. it should be kept in mind that they were beneath the groundwater table during the winter season from December 2000 to April 2001. The enhanced bromide concentration thus indicates that the tracer had leached from the unsaturated zone. Similar evidence of bromide leaching was found in the analysis of the drainage water samples derived from 1 m b.g.s. Figure 39C). The bromide breakthrough was similar to that detected in the suction cups located 1 m b.g.s. Still, the concentration during the leaching period 1999/2000 was much lower. Total recovery of bromide in drainage water during the monitoring period amounted to 1.9 kg/ha, indicating that only 9% of the bromide tracer had leached into the drains. Unlike the two sandy soils – where the majority of the applied bromide leached from the unsaturated zone during one winter season – a large part of the applied bromide was retained in the uppermost meter of the Faardrup soil. At the end of the monitoring period, elevated bromide concentrations could therefore be found in both groups of suction cups located 1 m b.g.s. This indicated that bromide continued to leach from the unsaturated zone as long as two years after application.

The results also showed a subsequent transport of bromide to a depth of 2 and 3.5 m b.g.s. Slightly elevated bromide concentrations of up to 1 mg/l were thus detected 2 m b.g.s. in the suction cups as well as in the horizontal wells 3.5 m b.g.s. (Figure 39A,B and D). Bromide was not detected in the downstream monitoring wells (Figure 39E).

Finally, it should be noted that during summer 2000 the very low soil water content precluded extraction of soil water by suction cups (Figure 38).

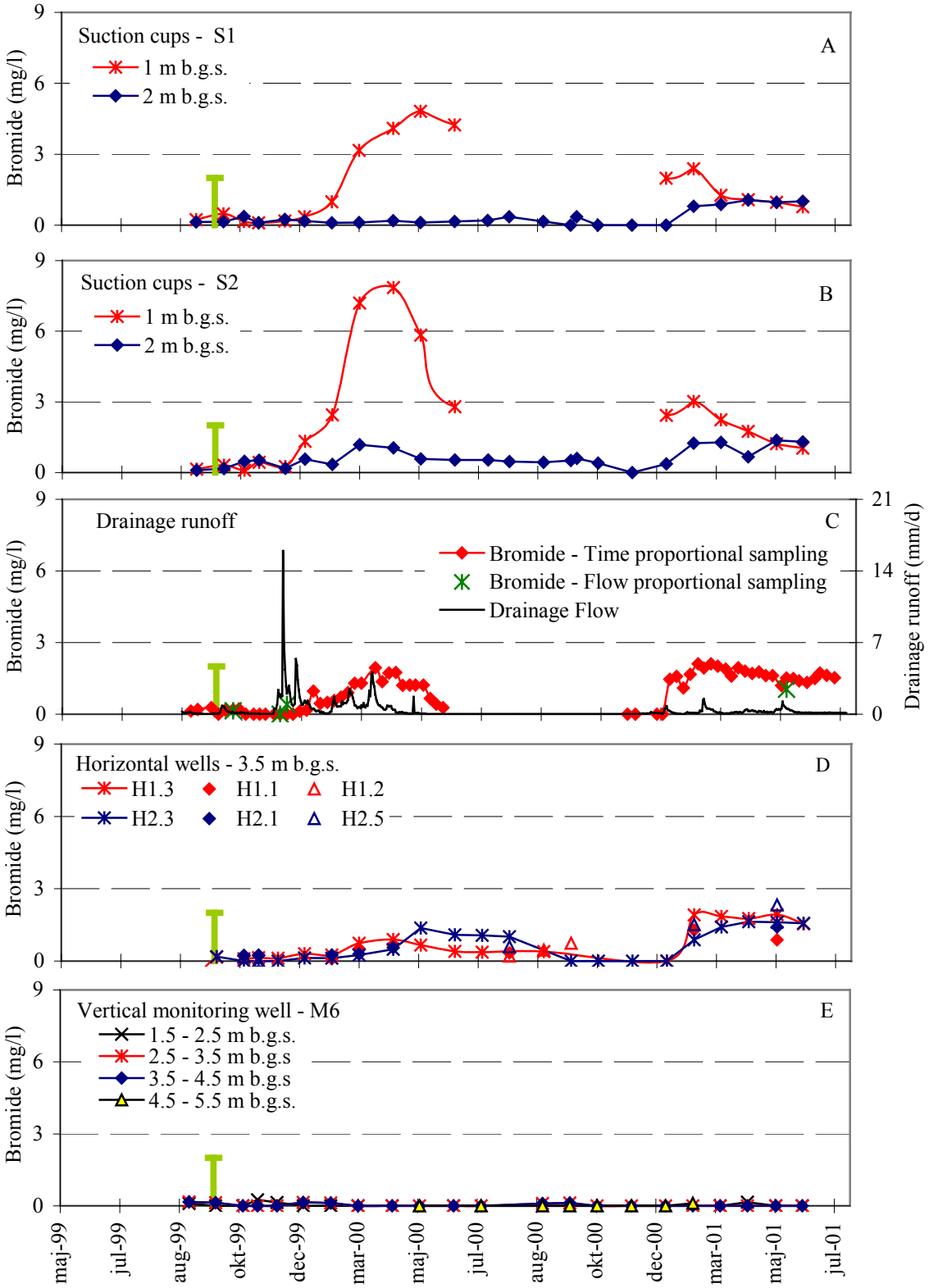

Figure 39. Bromide concentration at Faardrup. A and B refer to suction cups at S1 and S2. The bromide concentration is also shown for drainage runoff (C), the horizontal monitoring wells (D) and the vertical monitoring well M6 (E). The green vertical line indicates the time of bromide application.

6.2.3 Pesticide leaching

The leaching risk of fenpropimorph, propiconazole, fluroxypyr and pirimicarb will not be evaluated until the 2002 monitoring results become available, i.e. when two years of monitoring data have been collated. It should be noted, though, that none of the substances or their degradation products listed in Table 14 have been detected in any of the water samples analysed. Evaluation of the leaching risk of fluazifop-P-butyl, ethofumesate, metamitron, desmedipham, phenmedipham and their degradation products is also premature due to the fact that they have only recently been applied. Ethofumesate, MHPC, metamitron-desamino and metamitron were detected in drainage water on two occasions though (18 and 26 June) (Table 15).

Table 14. Pesticides analysed at Faardrup. Degradation products are indicated in italic.

Crop	Product	Pesticides analysed	Date of application	Accumulated precipitation[1)] (mm)
Winter wheat				
	Roundup 2000	Glyphosate - *AMPA*	Aug 99	1376
	Briotril	Bromoxynil Ioxynil	Oct 00	1126
	Starane 180	Fluroxypyr	Apr 00	767
	Tilt Top	Propiconazole Fenpropimorph - *fenpropimorphic acid*	5, 31 May 00	707, 678
	Pirimor G	Pirimicarb - *pirimicarb-desmethyl* - *pirimicarb-desmethyl-formamido*	June 00	628
Fodder beet				
	Roundup 2000	Glyphosate - *AMPA*	Oct 00	484
	Goltix WG	Metamitron - *metamitron desamino*	May, June, July 01	70, 63,36
	Betanal Optima	Ethofumesate Desmedipham - *EHPC* Phenmedipham - *MHPC*	May, June, July 01	70, 63,36
	Fusilade X-tra	Fluazifop-P-butyl - *fluazifop (free acid)*	June 01	17

1) Accumulated from date of application until 1 July 2001

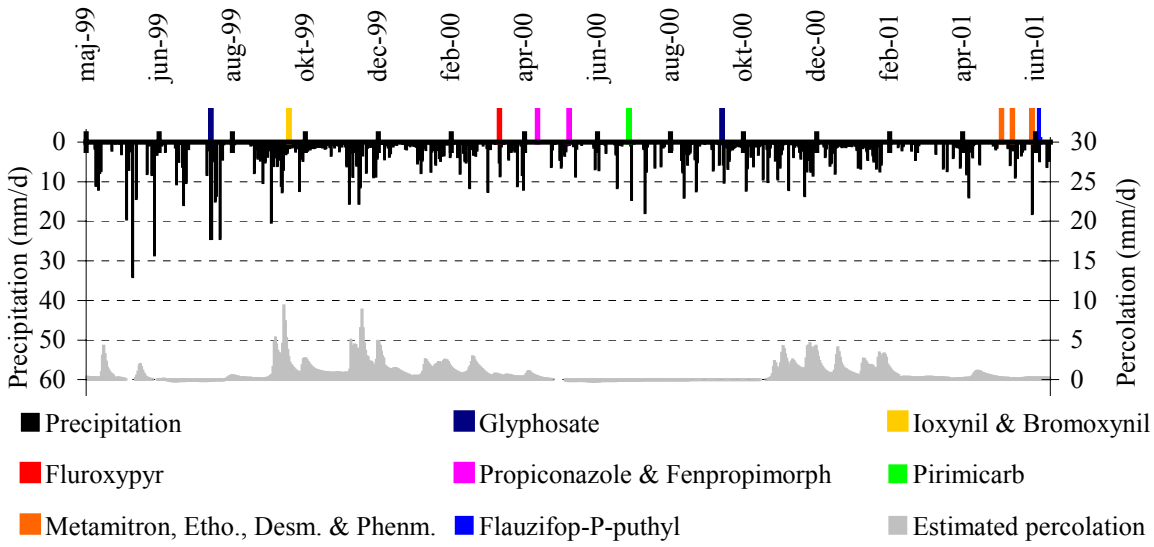

Figure 40. Pesticide application and precipitation (primary axis) together with estimated percolation 1 m b.g.s.(secondary axis) at Faardrup. Etho.: Euthofumesate, Desm.: Desmedipham, Phenm.: phenmedipham.

Ioxynil and bromoxynil, the active ingredients in Briotril, were not detected in any of the water samples. This is in concert with the degradation studies, which indicate that both compounds degrade rapidly in the Faardrup soil. The DT_{50} thus ranged from <1 to 5 days for bromoxynil and from 1 to 12 days for ioxynil (Section 8). The bromide tracer studies initiated a few days prior to Briotril application suggested that ioxynil and bromoxynil had a relatively long residence time in the root zone. The combination of a low DT_{50} and a relatively long residence time indicates that conditions are good for the degradation processes, thereby entailing a low risk that ioxynil and bromoxynil will leach from the soil.

Glyphosate, the active ingredient in Roundup, was applied twice at Faardrup (Figure 40). Based on nearly two years of monitoring data, the leaching risk of the glyphosate applied in 1999 is minor. Glyphosate and its degradation product AMPA were detected in low concentrations on a few occasions. Thus glyphosate was detected in a concentration of 0.01µg/l in drainage water and in a vertical monitoring well on 2 February 2000. AMPA was detected in a concentration of 0.019 and 0.012 µg/l in soil water samples from 1 m b.g.s., and in a concentration of 0.035µg/l in drainage water on 8 May 2001. However, it should be noted that monitoring of glyphosate and AMPA has not yet been completed, but will continue throughout the next monitoring period, thus providing two years of monitoring data for evaluation of the glyphosate applied in both 1999 and 2000.

Table 15. Concentration (µg/l) of MHPC, ethofumesate, metamitron and metamitron-desamino in drainage water at Faardrup.

Date	MHPC	Ethofumesate	Metamitron	Metamitron-desamino
18.06.01	0.19	0.35	0.7	0.15
26.06.01	0.03	0.02	0.1	0.02

6.3 Summary

The risk of pesticide leaching at Faardrup can be summarized as follows:

- With bromoxynil and ioxynil, the leaching risk was negligible.

- With fenpropimorph, propiconazole, fluroxypyr, pirimicarb, fluazifop-P-butyl, ethofumesate, metamitron, desmedipham, phenmedipham and glyphosate the leaching risk cannot be fully evaluated at present as the potential leaching period extends beyond the current monitoring period. Glyphosate, AMPA, ethofumesate, MHPC, metamitron-desamino and metamitron were detected at Faardrup, but only in a few water samples.

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. 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 19–24%, 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 42). 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 and analysis methods is provided in Appendixes 1–2. The monitoring design and test site are described in detail in Lindhardt *et al.* (2001).

7.1.2 Agricultural management

Herbicide spraying was carried out on 9 May 2000 using metsulfuron-methyl, on 5 June using flamprop-M-isopropyl and on 14 June using tribenuron-methyl. Fungicide spraying was carried out on 9 June and 26 June with propiconazole and fenpropimorph. The pesticide dimethoat was sprayed on 9 June. The crop was harvested on 8 August yielding just 39.8 hkg/ha of grain and 10.2 hkg/ha of straw (85% and 100% dry matter, respectively), which is about half of the normal yield for the location. The low yield is probably attributable to the fact that installation of measuring equipment had prevented autumn ploughing, and the field was instead ploughed in spring. As a consequence seedbed establishment was poor, as reflected in the very low final plant number (only 142 plants/m^2). The harvested field was ploughed in November 2000, and field peas sown on 11 April. Weeds were spayed with bentazone and pendimethalin on 1 May and pests with pirimicarb. It was intended that fluazifop-P-butyl should be sprayed to combat wild oats, but this was erroneously omitted. Due to heavy infestation, the wild oats had to be weeded out by hand. From

the beginning of June the field was heavily invaded by wood pigeons (L. Columba palumbus). According to an official from the Danish Forest and Nature Agency, problems with wood pigeons are widespread on Zealand. In this particular year, the late sowing caused by rainy conditions further aggregated the problem caused by the wood pigeons. At the time they need large amounts of food for their young, the height of the pea plants would normally have kept them from landing in the field. This was not the case, however. In spite of considerable effort to control bird damage using advanced scarecrows, balloons painted as birds of prey, and culling, pea yield at harvest on 19 August was only 26.6 hkg/ha (86% dry matter), which is around half of the normal yield. Management practice at the site is detailed in Appendix 3 (Table A3.6).

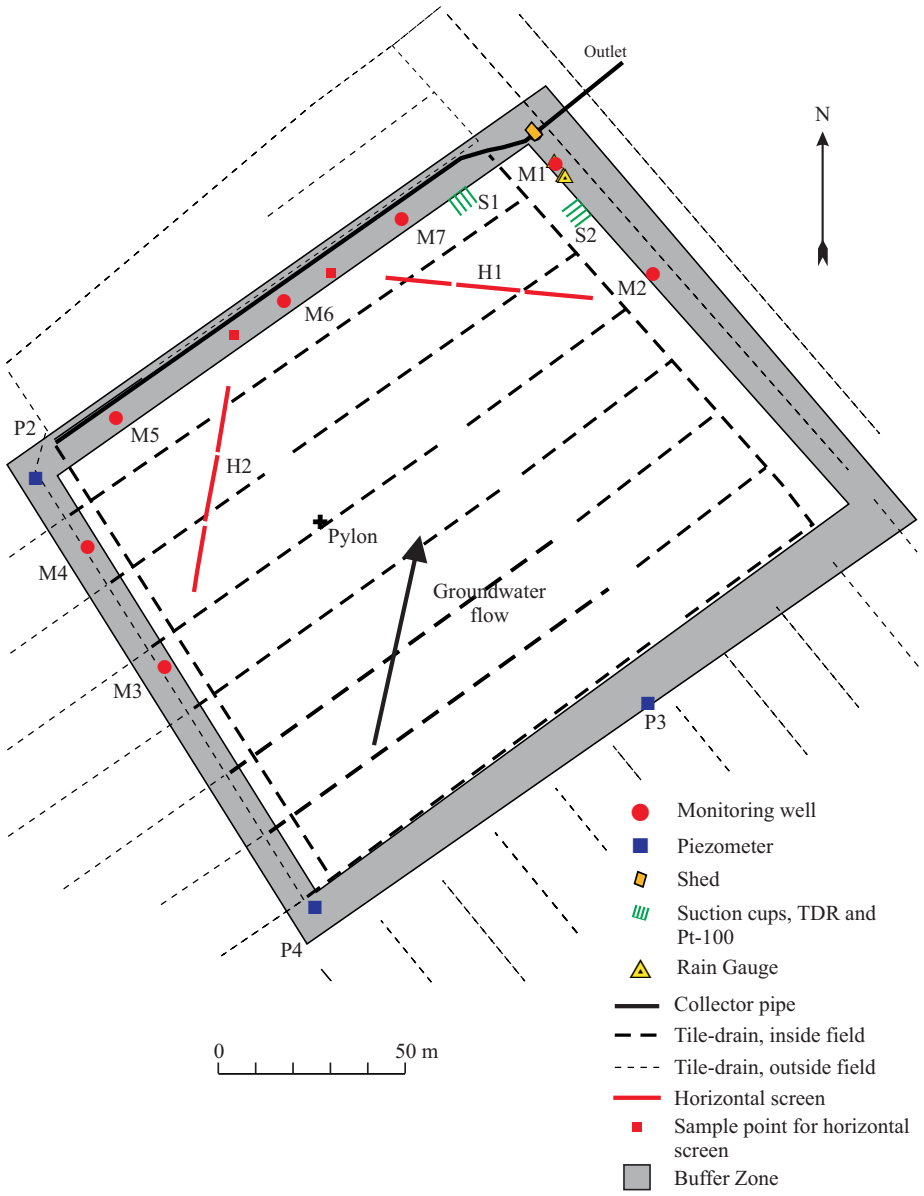

Figure 41. Overview of the Slaeggerup site. The innermost white area indicates the cultivated land, while the grey area indicates the surrounding buffer zone. The positions of the various installations are indicated, as is the direction of groundwater flow (by an arrow).

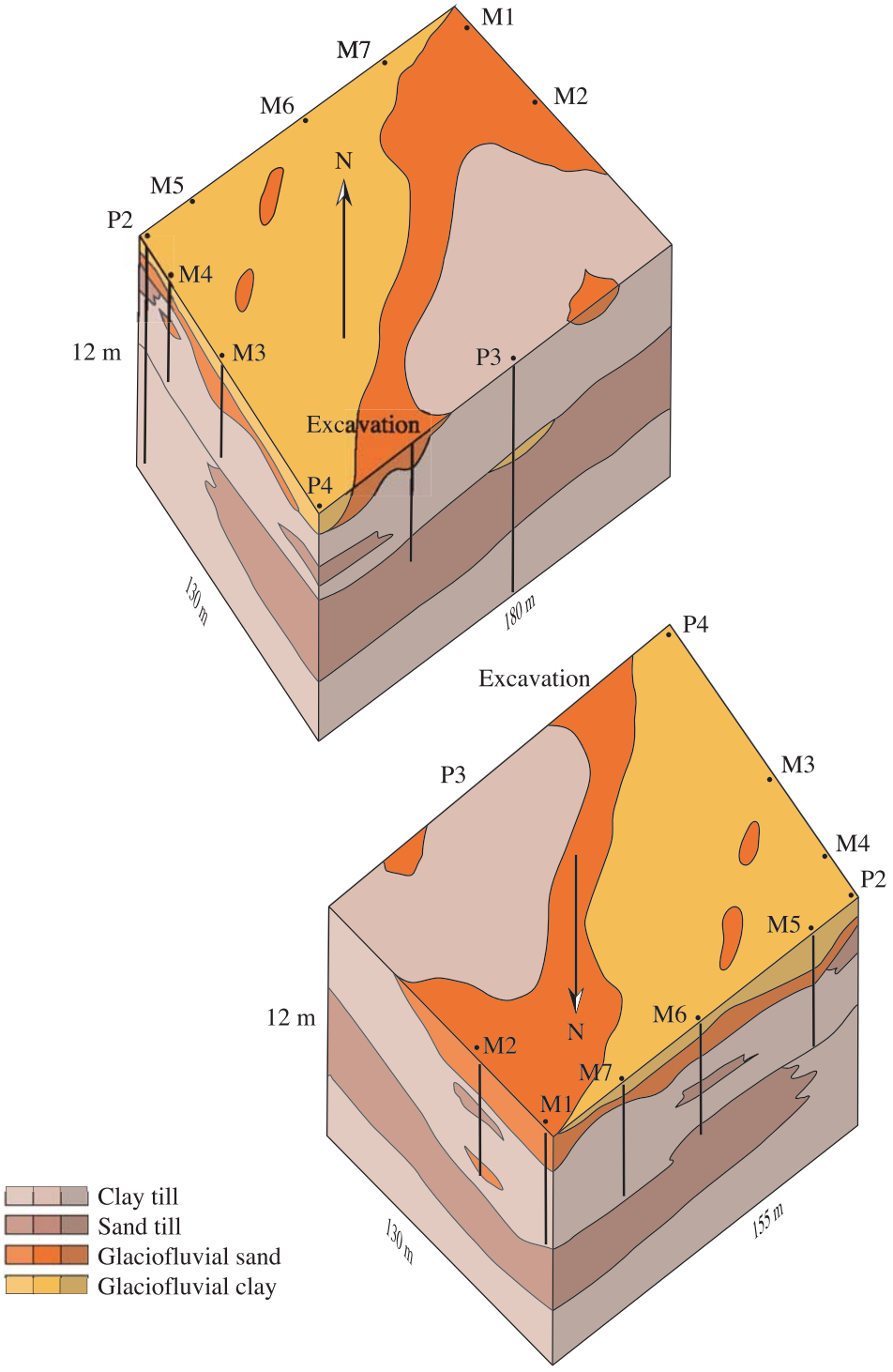

Figure 42. Geological description of the Slaeggerup site (Lindhardt *et al.,* 2001).

7.1.3 Model set-up and calibration

The MACRO model was 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 was used to simulate the water flow in the unsaturated zone during the full monitoring period April 2000–June 2001 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 time series of soil water content measured at three different depths (25, 60 and 110 cm b.g.s.) from the two profiles S1 and S2 (see Figure 41). 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. Data acquisition and model set-up is described in Appendix 5.

7.2 Results and discussion

7.2.1 Soil water dynamics and water balances

The model simulations were generally consistent with the observed data, thus indicating a good model description of the overall soil water dynamics in the unsaturated zone. The model was able to match the measured groundwater table well. The dynamics and level of the groundwater table were captured well by the model.

Measured drainage flow during the winter period was very low (11 mm). The model simulation yielded a similar figure (12 mm), but the modelled drainage flow was delayed compared to the measured drainage flow. The measured drainage flow started to accumulate in mid December 2000, at which time the groundwater table was located 2 m b.g.s. Thus it was not possible to match the dynamics of the measured drainage flow without an unreasonable increase in groundwater level or an unreasonably low drain depth. The overall trends in soil water content could be modelled successfully (Figure 43D, E and F).

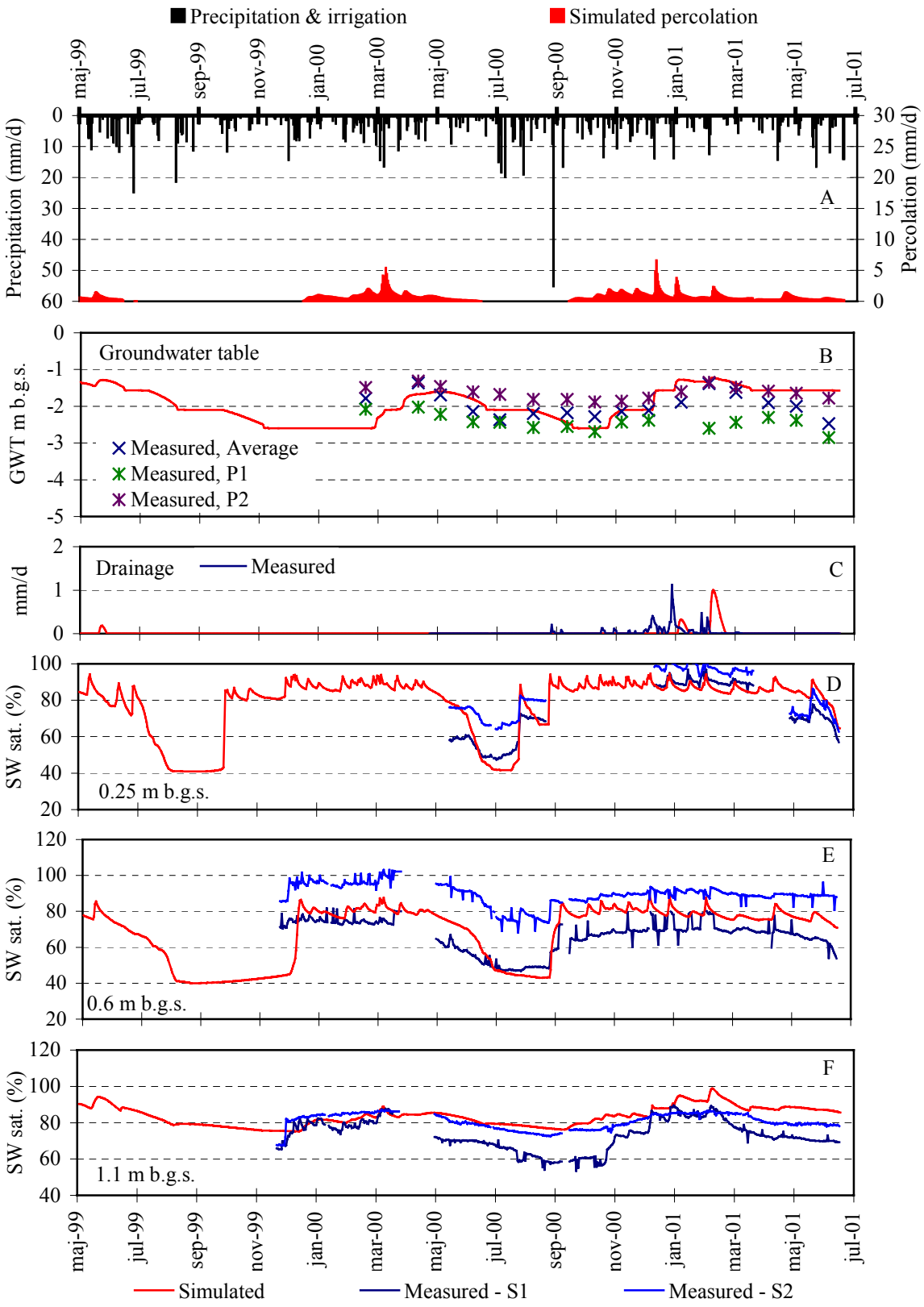

Figure 43. Soil water dynamics at Slaeggerup: Locally measured precipitation and simulated percolation at 1 m b.g.s. (A), simulated and measured groundwater level (B), simulated and measured drainage flow (C), and simulated and measured soil water saturation (SW sat.) at 3 different soil depths (D, E and F). Measured data in B refer to piezometers located in the buffer zone. Measured data in D, E and F refer to TDR probes installed at S1 and S2 (see Figure 41).

Table 16. 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	468	389	–	0	79 [4)]
1.7.00–30.6.01	660	636	339	11	12	286

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 monitoring period (April 2000–June 2001) was close to normal at Slaeggerup, with precipitation input being only 4% less than the yearly normal. The previous year was very dry with 21% less precipitation than normal. Precipitation was particularly sparse from June to September 2000, whereas October and November 2000 and especially April 2001 was wet months (Appendix 4). The modelled, accumulated drainage flow corresponded well to the measured drainage flow. The simulated groundwater recharge differed significantly between the two years (79 mm in 1999–2000 versus 286 mm in 2000–2001), reflecting the large precipitation deficit during the first period.

Bromide tracer studies could not be carried out at Slaeggerup because the water supply authorities refused 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 8 pesticides and 5 metabolites (Figure 44 and Table 17). An evaluation of their leaching risk is thus preliminary.

Fenpropimorph-acid and flamprop (free acid) were found in concentrations of 0.25 and 0.35 µg/l, respectively, in a single flow-proportional drainage water sample on 5 September 2000. This occurred in connection with a major storm event and subsequent flow of drainage water (Figure 41A and C). In addition, flamprop-M-isopropyl was detected in two flow-proportional samples in concentrations of 0.02 µg/l on 5 September 2000 and 0.014 µg/l on 9 February 2001, as well as on 3 consecutive time-proportional samples in concentrations between 0.027 and 0.035 µg/l. Bentazone was detected in a concentration of 0.01 µg/l on 16 May 2001 in soil water sampled 1 m b.g.s. at S2 as well as in the two uppermost screens of the vertical well M6.

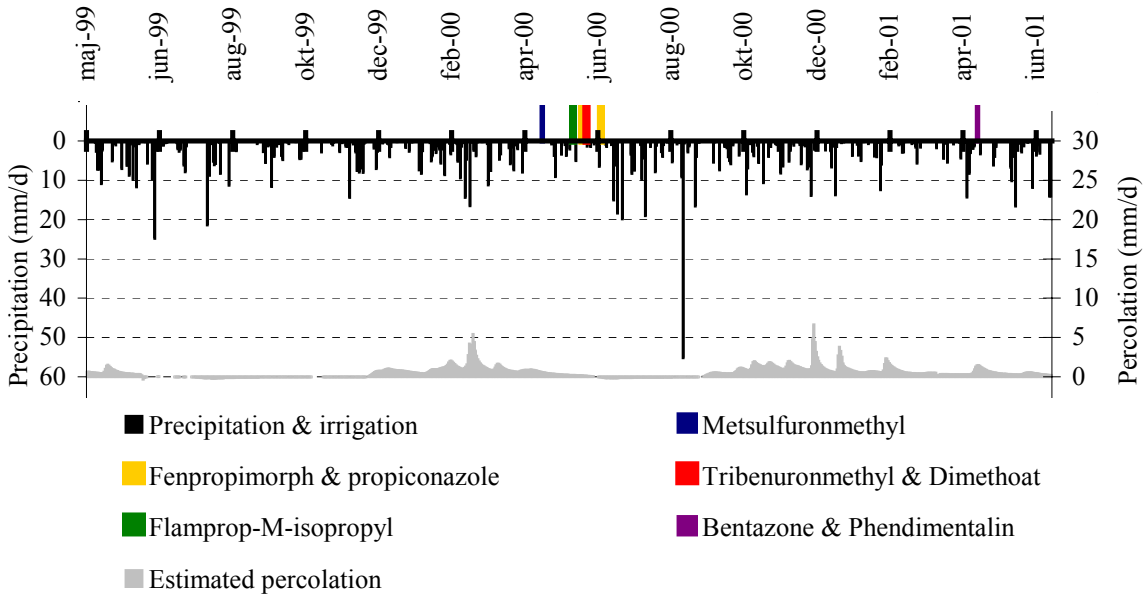

Figure 44. Pesticide application and precipitation (primary axis) together with estimated percolation 1 m b.g.s. (secondary axis) at Slaeggerup.

Table 17. Pesticides analysed at Slaeggerup. Degradation products are indicated in italic.

Crop	Product	Pesticides analysed	Date of application	Accumulated precipitation [1] (mm)
Spring barley				
	Ally	Metsulfuron-methyl - *triazinamin*	May 00	692
	Barnon Plus 3	Flamprop-M-isopropyl - *flamprop (free acid)*	June 00	668
	Tilt Top	Propiconazole Fenpropimorph - *fenpropimorphic acid*	June, July 00	662, 651
	Perfection 500 S	Dimethoat	June 00	668
	Express	*triazinamin-methyl* (from tribenuron-methyl)	June 00	662
Peas				
	Stomp SC	Pendimethalin	May 01	111
	Basagran 480	Bentazone - *2-amino-N-isopropyl-benzamid*		

1) Accumulated from date of application until 1 July 2001

7.3 Summary

The risk of pesticide leaching at Slaeggerup cannot be fully evaluated at present as the potential leaching period extends beyond the current monitoring period. Fenpropimorphic acid, flamprop-M-isopropyl, flamprop (free acid) and bentazone were detected at Slaeggerup, but only in a few water samples.

8 Degradation and sorption parameters

Information on degradation and sorption are of considerable importance for the elucidation of the fate of pesticides, including for the modelling of leaching. Site-specific information is usually sparse, however, and data from the literature often have to be used instead. To eliminate the uncertainty associated with the use of data from the literature and facilitate interpretation of the results of pesticide analyses, the present project incorporates studies on both half-life and K_d (K_{oc}) in Danish soils to demonstrate degradation and sorption, respectively. Microbial biomass and microbial activity of the soils at the sites were also determined to clarify the level of microbial activity in the soil. So far the degradation and sorption parameters have been determined for a combination of five pesticides and three soil types encompassing both plough layer and subsoil (Table 18). With a few of the pesticides, important degradation products were also included, e.g. fenpropimorphic acid.

Table 18. Soil-pesticide combinations hitherto included in the degradation and sorption studies.

Active ingredient	Trade name	Dosage (g a.i./ha)	Investigated sites
Bromoxynil (H)	Briotril, Oxitril	200	Faardrup, Slaeggerup
Fenpropimorph (F)	Tilt Top	375	Tylstrup, Jyndevad, Faardrup
Ioxynil (H)	Briotril, Oxytril	200	Faardrup
Metamitron (H)	Goltix WG	2,100	Silstrup, Faardrup
Propiconazole (F)	Tilt Top	125	Tylstrup, Jyndevad, Faardrup

H: Herbicide, I: Insecticide, F: Fungicide

8.1 Materials and methods

8.1.1 Soil sampling

Degradation and sorption were determined in the laboratory using pooled soil samples. Sampling was carried out just before or as close as possible to pesticide application. Soil samples were collected from the plough layer (0–20 cm) and the subsoil (80–100 cm). To avoid microbial and chemical contamination, the sampling equipment was cleaned with ethanol prior to use.

The plough layer samples were collected using a hand auger (2 cm inner diameter and 20 cm long). A sample based on 50 and 100 subsamples was collected from the plough layer, within the test field (Tylstrup, Silstrup, Estrup and Slaeggerup) or in the buffer zone if the area had already been sprayed (Jyndevad and Faardrup). Subsoil samples were collected from the walls of two 50 x 100 cm pits excavated in the buffer zone with the samples being collected horizontally. Each sample consisted of at least 2 kg of soil per substance per field per depth.

All samples were stored at 5°C after sampling until needed for the experiments. All results are expressed on dry weight soil basis. Prior to the experiments the soils were homogenized and sieved (2 mm), and any stones and plants were removed.

8.1.2 Microbial biomass and activity

Microbial biomass was measured using the substrate-induced respiration (SIR) method (Anderson and Domsch, 1978), which is a physiological method based on the increase in the respiration rate when glucose is added to the soil. Prior to the experiment, the concentration of glucose yielding the highest evolution of CO_2 was determined. CO_2 evolution was measured by gas chromatography. The microbial activity was measured by the degradation of ^{14}C-labelled Na-acetate. ^{14}C Na-acetate (5 µg/g) was added to the soil in an Erlenmeyer flask and the evolved $^{14}CO_2$ collected and counted using a scintillation counter. All studies were performed in quadruplicate.

8.1.3 Incubation of soil

The degradation studies were performed on mixed, homogenized soil from each field site. After homogenization, the water content of the soil was determined. The soil was air-dried and sieved. During the drying process the soil was mixed frequently to avoid excessive drying of part of the soil. For each degradation experiment, 10 replicates of each soil were prepared in Erlenmeyer flasks. An aquatic solution of the test pesticide was added to each flask and the water content adjusted to 40–60% of the water-holding capacity (WHC). The amount of pesticide added to each flask is indicated on the figures. The plough layer (0–20 cm) and subsoil (80–100 cm) samples were incubated at 20°C and 10°C, respectively. The

Erlenmeyer flasks were closed with rubber stoppers and hydrophobic cotton, which allowed diffusion of air and minimized desiccation of the soil during incubation.

At certain time intervals the incubation was discontinued for one replicate at a time, and the soil sample stored at -18°C until analysis. The time intervals were set for each pesticide according to the half-life reported in the literature, ensuring that at least three half-lives were covered. Each degradation experiment was performed in duplicate.

8.1.4 Analysis

Analysis of bromoxynil and ioxynil was performed by extraction in an ASE (Accelerated Solvent Extraction) apparatus: 1.5 g hydromatrix was added to each duplicate soil sample (25 g) in ASE tubes, and the extraction performed using 0.42% phosphonic acid in methanol at 110°C and 2000 psi for 7 min. The extract was concentrated in a vacuum centrifuge and analysed in HPLC/DAD using a Nucleosil 5 C18 column, a gradient of acetonitril/10 mM acetic acid, and a flow rate of 0.5 ml/min. The detection limit was 3.1 µg/kg soil. Blanks and recovery were analysed in each run of the ASE apparatus.

Analysis of metamitron and propiconazole in the adsorption experiment was performed by direct injection of the supernatant on LC/MS after equilibration and centrifugation.

Analysis of fenpropimorphic acid was performed by transferring 50 g of soil to Falcon tubes and apply 50 ml methanol plus 5 ml 6N HCl. The suspension was treated by ultrasonication 3 x 5 minutes and shaken on a Mastermixer for 4 hours. After centrifugation, 1 ml was removed and water was applied to give a methanol/water-proportion of 1:1. The extract was analysed by LC/MS.

Propiconazole was analysed by transferring 50 g of soil to Falcon tubes and apply 50 ml methanol. The suspension was treated by ultrasonication for 3 x 5 minutes and shaken for 4.5 hours on a Mastermixer. After centrifugation, 1 ml of the supernatant was removed and water applied to give a 1:1 methanol/water mixture. The extract was analysed by LC/MS.

Stability tests were performed by adding the pesticides to soil samples and then storing them at -18°C for a period corresponding to the storage period of the test samples. If the recovery was low, the analytical results were corrected on the basis of the recovery rates.

8.1.5 Degradation kinetics

In the registration procedures for pesticides and in many published degradation studies it is assumed that the degradation of pesticides follows simple first-order degradation kinetics. On this basis a half-life is estimated and used for further evaluation. A number of recent publications have shown that a two compartment $1^{st} + 1^{st}$ order model better describes the degradation processes (Fomsgaard, 1999). In a two-compartment model, one part of the added pesticide is rapidly degraded, while another part is adsorbed to the soil, and thus degraded much more slowly.

Once a sufficient number of data points had been obtained, a curve-fitting analysis was performed comparing the use of a simple 1st order model and a two compartment 1st + 1st order model. The modelling was performed using the software TableCurve 2D.
The mathematical expressions are:

1st order model: $$c(t) = a \cdot e^{-k_1 \cdot t}$$

1st + 1st order model: $$c(t) = a \cdot e^{-k_1 \cdot t} + b \cdot e^{-k_2 \cdot t}$$

Where:

c(t) = amount of pesticide remaining at time t

a = initial amount of pesticide degraded through one 1st order process

b = initial amount of pesticide degraded through the other 1st order process

t = time in days

k_1 *= degradation rate constant 1*

k_2 *= degradation rate constant 2*

8.1.6 Determination of sorption

Sorption was determined in both plough layer and subsoil samples. The soil samples were sieved (2 mm) and homogenized. To reduce microbial activity the soils were irradiated with 10 Kgray. Sorption experiments were carried out in a manner similar to that described in OECD (1997). The ratio between soil and 0.01 M $CaCl_2$ was fixed on the basis of literature values for K_d as described in Table 19. The ratio was selected in order to obtain an acceptable concentration ratio after equilibration. All experiments were performed at one concentration (three replicates) with unlabelled pesticides. After shaking the soil with 0.01 M $CaCl_2$ for 24 hours the suspension was centrifuged and the concentration of the pesticide in the aqueous phase determined by LC/MS. The pesticide concentration sorbed on soil was then calculated and the constants K_d and K_{oc} calculated as follows:

$$K_d = \frac{\mu g \ pesticide / g \ soil}{\mu g \ pesticide / ml \ solution}$$

$$K_{oc} = \frac{K_d \cdot 100}{total \ organic \ carbon}$$

Table 19. Pesticide concentrations and water:soil ratios applied in the sorption experiments.

		Pesticide concentration (mg/l)	Water:soil ratio
Plough layer (0–20 cm)			
	Bromoxynil, ioxynil, metamitron	0.5	5
	Propiconazole	0.5	12.5
Subsoil (80–10 cm)			
	Bromoxynil, ioxynil, metamitron	0.5	1
	Propiconazole	0.5	1

8.2 Results and discussion

8.2.1 Soil characteristics

As could be expected, the microbial biomass and the content of organic material were significantly greater in the plough layer than in the subsoil at all test sites (Table 20). The biomass was highest in the soil from Silstrup (641 mg biomass C/kg) and lowest in the sandy soil from Tylstrup and Jyndevad (142 and 194 mg biomass C/kg, respectively). The high microbial biomass at Silstrup might be due to the frequent application of manure at the site in previous years (Lindhardt *et al.,* 2001).

The microbial activity is expressed as the percentage ^{14}C evolved in $^{14}CO_2$ from ^{14}C-labelled acetate during 2 and 96 hours of incubation (Table 20). The evolution from plough layer soil is fastest in soil from Estrup (20% evolved after 2 hours) and slowest in soil from Faardrup (9% evolved after 2 hours). After 96 hours, almost the same percentage had evolved from all soils. In the subsurface soil, $^{14}CO_2$ evolution after 2 hours amounted to less than 2% in all soils, thus confirming the low microbial biomass in these soils. On the other hand, more than 40% of the ^{14}C from ^{14}C-labelled acetate hads evolved after 96 hours, thus indicating the potential for degradation of the very easily degradable acetate. The biomass and microbial activity data will be correlated to pesticide degradation data.

Table 20. Organic carbon, biomass and microbial activity determined in the plough layer (0–20 cm) and the subsoil (80–100 cm) at the PLAP sites.

		Tylstrup	Jyndevad	Silstrup	Estrup	Faardrup	Slaeggerup
Total organic carbon (%)							
	0–20 cm	2.0	1.9	2.2	3.2	1.3	1.2
	80–100 cm	0.5	0.1	0.2	0.3	0.1	0.1
Microbial biomass[1)] (mg C/kg soil)							
	0–20 cm	142	194	641	430	372	346
	80–100 cm	17	42	48	54	35	38
Microbial activity[2)] (% C^{14} evolved)							
	0–20 cm						
	- 2 hours	16	18	14	20	9	15
	- 96 hours	35	34	29	38	34	37
	80–100 cm						
	- 2 hours	1.8	1.3	0.9	0.8	0.8	0.7
	- 96 hours	45	55	41	53	40	36

[1)] *Determined by the SIR-method*

[2)] *Determined by the Na-acetate method*

All experiments were performed on homogenized soil samples. To confirm that the soils were properly mixed, $^{14}CO_2$ evolution from eight individual samples was determined after addition of acetate (two replicates). The evolution was almost identical during the whole

experimental period. Even though the ^{14}C-Na-acetate method is not very sensitive to minor differences in soil microbial activity, the identical evolution of $^{14}CO_2$ from the individual soil samples indicates that homogenization of the soil samples was satisfactory.

8.2.2 Bromoxynil, ioxynil and metamitron

In addition to degradation of bromoxynil at Slaeggerup, degradation and sorption parameters for bromoxynil, ioxynil and metamitron have been reported in Kjær *et al.* 2001. In the present report the results will thus only be summarized (Table 21). The primary data and further discussions can be found in Kjær *et al.* (2001).

The sorption parameters for bromoxynil and ioxynil were all in the lower end of the literature values. The data also confirmed the very low sorption generally found in the subsoil due to the low organic matter content. For metamitron, the K_d-value was 1.7 and 3.5 in soil from Faardrup and Silstrup, respectively, i.e. sorption was highest in the soil with the highest content of organic carbon (Table 21).

Table 21. Organic carbon, sorption and degradation parameters for bromoxynil, ioxynil and metamitron.

Pesticide	Field and soil depth	K_d (ml/g)	Organic carbon (%)	K_{oc} (ml/g)	DT_{50} (days)
Bromoxynil					
	Faardrup (0–20 cm)	1.16 ±0.02	1.3	85	<1
	Faardrup (80–100 cm)	N.D.*)	0.1	N.D.*)	<5
	Slaeggerup (0–20 cm)				<1
	Literature	2–13	–	108–634	1.5–52
Ioxynil					
	Faardrup (0–20 cm)	2.90 ±0.03	1.3	213	<1
	Faardrup (80–100 cm)	0.09 ±0.02	0.1	52	12
	Literature	2–20	–	235–321	1.5–75
Metamitron					
	Faardrup (0–20 cm)	1.69 ±0.22	1.3	124	
	Faardrup (80–100 cm)	0.13 ±0.01	0.1	75	
	Silstrup (0–20 cm)	3.47 ±0.1	2.2	160	
	Silstrup (80–100 cm)	0.41 ±0.05	0.2	177	
	Literature	1–7	–	17–700	

- The K_d values are means of triplicate measurements ±SD.
- N.D. Not detectable

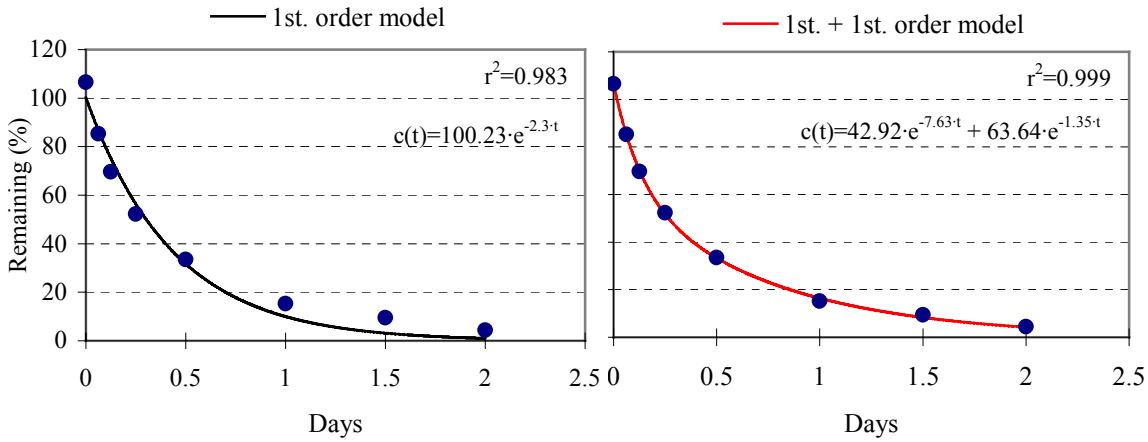

Figure 45. Degradation of bromoxynil in the plough layer (0–20 cm) from Slaeggerup. Dots indicate the experimental data, while the solid lines indicate the fitted curve for a 1st order model (left figures) and a two-compartment 1st + 1st order model (right figures). The initial bromoxynil content was 0.5 mg/kg.

The degradation studies confirmed that degradation occurred much faster in the plough layer than in the subsoil. Moreover, the degradation of both bromoxynil and ioxynil was very fast, and the DT_{50} values of both were much lower than reported in the literature (Table 21).

Degradation of bromoxynil in particular was remarkably fast in both the plough layer and the subsoil at Faardrup, so fast in fact that only a few measurable data points were obtained during the degradation experiment. With the plough layer only two measurable data points were obtained, the last of which was at 6 hours from the beginning of the incubation. The rest of the data points from day 4 onwards were indistinguishable from the blanks. With the subsoil, only three measurable data points were obtained, the last of which was on day 19. The rest of the data points from day 30 onwards were indistinguishable from the blanks. Due to the limited number of data points, moreover, it was not possible to fit curves to the experimental data.

The degradation of bromoxynil was also very fast at Slaeggerup, with a half life of less than one day (Figure 45 and Table 21). In this case the number of data points was sufficient to enable mathematical modelling. The half-life was thus 0.3 days when calculated using the 1st order model, and 0.2, 0.4 and 0.6 when using the two-compartment model.

8.2.3 Fenpropimorph and propiconazole

Degradation of fenpropimorph and propiconazole was determined in the plough layer and subsoil of Tylstrup, Jyndevad and Faardrup. The experimental data, illustrated in Figure 46 and Figure 47, were also subjected to a curve-fitting analysis comparing the use of a simple 1st order model with a two-compartment 1st + 1st order model (Figure 48 and Figure 49). The current results also encompass sorption parameters for propiconazole. The results are summarized in Table 22 to allow correlation of soil characteristics with degradation and sorption parameters for the two pesticides.

Table 22. Soil characteristics together with degradation and sorption parameters for fenpropimorph and propiconazole at Tylstrup, Jyndevad and Faardrup. Literature values are also included for comparison.

		Tylstrup	Jyndevad	Faardrup	Literature values
Plough layer					
(0–20cm)	**Soil characteristics**				
	- Total organic carbon (%)	2.0	1.9	1.3	
	- Biomass (mg C/kg soil)	142	194	372	
	- Microbial activity (% C^{14} evolved in 2 hours)	16	18	9	
	Propiconazole				
	- K_d (ml/g)	40 ±9	21 ±4	12 ±4	
	- K_{oc} (ml/g)	1,999	1,112	891	386–1,813
	- DT_{50} -1^{st} order (days)	310	191	106	14–430
	- DT_{50} -1^{st}+1^{st} order (days)	336(1)	157 (1)	98(1)	
		411(2)	24,945(2)	133(2)	
		410(3)	59,793(3)	144(3)	
	Fenpropimorph				
	- DT_{50} -1^{st} order (days)	379	123	15	16–145
	- DT_{50} -1^{st}+1^{st} order (days)	483(1)	66(1)	4(1)	
		623(2)		22(2)	
		624(3)		36(3)	
Subsoil					
(80—100 cm)	**Soil characteristics**				
	- Total organic carbon (%)	0.5	0.1	0.1	
	- Biomass (mg C/kg soil)	17	42	35	
	- Microbial activity (% C^{14} evolved in 2 hours)	1.8	1.3	0.8	
	Propiconazole				
	- K_d (ml/g)	3 ±0.4	1 ±0.4		–
	- K_{oc} (ml/g)	560	833		–

- The K_d values are means of triplicate measurements ±SD.

- Half-lives are calculated by simple 1^{st} order model and by two-compartment 1^{st} + 1^{st} model. Fitted curves and correlation coefficients are shown in Figure 48 and Figure 49

- (1), (2), (3) refers to the first, second and third half-live determined with the two-compartment 1^{st} + 1^{st} mode.

In the plough layer the degradation of both fenpropimorph and propiconazole was fastest in the Faardrup soil and decreased in the order Jyndevad and Tylstrup (Figure 46 and Figure 47). The fast degradation in the Faardrup soil may be due to the combination of elevated biomass concentration and lower sorption capacity, both of which favour the degradation processes. The biomass was highest in Faardrup soil, decreasing in the order Jyndevad and Tylstrup. K_d for propiconazole was highest in the Tylstrup and Jyndevad soils compared to the Faardrup soil (Table 22). These processes are discussed in further detail in Section 8.2.4.

The results also confirmed the very low degradation and sorption generally found in the subsoil. Apart from slight degradation of propiconazole in Faardrup soil, no degradation was thus detected in the subsoil (Figure 46 and Figure 47). Sorption of propiconazole was also low in the subsoil (Table 22).

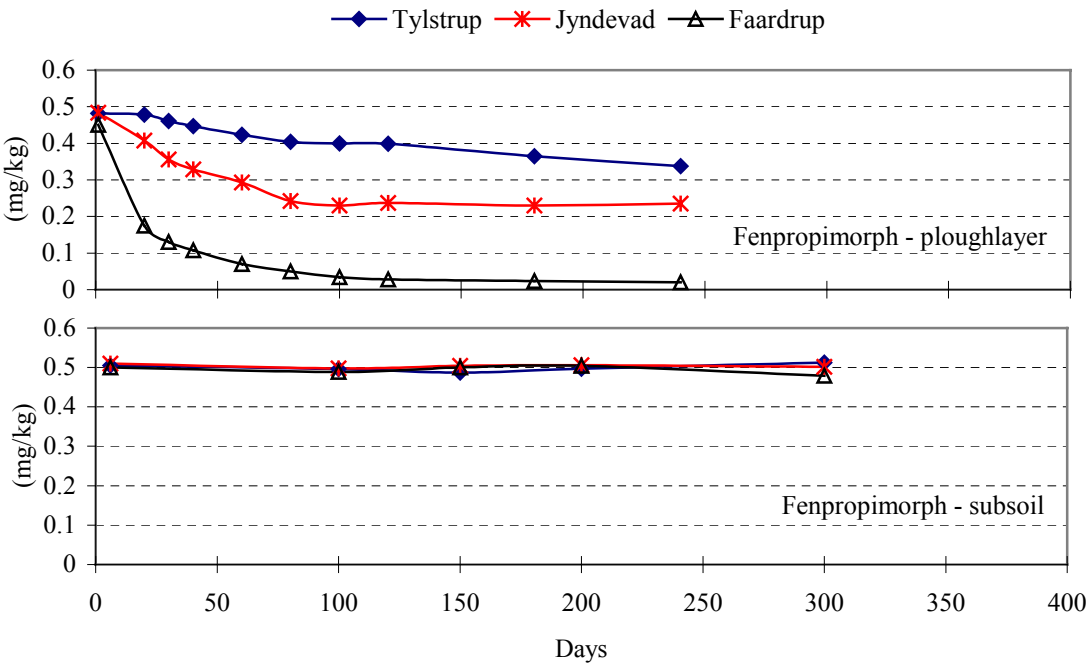

Figure 46. Degradation of fenpropimorph in the plough layer (0–20 cm) and subsoil (80–100 cm) from Tylstrup, Jyndevad and Faardrup. The initial fenpropimorph content was 0.5 mg/kg. The primary data are given in Appendix 13.

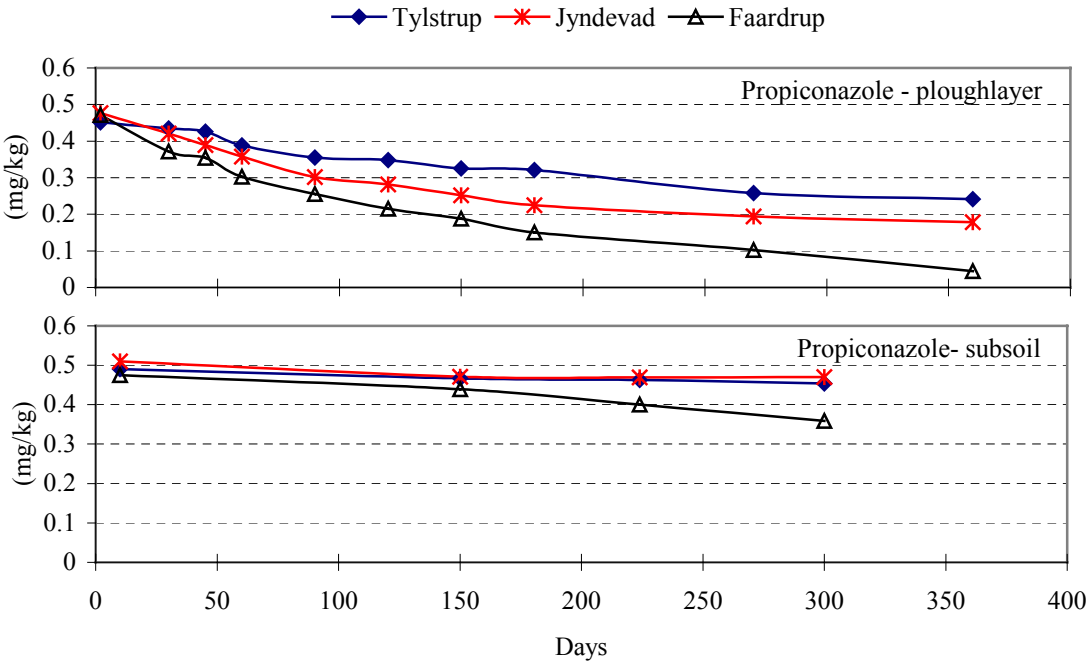

Figure 47. Degradation of propiconazole in plough layer (0–20 cm) and subsoil (80–100 cm) from Tylstrup, Jyndevad and Faardrup. The initial propiconazole content was 0.5 mg/kg. The primary data are given in Appendix 13.

The curve-fitting analysis showed that the degradation of fenpropimorph and propiconazole was best described by a two-compartment 1^{st} + 1^{st} order model. The coefficient of correlation of the two-compartment model was always higher than that of the 1^{st} order model (Figure 48 and Figure 49). This difference was most pronounced for fenpropimorph, where the results revealed large differences between the half-lives as calculated by the 1^{st} order model and by the two-compartment model. The differences between the two models were minor for propiconazole, although differences between the half-lives as calculated by the 1^{st} order model and by the two-compartment model were also seen (Table 22).

In Jyndevad soil, the degradation of fenpropimorph almost ceased when about 50% remained in the soil such that only one half-life value could be obtained (Figure 48). Degradation of propiconazole was also very slow in Jyndevad soil after the first half-life, as indicated by the very long half-life (Figure 49 and Table 22).

Fenpropimorphic acid is an important degradation product of fenpropimorph. The degradation product was identified in the plough layer soil (Table 23), but not in the subsoil. Fenpropimorphic acid did not accumulate, accounting for only 10% or less of the total amount of fenpropimorph shown in Appendix 13.

Table 23. Concentrations of fenpropimorphic acid in the plough layer from Tylstrup, Jyndevad and Faardrup after incubation for up to 240 days. Values are mg/kg.

	1	20	30	40	60	80	100	120	180	240
Tylstrup	n.d.	n.d.	n.d.	n.d.	n.d.	0.008	0.010	0.036	0.037	0.015
Jyndevad	n.d.	0.010	0.013	0.016	0.02	0.019	0.018	0.028	0.023	0.023
Faardrup	n.d.	0.019	0.012	0.017	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

n.d.: not detectable

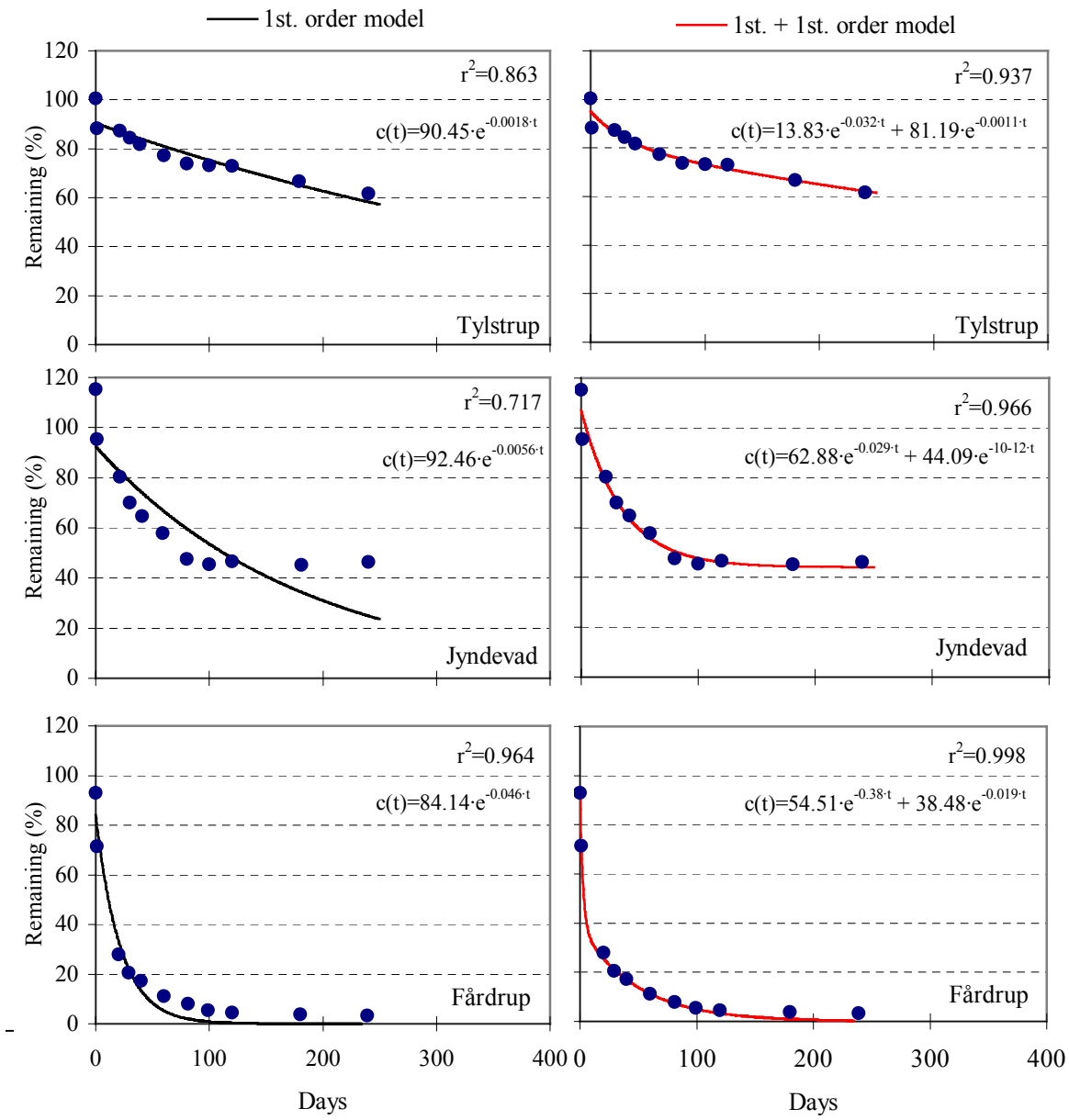

Figure 48. Degradation of fenpropimorph in the plough layer (0–20 cm) from Faardrup, Jyndevad and Tylstrup. Dots indicate the experimental data, while the solid lines indicate the fitted curve for a 1st order model (left figures) and a two-compartment 1st + 1st order model (right figures). The initial fenpropimorph content was 0.5 mg/kg. Calculated half-lives appear in Table 22.

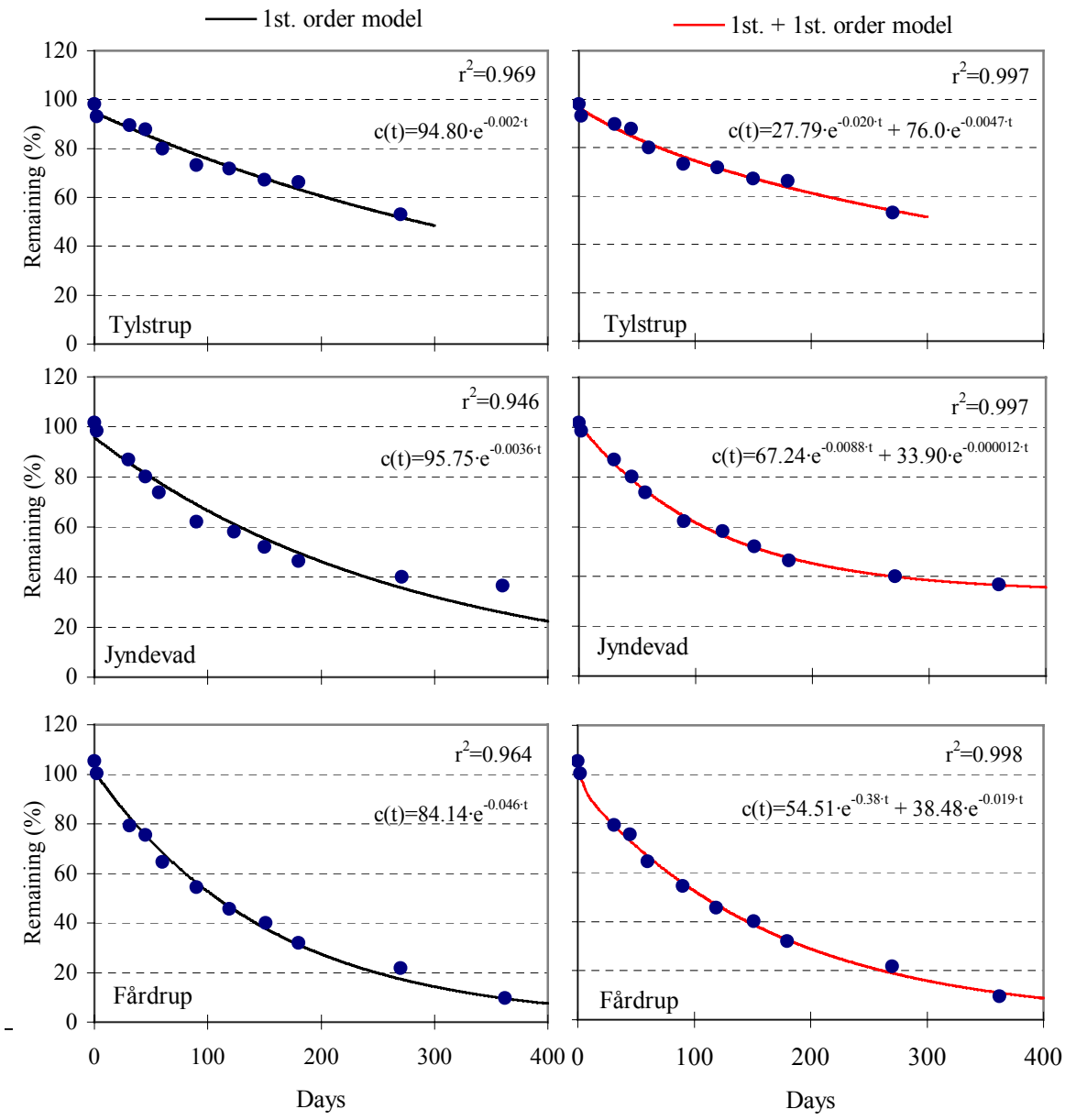

Figure 49. Degradation of propiconazole in the plough layer (0–20 cm) from Faardrup, Jyndevad and Tylstrup. Dots indicate the experimental data, while the solid lines indicate the fitted curve for a 1st order model (left figures) and a two-compartment 1st + 1st order model (right figures). The initial propiconazole content was 0.5 mg/kg. Calculated half-lives appear in Table 22.

8.2.4 Discussion of degradation kinetics

The curve-fitting analysis showed that the degradation processes were best described by a two compartment 1^{st} + 1^{st} order model, whereas a 1^{st} order model often provided a less satisfactory description of the degradation processes (Figure 48 and Figure 49).

In the two-compartment model, the first compartment – having fast degradation – is expected to occur within the soil-water phase, where microorganisms have easy access to the pesticide. In the second compartment, degradation is slow. Here the pesticide is adsorbed to soil particles, with the degradation rate being governed by the slow desorption-diffusion processes. The distribution of pesticide among compartments is governed by the structure of the pesticide as well as by the amount and type of organic material present in the soil. The speed at which the pesticide can be transformed in the first compartment before it is sorbed in the second compartment is affected by the velocity k_1.

Results from the two-compartment models of fenpropimorph and propiconazole show that a high proportion of the pesticide is transformed in the second compartment in the Tylstrup soil, thus indicating that a higher amount of the pesticide was adsorbed. The Tylstrup and Jyndevad soils were also found to a the higher organic carbon content and a higher K_d value for propiconazole than the Faardrup soil. It can thus be concluded that within the first compartment, degradation correlated with sorption as could be expected, e.g. propiconazole sorption and organic carbon decreased in the order Tylstrup to Jyndevad to Faardrup, and the rate of degradation increased as shown by the decreased half-lives calculated by both the 1^{st} order model and the two-compartment model (Table 22). The situation is more complicated when comparing with the two-compartment half-lives. To be able to explain all the relations between compartments and degradation rates it would be necessary to undertake comprehensive modelling studies and further studies of the structure and the binding mechanisms of the compounds.

The two-compartment model cannot be solved analytically, which means that one single DT_{50} cannot be calculated. Half-lives can thus only be given if they are found in the curve or calculated through an iterative process. The simple 1^{st} order equation can be solved analytically such that $DT_{50} = \ln 2/k$, which means that the half-life will be the same irrespective of the time in the process. In contrast, the half-life according to the two-compartment 1^{st} + 1^{st} order process increases with time because the rate constant for the second compartment becomes increasingly dominant with time. The error that is introduced by using a simple 1^{st} order model for the calculation of half-life varies among the soils and compounds.

If the pesticides from the second compartment were only mobilized due to the use of a strong extraction technique, they would never have been available for use by the microorganisms or to leach to the groundwater. As a consequence, the pesticide persistence would be overestimated . If, on the other hand, the pesticides were truly available to the soil microorganisms or to leach to the groundwater, then the pesticide persistence would be underestimated with the use of a simple 1^{st} order process. For example, 3 half-lives for fenpropimorph in Faardrup soil calculated using the 1^{st} order model is only 45 days, while the two-compartment 1^{st} + 1^{st} order model more correctly yields 62 days (4+22+36), as indicated in Table 22.

8.3 Summary

Sorption and degradation parameters were determined on various combinations of pesticides and soil types representative of the PLAP programme. The results confirmed the low microbial activity, sorption and degradation rates generally found in subsoil. Both degradation rates and sorption differed markedly between soils, thus stressing the importance of having site-specific parameters when modelling the leaching of pesticides.

The sorption values for bromoxynil and ioxynil were in the lower end of the literature range. The DT_{50} of ioxynil and bromoxynil were remarkably low, ranging from <1 day in the plough layer and from <5 to 12 days in the subsoil. The rates of degradation were always better described by a two-compartment 1^{st} + 1^{st} order model than with the usual 1^{st} order model, especially in the case of fenpropimorph. Degradation often has one initial fast degradation rate with a short half-life followed by slower degradation rates with longer half-lives. An error is thus introduced if the simple 1^{st} order half-life is used in the evaluation of pesticide persistence. Further analysis of the significance of the introduced error for risk assessment of pesticide leaching is thus required.

9 Pesticide analysis quality assurance

Scientifically valid methods of analysis are essential for the integrity of the PLAP programme. The field monitoring work has therefore been supported by intensive quality assurance entailing continuous evaluation of the analyses employed.

9.1 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 order to validate the stability of spiked water samples, one of the laboratories has carried out comparative studies of analyses of parallel series of samples spiked either in the laboratory or in the field. 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 Danish Aquatic Monitoring and Assessment Programme (NOVA-2003).

9.1.1 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.

9.1.2 External QA

Every third month, two 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 24). Fresh ampoules were used for each preparation of a set of low and high standard solution. 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 24. 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 24. Pesticide concentrations in the spike solution and in the high-level and low-level control samples.

	Compound	Spike solution (mg/l)	High-level control (ng/l)	Low-level control (ng/l)
Mixture 1	Dimethoat	1	117	50
	Ethofumesate	1	117	50
	Fenpropimorph	1	117	50
	Metamitron	1	117	50
	Propiconazole	1	117	50
	Pirimicarb	1	117	50
Mixture 2				
	Bromoxynil	1	117	50
	Desmedipham	1	117	50
	Flamprop (free acid)	1	117	50
	Fluazifop (free acid)	1	117	50
	Fluroxypyr (free acid)	1	117	50
	Ioxynil	1	117	50
	Phenmedipham	1	117	50

9.1.3 Stability tests

In February–March 2001, one laboratory compared samples spiked in the laboratory with samples spiked in the field. Identical spike solutions were used to spike water samples from an upstream ground water station either in the laboratory or in the field. Samples spiked in the field were transported to the laboratory and kept refrigerated until extraction. Laboratory spikes and field spikes were extracted in one series the day the laboratory spikes were prepared. The extracts were also analysed in one series. Differences in measured concentrations due to uncertainty of the analytical method are thus reduced to the intra- series variation. Spike concentrations were twice the concentration of the internal control samples that were analysed parallel to the stability test samples, e.g. 0.08 to 0.16 µg/l. Stability tests were performed at two occasions at the experimental sites Silstrup, Estrup and Slaeggerup and once at Tylstrup. The interval between field spiking and extraction and between extraction and analysis varied from 4 to 12 days.

9.2 Results and discussion

9.2.1 Internal QA

The internal QA data have been analysed to obtain an impression of the day-to-day variation and within-day variation. The statistical analysis encompasses all duplicate pesticide analyses, single analyses being excluded. One-way analysis of variance was used to separate day-to-day variation from within-day variation. The results are presented in Table 25.

With more than half of the pesticides the day-to-day variation accounted for most of the uncertainty. Thus when s_t exceeded 10, this was due to a high day-to-day variation. $F>F_{critical}$ indicates that the day-to-day variation is significantly higher than the within-day variation (95% confidence interval). $F<F_{critical}$ indicates that the random errors dominate the overall uncertainty.

Table 25. One-way analysis of variance of pesticide analyses.

	Pesticide	s_w [1] (µg/l)	s_b [1] (µg/l)	s_t [2] (µg/l)	F	$F_{critical}$	n
Laboratory 1							
	3-aminophenol (D)	0.007	0.006	0.010	0.74	3.23	9
	Desmedipham	0.004	0.009	0.010	4.48	2.85	11
	Dimethoat	0.002	0.004	0.004	3.49	2.51	14
	Ethofumesate	0.001	0.002	0.002	1.26	2.85	11
	Fenpropimorph	0.002	0.003	0.004	2.40	2.06	22
	Fenpropimorphic acid (D)	0.005	0.015	0.016	7.31	2.29	17
	Flamprop (free acid)	0.003	0.006	0.007	4.61	2.51	14
	Flamprop-M-isopropyl	0.002	0.004	0.005	5.21	2.51	14
	Fluazifop-P (free acid)	0.006	0.011	0.012	3.13	5.19	5
	Linuron	0.004	0.003	0.005	0.48	2.72	12
	Metamitron	0.004	0.010	0.010	4.87	4.39	6
	Metamitron-desamino (D)	0.010	0.024	0.026	6.09	3.50	8
	Metribuzin	0.001	0.003	0.003	5.18	2.72	12
	Metribuzin-desamino (D)	0.009	0.031	0.032	12.88	5.19	7
	Metribuzin-desamino-diketo (D)	0.006	0.017	0.018	7.30	2.72	12
	Metribuzin-diketo (D)	0.020	0.022	0.029	1.24	2.72	12
	Metsulfuron-methyl	0.004	0.007	0.008	2.83	3.50	8
	MHPC (D)	0.004	0.008	0.008	4.42	3.02	10
	Pendimethalin	0.001	0.002	0.002	1.33	3.23	9
	Phenmedipham	0.002	0.003	0.004	3.75	4.39	6
	Pirimicarb	0.001	0.002	0.002	1.50	2.85	11
	Pirimicarb-desmethyl (D)	0.008	0.013	0.015	2.62	1.99	24
	Propiconazole	0.003	0.005	0.005	3.12	2.06	22
	Triasulfuron	0.004	0.009	0.009	4.97	3.23	9
	Triazinamin (D)	0.002	0.010	0.010	16.05	2.51	14
	Triazinamin methyl (D)	0.003	0.005	0.006	2.53	2.60	13
Laboratory 2							
	AMPA (D)	0.004	0.008	0.009	3.71	1.61	49
	Bromoxynil	0.001	0.006	0.007	19.51	2.02	23
	Desethylterbuthylazine (D)	0.005	0.009	0.011	3.11	9.55	3
	Ethofumesate	0.003	0.008	0.009	9.21	3.23	9
	ETU (D)	0.010	0.017	0.020	3.12	3.87	7
	Fenpropimorph	0.002	0.002	0.003	1.09	2.72	19
	Fluroxypyr	0.003	0.006	0.007	3.33	2.85	11
	Glyphosate	0.003	0.007	0.008	4.96	1.59	51
	Ioxynil	0.001	0.005	0.005	10.62	2.51	14
	Metamitron	0.002	0.014	0.015	73.89	3.23	9
	Phenmedipham	0.002	0.003	0.004	1.19	6.59	4
	Pirimicarb	0.003	0.007	0.008	7.26	2.14	20
	Propiconazole	0.006	0.010	0.012	3.19	1.81	32

1) s_w and s_b are the within-day and day-to-day standard deviation, respectively

2) s_t is the total standard deviation calculated as $s_t = \sqrt{s_w^2 + s_b^2}$ (Lund et al., 1994)

n= number of duplicate analyses, D= degradation product

The overall standard deviations (s_t) of the various pesticide analyses lie within the range 0.002–0.032 µg/l. Reproducibility of the degradation products was found to be poorer than that of the mother compounds. Standard deviation for mother- and degradation products was in the range 0.002–0.015 µg/l and 0.009–0.032 µg/l, respectively. The reproducibility of metamitron-desamino, metribuzin-desamino, metribuzin-diketo and ETU analyses were particularly poor, $s_t \geq 0.02$.

9.2.2 External QA

Table 26 provides an overview of the recovery of all spiked samples based on 1–5 observations. Recovery of the spiked samples is generally good, an exception being desmedipham and phenmedipham.

Table 26. Average recovery (%) at low/high concentration level indicated for each site. Recovery refers to the ratio of the observed and nominal concentrations.

Pesticide	Tylstrup	Jyndevad	Silstrup	Estrup	Faardrup	Slaeggerup
Bromoxynil					92/94	
Desmedipham*			48/39		**0/9**	
Dimethoat	82/91		**82/91**	87/88		91/92
Ethofumesate			85/93		114/94	
Fenpropimorph	86/94	110 /103	**90/97**	64/48	95/91	72/69
Flamprop (free acid)			**74/85**	79/84		68/82
Fluazifop-P (free acid)			63/88		**74/69**	
Fluroxypyr					90/91	
Ioxynil					89/94	
Metamitron*			71/81		**84/56**	
Phenmedipham*			34/27		**0/12**	
Pirimicarb			88/92		**96/92**	
Propiconazole	94/91	106/101	138/119	95/82	95/91	81/87

** indicates that the compound was partly transformed into a degradation product as shown in Appendix 14*
Values in bold indicate that recovery is based on a single observation.

The low recovery reported for desmedipham, phenmedipham and metamitron is presumably due to stability problems. Degradation products were thus detected in the spiked samples, indicating that the corresponding mother compounds were unstable during the interval between preparation of the spike solution and the time of analysis. This problem is further discussed in Section 9.2.3. In Appendix 14, degradation products detected in spiked samples are marked on the control cards for both the mother compound and the degradation product. The concentration of the degradation product should be added to the concentration of the mother compound to obtain a more realistic picture of the recovery.

Fenpropimorph and propiconazole were included in the monitoring programme at all six field sites, and it is therefore possible to compare the matrix influence on the results. Recovery of propiconazole varies from site to site, but the relative standard deviation does not exhibit site-specific differences. With fenpropimorph, both recovery and relative standard deviation exhibit site-specific differences (Table 27). Thus recovery is low at site 4, while relative standard deviation is high. It is likely that the differences are due to differences in water composition at the different sites.

In conclusion, the observed differences in recovery between field sites are likely to be caused by differences in matrix composition, although inter-laboratory differences have also been observed. Differences in metamitron recovery between field sites are partly explained by differences in transport and storage condition resulting in different stability of the sample.

Table 27. Average recovery and relative standard deviation (rel. SD) of fenpropimorph and propiconazole in spiked samples from all experimental fields.

	Tylstrup		Jyndevad		Silstrup		Estrup		Faardrup		Slaeggerup	
	low	high	low	High	low	high	low	high	low	high	low	high
Fenpropimorph												
Recovery (%)	86	94	110	103	90	97	64	48	95	91	72	69
Rel. SD (%)	13	11	7.1	17	–	–	20	46	1.2	5.4	23	35
n	5	5	5	5	1	1	5	5	3	3	5	5
Propiconazole												
Recovery (%)	94	91	106	101	138	119	95	82	95	91	81	87
Rel. SD (%)	15	12	17	16	–	–	18	11	20	20	19	5
n	5	5	5	5	1	1	5	5	3	3	5	5

n= number of external QA samples per site

Nine pesticides and ten degradation products were detected in samples from the experimental fields, and QA data connected to these findings are of special interest. Recovery of pesticides in both internal and external QA samples was found to be acceptable for all pesticides detected in field samples (Table 28). Thus, bentazone, glyphosate and all of the degradation products (marked D in Table 28) were absent in the pesticide spike mixture. The quality assessment of these analyses is therefore entirely based upon the internal QA data. However, ETU was included in the external QA sample the first experimental year (Kjær *et al*., 2001). Results from the external QA samples are shown together with the internal QA samples in Appendix 14.

Table 28. Average recovery (%) at low/high concentration level indicated for those pesticides identified in at least one sample. Recovery refers to the ratio of the observed and nominal concentrations**.**

Pesticide	Tylstrup	Jyndevad	Silstrup	Estrup	Faardrup	Slaeggerup
AMPA		*		*	*	
Bentazone						*
Ethofumesate			89/93		114/94	
ETU	*					
Fenpropimorph		110/103		64/48		
Fenpropimorphic acid (D)						*
Flamprop (free acid)				79/84		68/82
Flamprop-M-isopropyl				*		*
Glyphosate				*		
Metamitron			71/81			
Metamitron-desamino (D)			*		*	
Metribuzin-desamino-diketo (D)	*	*				
Metribuzin-diketo (D)	*	*				
MHPC					*	
Pirimicarb			88/92			
Pirimicarb-desmethyl (D)			*			

**) No external QA samples available*
D = degradation product

Metsulfuron-methyl was detected in one control sample, where it should not be present, at a concentration of 0.01 µg/l. Metamitron-desamino was detected in one blank sample at a concentration of 0.05 µg/l. Metamitron-desamino was detected in several samples, not all of which were from the batch with the positive blank sample. The findings in the samples are regarded as true positive findings. No other pesticides were detected in blank samples indicating that the samples did not become contaminated in the laboratory.

All the pesticides in the spiked samples were detected in all samples. In one spiked sample the laboratory reported a very low value for one compound, missed one compound and gave a positive result for a non-present compound. Subsequent inspection of the raw data revealed that the reported data was erroneous. Correction was only possible because the sample was a QA sample.

9.2.3 Stability tests

The ratio of pesticide concentration in samples spiked to the same concentration on different days and analysed simultaneously reflects the stability of the spiked samples. Table 29 displays the above-mentioned ratio for seven series of samples. The interval between spiking in the field and extraction of the samples was 5–9 days while that from extraction to analysis was 4–12 days. The concentration of the metabolite metamitron-desamino (from metamitron) and MHPC (from desmedipham and phenmedipham) is very low in the laboratory spikes, so the field:laboratory spike ratio is negligible and therefore omitted from the table.

By far the majority of the analysed compounds were relatively stable, and their stability was not markedly affected by transport and storage conditions. Metamitron, desmedipham and phenmedipham were found to be unstable, however. Degradation products were detected in the spiked solution, and stability was therefore markedly affected by transportation and storage conditions.

The first round at Silstrup revealed that the stability of metamitron was low (50%). This is in accordance with the finding of a relatively high concentration of the degradation product metamitron-desamino in the field spike (0.075 µg/l). The stability of fluazifop-P (free acid) was also low. No degradation products of this compound are included in the analysis method. Desmedipham and phenmedipham were less stabile in round one than in round two. The corresponding metabolite of phenmedipham, MHPC, was identified, but quantification was not possibly as the concentrations were below the detection limit of 0.02 µg/l. However, 0.02 µg/l corresponds to 23% of the phenmedipham, so the low concentrations detected may still be due to degradation of the mother compound. This could also be the case for desmedipham, although the metabolite EHPC was not analysed in these samples.

Table 29. Ratio (%) between concentrations of pesticides determined in parallel samples of field spikes (FS) and laboratory spikes (LS). Concentration level 0.08– 0.16 µg/l.

	Silstrup FS/LS		Estrup FS/LS		Slaeggerup FS/ LS		Tylstrup FS/LS
Pesticide	1 round	2 round	1 round	2 round	1 round	2 round	1 round
Bentazone			99	100	103	105	92
Desmedipham	82	91					
Dimethoat			101	106	103	104	
Ethofumesate	90	99	104	106	97	110	
Fenpropimorph	92	98	115	88	98	78	98
Flamprop (free acid)			96	97	89	97	
Flamprop-m-isopropyl	98	105	106	100	102	108	
Fluazifop-P (free acid)	64	106	n.a.	102	n.a.	100	
Linuron							93
Metamitron	50	80					
Metamitron GC/MS	51	95	106	93	92	91	101
Metribuzin			104	102	95	102	101
Metsulfuron-methyl			95	105	97	93	
Pendimethalin			100	103	100	113	101
Phenmedipham	84	93					
Pirimicarb	98	102	132	100	95	86	96
Propiconazole	96	105	105	96	108	106	85
Triasulfuron							100
Days between spiking	9	5	5	7	6	7	6
Days between extraction and analysis	12	4	10	5	10	5	4

FS = a sample spiked in the field; LS = a sample spiked in the laboratory; n.a = not analysed.

With these compounds the stability of the first field spike at Silstrup was lower than for any other sample. The sample was stored for 9 days before extraction and for 12 days from extraction to analysis. The test samples from Estrup and Slaeggerup were stored for 5–7 days before extraction and for a further 5 or 10 days before analysis. Results from these experiments indicate that storage of the extract in the freezer for up to 10 days does not influence the stability. The stability of metamitron in these tests is significantly better than in the first round at Silstrup. Comparing data from Silstrup, Estrup and Slaeggerup does not explain the low stability of the first round of samples at Silstrup. In contrast to what would be expected if the storage time was as important as suggested by the difference between Silstrup first and second round, there was no significant difference between storage of samples in 5 or 7 days. However, formation of the degradation products metamitron-desamino and MHPC in QA samples can be used as an indicator for sub-optimal transport/storage conditions.

9.3 Summary

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

- Reproducibility of the pesticide analyses was good, standard deviation ranging from 0.002–0.015 µg/l.
- Reproducibility of the degradation products was poorer than that of the mother compounds, ranging from 0.009–0.032µg/l.
- Recovery of pesticides in both internal and external QA samples was acceptable for all pesticides detected in field samples.
- Variations in recovery of the same compound in spiked samples from all field sites indicate uncertainties in analysis caused by differences in matrix composition.
- No contamination of samples generally occurred during collection, storage and analysis. However, two cases of "false positive" were observed in blank or spiked samples.
- Stability tests indicated that by far the majority of the analysed compounds did not exhibit stability problems. However, the occurrence of degradation products in some of the spiked samples indicate that a few of the compounds are unstable, and conditions during transport and storage are important.

10 Summary of monitoring results

The majority of the applied pesticides (13 of 21) did not leach during the current monitoring period. It should be noted, though, that evaluation of the leaching risk of many of these pesticides is still preliminary as the potential leaching period extends beyond the current monitoring period. This is the case for those pesticides marked with a single + or – in Table 30.

The monitoring data indicate unacceptable leaching by two of the applied pesticides. Thus glyphosate and its degradation product AMPA and two degradation products of metribuzin leached from the root zone (1 m b.g.s.) in average concentrations exceeding the maximum allowable concentration of 0.1 µg/l (Table 30). The monitoring data also indicate leaching of a further six pesticides, but it is too early to determine whether this will reach unacceptable levels as the potential leaching period extends beyond the current monitoring period. 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.

A more complete evaluation integrating the monitoring data with both sorption and degradation studies and modelling of pesticide transport will be made once a more comprehensive data set covering the entire leaching period of a greater number of pesticides becomes available.

Table 30. Pesticide leaching at the six PLAP sites. The number of pluses or minuses indicates the number of leaching seasons in which the pesticide was included in PLAP programme and whether or not evidence of leaching was detected. Pesticides applied in spring 2001 are not included in the table.

	Tylstrup	**Jyndevad**	**Silstrup**	**Estrup**	**Faardrup**	**Slaeggerup**
Top soil classification	Loamy sand	Sand	Sandy loam	Sandy loam	Sandy loam	Sandy loam
Metribuzin	++	++[1)]				
Glyphosate		– –		+	– –	
Ethofumesate			+			
Metamitron			+			
Flamprop-M-isopropyl				+		+
Pirimicarb	–		+		–	
Propiconazole	–	–		+	–	–
Fenpropimorph	–	–		–	–	+
Dimethoat				–		–
Metsulfuron-methyl				–		–
Triazinamin-methyl	–	– –		–		–
(tribenuron methyl)						
Pendimethalin	–		–			
Fluazifop-P			–			
Desmedipham			–			
Phenmedipham			–			
Bromoxynil					– –	
Fluroxypyr					–	
Ioxynil					– –	
ETU *(Mancozeb)*	– –					
Linuron	– –					
Triasulfuron	–					

[1)] *Deriving from previous application*

\+ *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 products) detected in either several consecutive samples or in a single sample in concentrations exceeding 0.1 µg/l; average concentration below 0.1 µg/l*

– *Pesticide not detected, or only detected in very few samples in concentrations below 0.1 µg/l*

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Appendix 1. Sampling procedure

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 were 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. 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 completely the day before sampling. With the horizontal monitoring wells sampling was performed using a peristaltic pump, allowing a purge volume of 200 l equivalent to 1.6 times the volume of the screen.

Soil water samples were 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 were 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 flow event. For each storm event, analysis of pesticides and inorganic chemicals (Br, Cl, K, NO_3, 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) was 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 following equation:

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

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

$$M_i = Cf_i \cdot Vf_i \quad If\ a\ flow\ event\ occurs\ within\ the\ i'te\ week$$

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 and Ca, pH and conductivity are measured monthly, whereas HCO_3, Fe, Mg, Mn, DOC, Na, NO_3, NO_2, PO_4, total-P, dissolved total-P, suspended matter and SO_4 are measured four times a year. At the loamy sites inorganic analysis is moreover performed on drainage water samples, as described above.

Pesticide analysis is 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, five monitoring wells and six screens of the horizontal monitoring wells is performed every fourth month (Table A1.1). At the loamy sites, pesticide analysis is also performed on drainage water samples, as described above.

Table A1.1 Pesticide monitoring programme in the horizontal (H) and vertical monitoring (M) wells.

Site	Monthly monitoring	Quarterly monitoring	Not measured
Tylstrup	M5, M4, M6	M1, M3, M4, M5, M6	M7, M2
Jyndevad	M1, M4	M1, M2, M4, M5, M7	M6, M3
Silstrup	M5, M6, 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	M4, M5, H1.2	M1, M3, M4, M5, M6, H1.1, H1.2, H1.3	M2, M7
Faardrup	M5, M6, H1.3, H2.3	M1, M2, M3, M4, M5, M6, H1.1, H1.2, H1.3, H2.1, H2.2, H2.3	M7
Slaeggerup	M5, M6, H2.2, H1.2	M1, M3, M5, M6, M7, H1.1, H1.2, H1.3, H2.1, H2.2, H2.3	M2, M4

The inorganic parameters were analysed using the following methods:

Total nitrogen: Inorganic and organic nitrogen compounds were oxidized to nitrate with peroxydisulphate in an alkaline environment under pressure in a sealed vessel as described in Cabera and Beare (1993).

Ammonia-N: Using nitroprusside as the catalyst, ammonia was reacted with salicylate-dichloroisocyanurate to form an emerald green complex, the absorbance of which was measured on a spectrophotometer. The method used is described in Croole and Simpson (1971) modified for water samples.

Calcium and magnesium: The calcium and magnesium content was measured by means of atomic absorption spectrophotometry after the metal content of the sample had been dissolved with nitric acid. The method is described in DS 259 (1982) and DS 238 (1985).

Sodium and potassium was measured by means of flame emission photometry according to EEC (1971).

Total-P and dissolved total-P: Total-P was measured on nonfiltered samples. Complex inorganic and organically bound phosphorus was transformed to orthophosphate by use of potassium peroxydisulphate in an acidic solution. Dissolution was performed under pressure in a sealed vessel. In the sulphate solution, orthophosphate forms a complex with molybdate and antimony that can be reduced to the heteropolycomplex molybdenum blue using ascorbinic acid. The absorbance of the complex at 880 nm is proportional to the phosphorus content (DS 292, 1985).

NO_3-N, NO_2-N, PO_4-P, SO_4-S, Cl, Br were measured by means of high performance liquid chromatography (HPLC). The basis for the method is anion exchange and detection using an electrochemical detector according to Vognsen (1996).

Suspended matter was determined by passing a maximum of 1 litre of water through a cellulose acetate and fibreglass filter (normally 0.150 l of filter is used). The detection limit was set to 5 mg/l. The method used is that described in DS 207 (1985).

The pesticide analyses were carried out at two commercial laboratories. At Miljøkemi the pesticides analyses were all performed on decanted water samples, whereas at Rovesta the samples were only decanted if unclear. The methods of analysis employed are tabulated below. The table also indicates whether or not the methods are accredited by DANAK, or approved by the Danish EPA for pesticide analysis within the framework of NOVA-2003 (The Danish Aquatic Environment Monitoring and Assessment Programme 1998–2003).

Table A2.1 Methods of pesticide analysis applied at Tylstrup, Silstrup, Estrup and Slaeggerup.

Pesticide	Extraction	Detection	Detection limit (µg/l)	Accredited by DANAK	Approved by Danish EPA	Laboratory
AMPA	[1)]	GC/MS	0.01		Yes	Miljøkemi
2-amino-N-isopropylbenzamid	LLE	GC/MS	0.02	No	No	Rovesta
3-aminophenol	LLE	GC/ECD	0.02	No	No	Rovesta
Bentazone	LLE	GC/MS	0.01	No	Yes	Rovesta
Desmedipham	LLE	GC/MS	0.02	No	No	Rovesta
Dimethoat	LLE	GC/MS	0.01	No	Yes	Rovesta
EHPC	LLE	GC/MS	0.02	No	No	Rovesta
Ethofumesate	LLE	GC/MS	0.01	No	Yes	Rovesta
ETU	LLE	GC/MS	0.01	No	Yes	Miljøkemi
Fenpropimorph	LLE	GC/MS	0.01	No	Yes	Rovesta
Fenpropimorphic acid	SFE	GC/MS	0.02	No	No	Rovesta
Flamprop (free acid)	LLE	GC/MS	0.01	No	No	Rovesta
Flamprop-M-isopropyl	LLE	GC/MS	0.01	No	No	Rovesta
Fluazifop-P (free-acid)	LLE	GC/MS	0.02	No	No	Rovesta
Glyphosate	[1)]	GC/MS	0.01		Yes	Miljøkemi
Linuron	LLE	GC/MS	0.01	No	Yes	Rovesta
Metamitron	LLE	GC/MS	0.02	No	Yes	Rovesta
Metamitron-desamino	SFE	GC/MS	0.02	No	No	Rovesta
Metribuzin	LLE	GC/MS	0.01	No	Yes	Rovesta
Metribuzin-desamino-diketo	LLE	GC/MS	0.02	No	No	Rovesta
Metribuzin-desamino	SFE	GC/MS	0.02	No	No	Rovesta
Metribuzin-diketo	LLE	GC/MS	0.02	No	No	Rovesta
Metsulfuron-methyl	LLE	GC/MS	0.02	No	Yes	Rovesta
MHPC	LLE	GC/MS	0.02	No	No	Rovesta
Pendimethalin	LLE	GC/MS	0.01	No	Yes	Rovesta
Phenmedipham	LLE	GC/MS	0.01	No	No	Rovesta
Pirimicarb	LLE	GC/MS	0.01	No	Yes	Rovesta
Pirimicarb-desmethyl	LLE	GC/MS	0.02	No	No	Rovesta
Pirimicarb-desmethyl-formamido	LLE	GC/MS	0.02	No	No	Rovesta
Propiconazole	LLE	GC/MS	0.01	No	Yes	Rovesta
Triasulfuron	LLE	GC/MS	0.02	No	No	Rovesta
Triazinamin	SFE	GC/MS	0.02	No	No	Rovesta
Triazinamin-methyl	SFE	GC/MS	0.01	No	No	Rovesta

[1)] *The water sample was first adjusted to pH 2 and subsequently concentrated following a two-step ion exchange and derivatization procedure*

Table A2.1 Methods of pesticide analysis applied at Jyndevad and Faardrup.

Site	Pesticide	Extraction	Detection	Detection limit (µg/l)	Accredited by DANAK	Approved by Danish EPA	Laboratory
Jyndevad							
	Triazinamin-methyl	SFE	LC/MS	0.02	No	No	Miljøkemi
	Fenpropimorph	SFE	LC/MS	0.01	Yes	Yes	Miljøkemi
	Fenpropimorphic acid	SFE	LC/MS	0.01	No	No	Miljøkemi
	Propiconazole	SFE	LC/MS	0.01	Yes	Yes	Miljøkemi
	AMPA	[1)]	GC/MS	0.01	No	Yes	Miljøkemi
	Glyphosate	[1)]	GC/MS	0.01	No	Yes	Miljøkemi
	Pyridate	SFE	LC/MS	0.02	No	No	Miljøkemi
	Desethylterbuthylazine	SFE	LC/MS	0.01	Yes	Yes	Miljøkemi
	Terbuthylazine	SFE	LC/MS	0.01	Yes	Yes	Miljøkemi
	PHPC	SFE	LC/MS	0.02	No	No	Miljøkemi
	Bromoxynil	SFE [2)]	GC/MS	0.01	No	Yes	Miljøkemi
	Ioxynil	SFE [2)]	GC/MS	0.01	No	Yes	Miljøkemi
	Fenpropimorph	SFE [2)]	GC/MS	0.01	No	Yes	Miljøkemi
	Fenpropimorphic acid	SFE [2)]	GC/MS	0.01	No	No	Miljøkemi
	Fluroxypyr-acid	SFE [2)]	GC/MS	0.01	No	No	Miljøkemi
Faardrup							
	AMPA	[1)]	GC/MS	0.01		Yes	Miljøkemi
	Glyphosate	[1)]	GC/MS	0.01		Yes	Miljøkemi
	Pirimicarb	SFE [2)]	GC/MS	0.01	No	Yes	Miljøkemi
	Pirimicarb-desmethyl	SFE [2)]	GC/MS	0.01	No	No	Miljøkemi
	Pirimicarb-desmethyl-formamido	SFE [2)]	GC/MS	0.02	No	No	Miljøkemi
	Propiconazole	SFE [2)]	GC/MS	0.01	No	Yes	Miljøkemi
	Ethofumesate	SFE [2)]	GC/MS	0.01	No	Yes	Miljøkemi
	Metamitron	SFE	LC/MS	0.01	Yes	Yes	Miljøkemi
	Metamitron-desamino	SFE	LC/MS	0.01	No	No	Miljøkemi
	Fluazifop-P (free acid)	SFE [2)]	GC/MS	0.01	No	No	Miljøkemi
	Fluazifop-P-butyl	SFE [2)]	GC/MS	0.01	No	No	Miljøkemi
	Desmedipham	SFE	LC/MS	0.01	No	No	Miljøkemi
	Phenmedipham	SFE	LC/MS	0.01	No	No	Miljøkemi
	MHPC	SFE	LC/MS	0.02	No	No	Miljøkemi
	EHPC	SFE	LC/MS	0.02	No	No	Miljøkemi

[1)] *The water sample was first adjusted to pH 2 and subsequently concentrated following a two-step ion exchange and derivatization procedure*

[2)] *The extract volume was methylated with diazomethane*

Table A3.1 Management practice at Tylstrup. The active ingredients of the various pesticides are indicated in parentheses.

Date	Management practice
19.11.98	Ploughing – 20 cm depth
04.05.99	Potatoes planted – cultivar Dianella
25.05.99	Herbicide application – 1.0 l/ha Afalon (linuron)
25.05.99	Herbicide application – 0.2 kg/ha Sencor WG (metribuzin)
27.05.99	Tracer application – 30 kg/ha potassium bromide
07.06.99	Herbicide application – 0.15 kg/ha Sencor WG (metribuzin)
11.06.99	Insecticide application – 0.3 l/ha Karate (lambda-cyhalothrin)
22.06.99–14.09.99	10 fungicide applications – each comprising 2.0 kg/ha Dithane DG (mancozeb)
12.09.99	Irrigation – 33 mm/ha
20.10.99	Potatoes harvested (tuber yield 475 hkg/ha, 24% dry matter)
22.10.99	Disc harrowed – 6 cm depth
01.11.99	Harrowed – 3 cm depth
11.11.99	Harrowed – 5 cm depth
25.11.99	Harrowed – 7 cm depth
17.03.00	Ploughed – 20 cm depth
24.03.00	Rolled with a concrete roller
28.03.00	Fertilization – 124 kg N/ha, 18 kg P/ha and 59 kg K/ha
29.03.00	Spring barley sown – cultivar Bartok
13.05.00	Herbicide application – 0.02 kg/ha Logran 20 WG (triasulfuron)
19.06.00	Fungicide application – 1.0 l/ha Tilt Top (propiconazole + fenpropimorph)
19.06.00	Insecticide application – 0.25 l/ha Pirimor G (pirimicarb)
07.07.00	Irrigation – 31 mm/ha
21.08.00	Harvest of spring barley (grain yield 73.3 hkg/ha; 85% dry matter. Straw yield 28.6 hkg/ha; 100% dry matter)
14.09.00	Ploughing – 25 cm depth
01.10.00	Winter rye sown – cultivar Dominator
02.11.00	Herbicide application – 2 tablets/ha Express (tribenuron-methyl)
02.11.00	Herbicide application – 2.0 l/ha Stomp SC (pendimethalin)
14.05.01	Fungicide application – 0.5 l/ha Tilt Top (propiconazole + fenpropimorph)
31.05.01	Irrigation – 23 mm/ha
13.06.01	Fungicide application – 0.5 l/ha Tilt Top (propiconazole + fenpropimorph)
21.06.01	Irrigation – 21 mm/ha
28.08.01	Winter rye harvested (grain yield 63.6 hkg/ha; 85% dry matter. Straw yield 36.0 hkg/ha; 100% dry matter)

Table A3.2 Management practice at Jyndevad. The active ingredients in the various pesticides are indicated in parentheses.

Date	Management practice
10.03.99	Rotary cultivated – 5 cm depth
10.03.99	Ploughed – 20 cm depth
15.03.99	Rolled with a concrete roller
25.03.99	Spring barley sown – cultivar Alexis
20.04.99	Fertilization – 49 kg N/ha (ammonium nitrate limestone)
22.04.99	Fertilization – 17 kg P/ha and 87 kg K/ha
07.05.99	Fertilization – 85 kg N/ha (ammonium nitrate limestone)
10.05.99	Herbicide application – 0.015 kg/ha of Logran 20 WG (triasulfuron)
29.05.99	Irrigation – 31 mm/ha
09.08.99	Spring barley harvested (grain yield 47.7 hkg/ha; 85% dry matter. Straw yield 40.3 hkg/ha; 100% dry matter)
22.09.99	Herbicide application – 2.0 l/ha of Roundup 2000 (glyphosat)
05.10.99	Rotary cultivated – 5 cm depth
11.10.99	Ploughed – 20 cm depth
11.10.99	Rolled with a concrete roller
13.10.99	Winter rye sown – cultivar Dominator
12.11.99	Tracer application – 30.0 kg/ha of potassium bromide
12.11.99	Herbicide application – 0.0075 kg/ha of Express (tribenuron-methyl)
04.04.00	Fertilization – 115 kg N/ha, 16 kg P/ha and 55 kg K/ha
05.04.00	Fungicide application – 0.5 l/ha of Tilt Top (propiconazole + fenpropimorph)
05.05.00	Irrigation – 29 mm/ha
07.06.00	Fungicide application – 0.5 l/ha of Tilt Top (propiconazole + fenpropimorph)
09.08.00	Spring barley harvested (grain yield 56.2 hkg/ha; 85% dry matter. Straw yield 38.1 hkg/ha; 100% dry matter)
24.04.01	Cattle slurry applied – 49 tonnes/ha, 68 kg total-N/ha, 34 kg P/ha and 196 kg K/ha
26.04.01	Ploughing – 20 cm depth
30.04.01	Maize sown – cultivar Loft
30.04.01	Fertilization – 59 kg/ha (ammonia nitrate)
30.04.01	Fertilization – 21 kg N/ha and 40 kg P/ha
14.05.01	Fungicide application – 1.5 l/ha Lido (terbuthylazine + pyridate)
30.05.01	Fungicide application – 1.5 l/ha Lido (terbuthylazine + pyridate)
01.10.01	Maize harvested (cob yield 84.4 hkg/ha, 100% dry matter. Stalk yield 67.0 hkg/ha 100% dry matter)

Table A3.3 Management practice at Silstrup. The active ingredients in the various pesticides is indicated in parentheses.

Date	Management practice
19.04.00	Fertilization – Cattle slurry 36.5 tonnes/ha. 150 kg total-N/ha, 36 kg P/ha and 162 kg K/ha
19.04.00	Ploughing – 22 cm depth
04.05.00	Fodder beat sown – cultivar Kyros
15.05.00	Fertilization – 103 kg N/ha, 26 kg P/ha and 78 kg K/ha
22.05.00	Herbicide application – 1 l/ha Goltix WG and 1 l/ha Betanal Optima (metamitron, phenmedipham, desmedipham and ethofumesate)
22.05.00	Tracer application – 30 kg/ha potassium bromide
15.06.00	Herbicide application 1 l/ha Goltix WG and 1 l/ha Betanal Optima (metamitron, phenmedipham, desmedipham and ethofumesate)
28.06.00	Herbicide application – 1.5 l/ha Fusilade X-tra (fluazifop-P-butyl)
05.07.00	Insecticide application – 0.3 kg/ha Pirimor G (pirimicarb)
12.07.00	Herbicide application – 1 l/ha Goltix WG and 1 l/ha Betanal Optima (metamitron, phenmedipham, desmedipham and ethofumesate)
15.11.00	Fodder beet harvested (beet yield 134.5 hkg/ha; 100% dry matter)
01.04.01	Ploughing – depth 18 cm
08.05.01	Fertilization – 91 kg N/ha, 13 kg P/ha and 34 K kg/ha
09.05.01	Spring barley sown – cultivar Otira
22.05.01	Fertilization – 27 kg N/ha, 4 kg P/ha and 10 kg K/ha
09.06.01	Herbicide application – 2 tablets/ha Express (tribenuron-methyl)
21.06.01	Herbicide application – 3 l/ha Barnon Plus 3 (flamprop-M-isopropyl)
21.06.01	Fungicide application – 0.5 l/ha Tilt Top (propiconazole + fenpropimorph)
04.07.01	Fungicide application – 0.5 l/ha Tilt Top (propiconazole + fenpropimorph)
05.09.01	Spring barley harvested (grain yield 74.8 hkg/ha; 85% dry matter. Straw yield 28.6 hkg/ha 100% dry matter)

Table A3.4 Management practice at Estrup. The active ingredients in the various pesticides are indicated in parentheses.

Date	Management practice
11.04.00	Ploughing – depth 22 cm
12.04.00	Spring barley sown – cultivar Barke
27.04.00	Fertilizer application – 131 kg N/ha, 19 kg P/ha and 63 kg K/ha
15.05.00	Herbicide application – 1 tablet/ha Ally (metsulfuron-methyl)
15.05.00	Application of 2 l/ha manganese sulphate
15.05.00	Tracer application – 30 kg/ha potassium bromide
31.05.00	Herbicide application – 3.0 l/ha Barnon Plus 3 (flamprop-M-isopropyl)
07.06.00	Application of 2 l/ha manganese sulphate
15.06.00	Fungicide application – 0.5 l/ha Tilt Top (propiconazole + fenpropimorph)
15.06.00	Insecticide application – 0.4 l/ha Perfection 500 S (dimethoat)
05.07.00	Fungicide application – 0.5 l/ha Tilt Top (propiconazole + fenpropimorph)
05.07.00	Insecticide application – 0.4 l/ha Perfection 500 S (dimethoat)
28.08.00	Spring barley harvested (grain yield 52.6 hkg/ha; 85% dry matter. Straw yield 13.1 hkg/ha; 100% dry matter)
13.10.00	Herbicide application – 4.0 l Roundup Bio (glyphosate)
23.10.00	Ploughing – depth 20 cm
01.05.01	Fertilizer application – 20 kg P/ha and 105 kg K/ha
02.05.01	Peas sown – cultivar Julia
22.05.01	Herbicide application – 1.0 l/ha Basagran 480 (bentazone)
22.05.01	Herbicide application – 1.5 l/ha Stomp (pendimethalin)
27.06.01	Insecticide application – 0.25 kg/ha Pirimor G (pirimicarb)
22.08.01	Peas harvested (seed yield 51.8 hkg/ha; 86% dry matter)

Table A3.5 Management practice at Faardrup. The active ingredients in the various pesticides are indicated in parentheses.

Date	Management practice
11.08.99	Herbicide application – 2.0 l/ha Roundup 2000 (glyphosate)
10.09.99	Stubble harrowed – 10 cm depth
19.09.99	Ploughed – 20 cm depth
19.09.99	1st seed bed preparation – with power harrow, 5 cm depth
20.09.99	2nd seed bed preparation – with power harrow, 5 cm depth
20.09.99	Winter wheat sown – cultivar Stakado
05.10.99	Tracer application – 30 kg/ha potassium bromide
14.10.99	Herbicide application – 1.0 l/ha Briotril (ioxynil and bromoxynil)
21.03.00	Fertilization – 70 kg N/ha, 10 kg P/ha and 25 kg K/ha
08.04.00	Herbicide application – 0.8 l/ha Starane 180 (fluroxypyr)
19.04.00	Fertilization – 99 kg N/ha, 14 kg P/ha and 36 kg K/ha
05.05.00	Fungicide application – 0.5 l/ha Tilt Top (propiconazole + fenpropimorph)
31.05.00	Fungicide application – 0.5 l/ha Tilt Top (propiconazole + fenpropimorph)
19.06.00	Insecticide application – 0.25 l/ha Pirimor G (pirimicarb)
28.08.00	Winter wheat harvested (grain yield 92.7 hkg/ha; 85% dry matter. Straw yield 76.2 hkg/ha; 100% dry matter,)
04.10.00	Herbicide application – 2.0 l/ha Roundup 2000 (glyphosate)
16.10.00	Ploughing – depth 20 cm
02.05.01	Fertilization – 110 kg N/ha, 21 kg P/ha and 63 kg K/ha
02.05.01	Sugar beet sown – cultivar Havana
21.05.01, 30.05.01 & 15.06.01	Herbicide application – 1 l/ha Goltix WG and 1.5 l/ha Betanal Optima (metamitron, phenmedipham, desmedipham and ethofumesate)
21.06.01	Herbicide application – 1.5 l/ha Fusilade X-tra (fluazifop-P-butyl)
17.07.01	Insecticide application – 0.3 l/ha Pirimor G (pirimicarb)
24.10.01	Sugar beet harvested (beet yield 147.9 hkg/ha; 100% dry matter)

Table A3.6 Management practice at Slaeggerup. The active ingredients in the various pesticides are indicated in parentheses.

Date	Management Practice
05.04.00	Ploughing – depth 22 cm
07.04.00	Fertilization – 81.8 kg N/ha, 20.5 kg P/ha and 61.4 kg K/ha
08.04.00	Spring barley sown – cultivar Optic
09.05.00	Herbicide application – 1 bag/ha Ally (metsulfuron-methyl)
05.06.00	Herbicide application – 3.0 l/ha Barnon Plus 3 (flamprop-M-isopropyl)
09.06.00	Fungicide application – 0.5 l/ha Tilt Top (propiconazole + fenpropimorph)
09.06.00	Pesticide application – 0.6 l/ha Perfection 500 (dimethoat)
14.06.00	Herbicide application – 2 tablets/ha Express (tribenuron-methyl)
26.06.00	Fungicide application – 0.5 l/ha Tilt Top (propiconazole + fenpropimorph)
22.08.00	Spring barley harvested (grain yield 39.8 hkg/ha; 85% dry matter. Straw yield 10.2 hkg/ha; 100% dry matter)
20.11.00	Ploughing – depth 22 cm
11.04.01	Peas sown – cultivar Pinocchio
01.05.01	Fertilization – 7.5 kg P/ha and 39.3 kg K/ha
01.05.01	Herbicide application – 1.0 l/ha Basagran 480 (bentazone)
01.05.01	Herbicide application – 1.5 l/ha Stomp SC (pendimethalin)
01.07.01	Insecticide application – 0.25 kg/ha Pirimor G (pirimicarb)
19.08.01	Peas harvested (seed yield 26.6 hkg/ha; 86% dry matter)

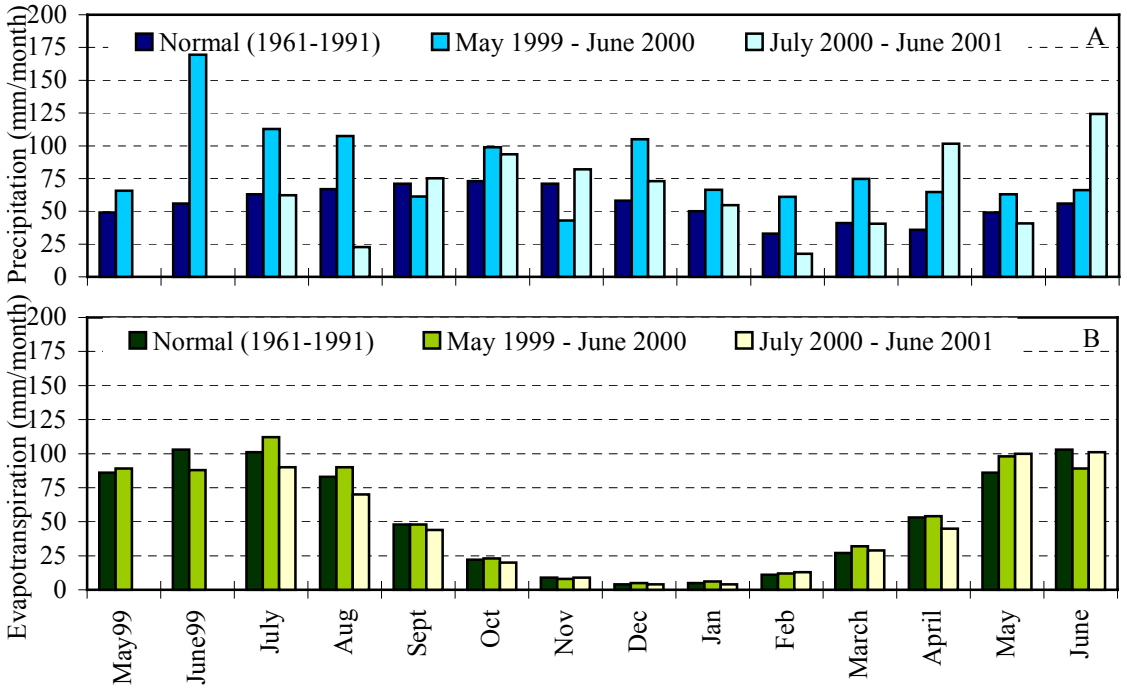

Figure A4.1. Monthly precipitation measured 1.5 above ground (A) and potential evapotranspiration (B) at Tylstrup for the monitoring period May 1999–June 2001. Normal values (1961–1990) compared to locally measured (precipitation) or calculated (evapotranspiration).

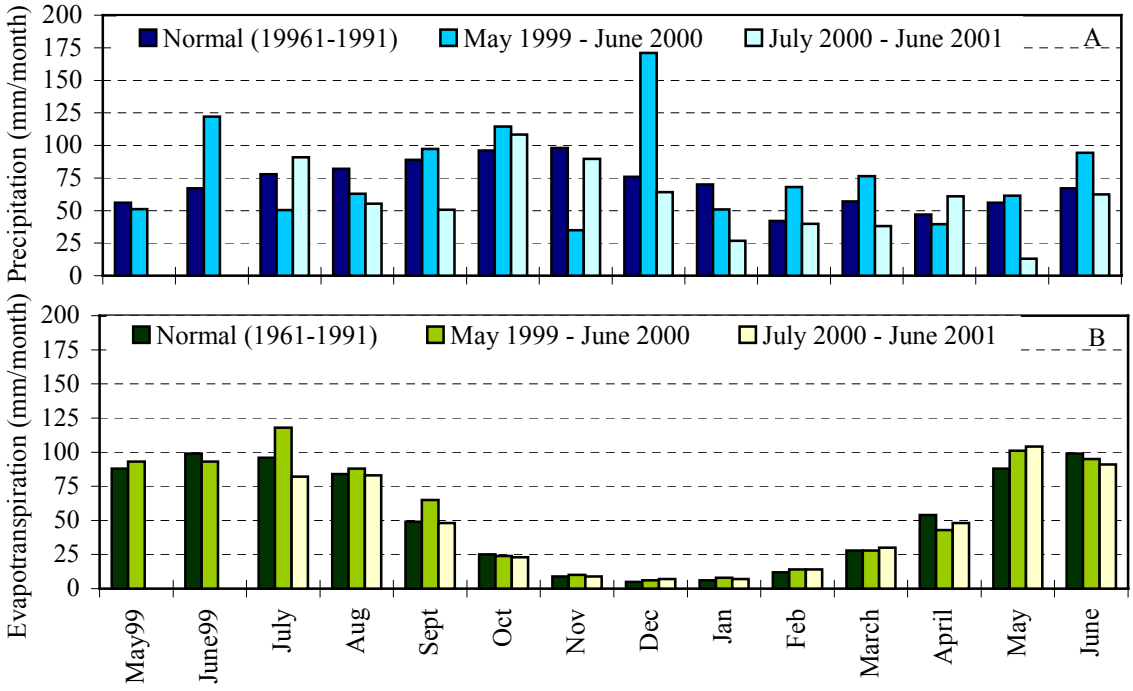

Figure A4.2. Monthly precipitation measured 1.5 above ground (A) and potential evapotranspiration (B) at Jyndevad for the monitoring period May 1999–June 2001. Normal values (1961–1990) compared to locally measured (precipitation) or calculated (evapotranspiration).

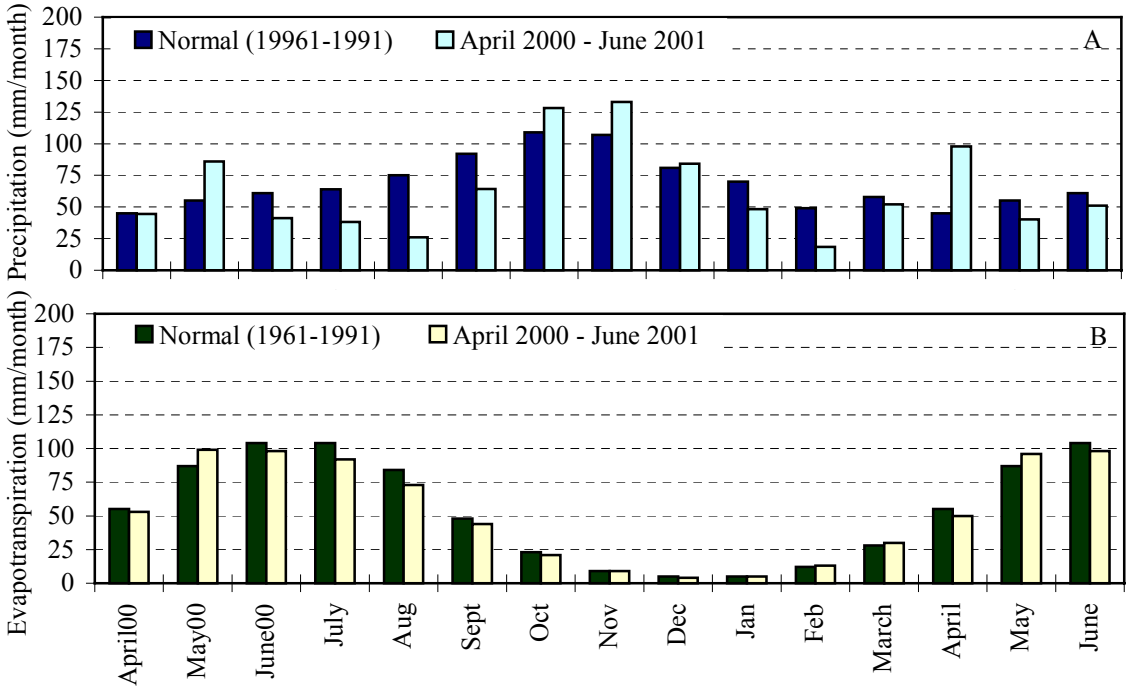

Figure A4.3. Monthly precipitation measured 1.5 m above ground (A) and potential evapotranspiration (B) at Silstrup for the monitoring period April 2000–June 2001. Normal values (1961–1990) compared to locally measured (precipitation) or calculated (evapotranspiration).

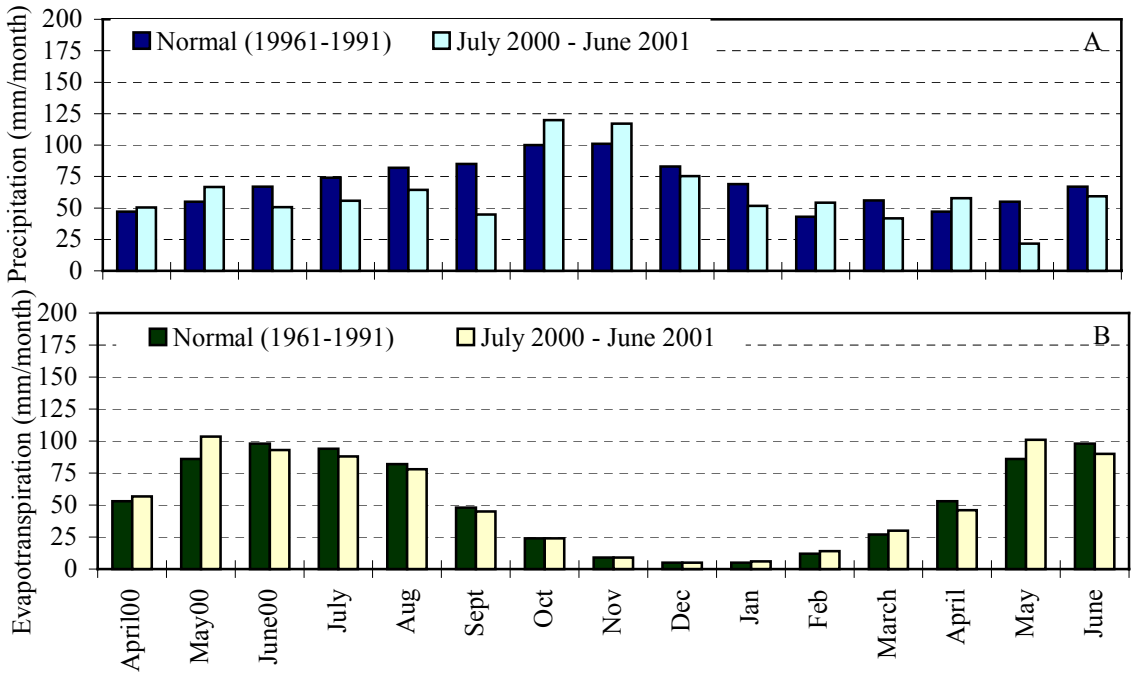

Figure A4.4. Monthly precipitation measured 1.5 above ground (A) and potential evapotranspiration (B) at Estrup for the monitoring period June 2000- June 2001. Normal values (1961–1990) compared to locally measured (precipitation) or calculated (evapotranspiration).

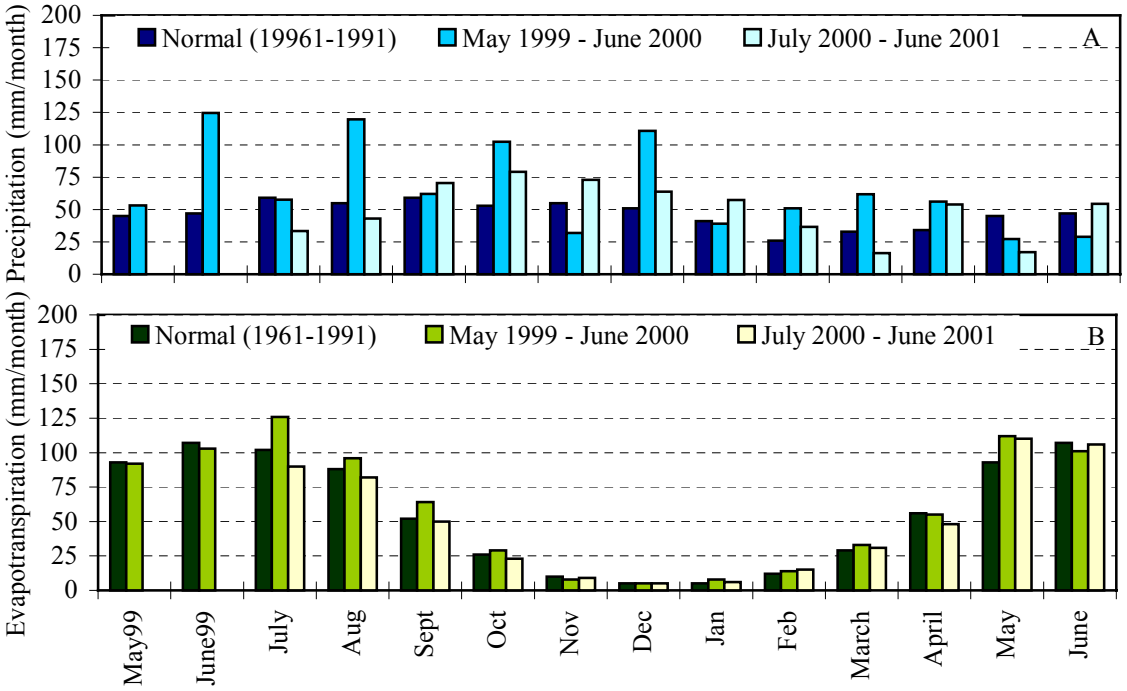

Figure A4.5. Monthly precipitation measured 1.5 above ground. (A) and potential evapotranspiration (B) at Faardrup for the monitoring period May 1999–June 2001. Normal values (1961–1990) compared to locally measured (precipitation) or calculated (evapotranspiration).

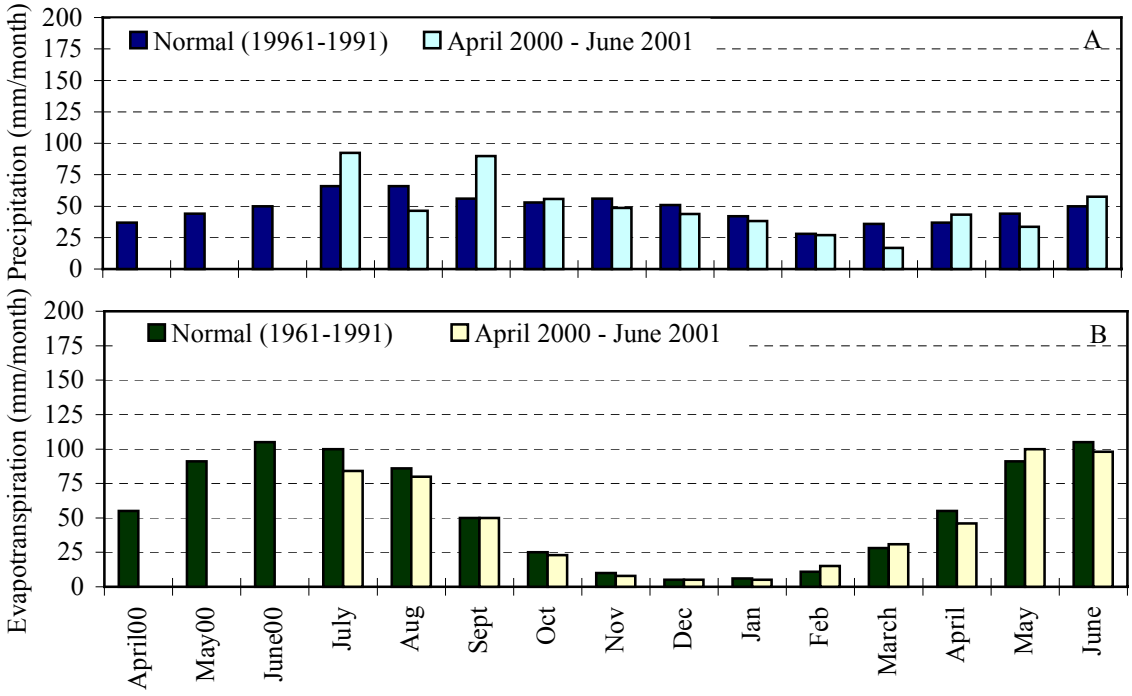

Figure A4.6. Monthly precipitation measured 1.5 above ground (A) and potential evapotranspiration (B) at Slaeggerup for the monitoring period April 2000–June 2001. Normal values (1961–1990) compared to locally measured (precipitation) or calculated (evapotranspiration).

The MACRO model is a one-dimensional physically based numerical model for water flow and reactive solute transport in structured soils (Jarvis, 2000). The model describes coupled unsaturated-saturated non-steady state water flow in cropped soils including lateral flow to field drains. The model is a dual-permeability model dividing the flow field into two separate domains, each characterized by a degree of saturation, conductivity, flux and solute concentration. No assumptions of macropore geometry are made, and any variability of the properties thus has to be lumped into effective parameters representative of the actual scale. The model is further described in Jarvis (2000).

The model has been applied to each of the six field sites covering the soil profile to a depth of 5 m b.g.s., always including the groundwater table. Wherever possible, field and laboratory observed data on physical and hydraulic properties characterizing the sites were used as input to the model, with literature values being used for the remaining parameters (primarily the mass transfer coefficient and crop-related parameters).

Discretization: The soil profile is divided into the maximum permitted 22 increments covering the three (four at Estrup) main horizons described in the pedological profiles (Lindhardt *et al.*, 2001). The increment thickness ranges from 2 cm at the surface to 50 cm below 1.5 m. Each horizon is characterized by 4–10 increments having the same soil hydraulic properties. To increase the stability of the numerical scheme, the increments are thinnest when the horizons change.

Meteorological data: The driving variables are daily precipitation, daily maximum and minimum temperatures and daily potential evapotranspiration. The precipitation is measured on site, whereas the temperature data are from DIAS meteorological stations located 1–3 km from each test site. The potential evapotranspiration is calculated using a modified Makkink equation (Aslyng and Hansen, 1982). The potential evapotranspiration is defined as the evapotranspiration from well-growing short grass adequately supplied with water. Potential evapotranspiration and locally measured precipitation are shown in Appendix 2 on a monthly basis for the two monitoring periods.

Initial conditions: The initial conditions in terms of soil water content and soil temperature were assessed from previous simulations. A spin-up period of 5 years was applied before any results were evaluated, leaving the initial conditions less important**.**

Boundary conditions: The bottom boundary condition is an empirical approach where a deep percolation rate is given as a function of the water table height in the soil profile. This is one of two possible boundary conditions allowing a fluctuating water table in the profile. The flow is controlled by an empirical coefficient, which seems to be related to the hydraulic conductivity of the soil. This parameter was assessed through calibration.

Dispersive properties: Solute transport parameters (e.g. diffusion coefficient, dispersivity and mixing depth) were set to the default values in the model. These parameters were not subjected to any calibration.

Crop parameters: The parameters characterizing the crop development derives from the MACRO crop database available on
http://arno.ei.jrc.it:8181/focus/models/MACRO/download.html.

Agricultural management: Information about crop type, date of emergence, date of harvest and irrigation were registered at the six fields (Appendix 3). The bromide tracer was applied as an irrigation event with a known high concentration of bromide. The amount of irrigation is calculated from the amount of bromide applied at the site and the measured concentration in the applied water. No tracer has been applied at Slaeggerup.

Drainage parameters: The parameters characterizing the drainage system (drain depth and spacing) are specified for the four clayey sites. According to Lindhardt *et al.* (2001), drain spacing ranges from 13 to 18 m. The drain depth typically varies across the field, and it is therefore difficult to represent this by one soil column. The drain depth is found by calibration with a resulting depth of 1 to 1.3 m b.g.s.

Soil hydraulic properties: In MACRO, the soil hydraulic properties (soil retention and unsaturated conductivity curves) for each horizon is described by two sets of equations representing the relationships in either the macropores or the matrix, see Table A5.1. The equations are based on effective saturations defined in the table.

Table A5.1 Equations describing unsaturated hydraulic conductivity and retention curves in MACRO

	Matrix	Macropores
Effective saturation	$S_{mi} = \frac{\theta_{mi} - \theta_r}{\theta_b - \theta_r}$	$S_{ma} = \frac{\theta_{ma}}{\theta_s - \theta_b}$
Soil water retention curve	$\psi_{mi} = \psi_b S_{mi}^{-\frac{1}{\lambda}}$	$\psi(\theta)$ is not required, gravity flow is assumed
Unsaturated hydraulic conductivity curve	$K_{mi} = K_b S_{mi}^{n+2+\frac{2}{\lambda}}$	$K_{ma} = K_{s(ma)} S_{ma}^{n^*}$

S_{mi} and S_{ma} are effective saturation in matrix and in macropores, respectively
θ_s and θ_r are saturated and residual water content, respectively
θ_{mi} and θ_{ma} are the water content in matrix and in macropores, respectively.
θ_b is the boundary soil water content, when matrix is saturated but the macropores empty
ψ_{mi} is the soil water tension in matrix
ψ_b is the boundary soil water tension when matrix is saturated but the macropores empty
λ is the pore size distribution factor in matrix (from Brooks and Corey's formulation)
K_{mi} and K_{ma} are the hydraulic conductivity in matrix and in macropores, respectively
$K_{s(ma)}$ is the saturated hydraulic conductivity when the soil is fully saturated
K_b is the boundary hydraulic conductivity when matrix is saturated but the macropores are empty
n and n are the tortuosity factor in matrix and in macropores, respectively*

Each site is represented by one soil column divided into 3–4 horizons. Spatial variability within the field was aggregated and accounted for in effective parameter values assessed from measured data. Measured data for θ_s, K_s, γ (soil bulk density) were available from each horizon. Measurements are made on several soil samples from each horizon from 2–3 pedological profiles described in Lindhardt *et al.* (2001). Measured data for tension, unsaturated conductivity and soil water content were subsequently fitted with the parameter-estimating program RETC (version 6.0) in order to retrieve the remaining parameters (λ, θ_r). Measured data and parameterized curves of the hydraulic conductivity function and retention are illustrated in Figure A5.2–A5.7.

In MACRO the total porosity is partitioned into macropores and matrix at a given water content and tension (θ_b and ψ_b), characterized by a 'boundary' hydraulic conductivity K_b (see Figure A5.1). The boundary is defined as the water content or tension where matrix is fully saturated and the macropores empty. It is difficult to identify this 'boundary' in experimental data. To estimate these model parameters it is thus assumed that the boundary soil water tension ψ_b is equivalent to the air entry pressure estimated when fitting the Brooks and Corey formulation of the retention curve to the measured data. Assuming that (θ_b, ψ_b) lies on the fitted retention curve, corresponding estimates of the boundary water content θ_b is generated once ψ_b is determined, see Figure A3.1.

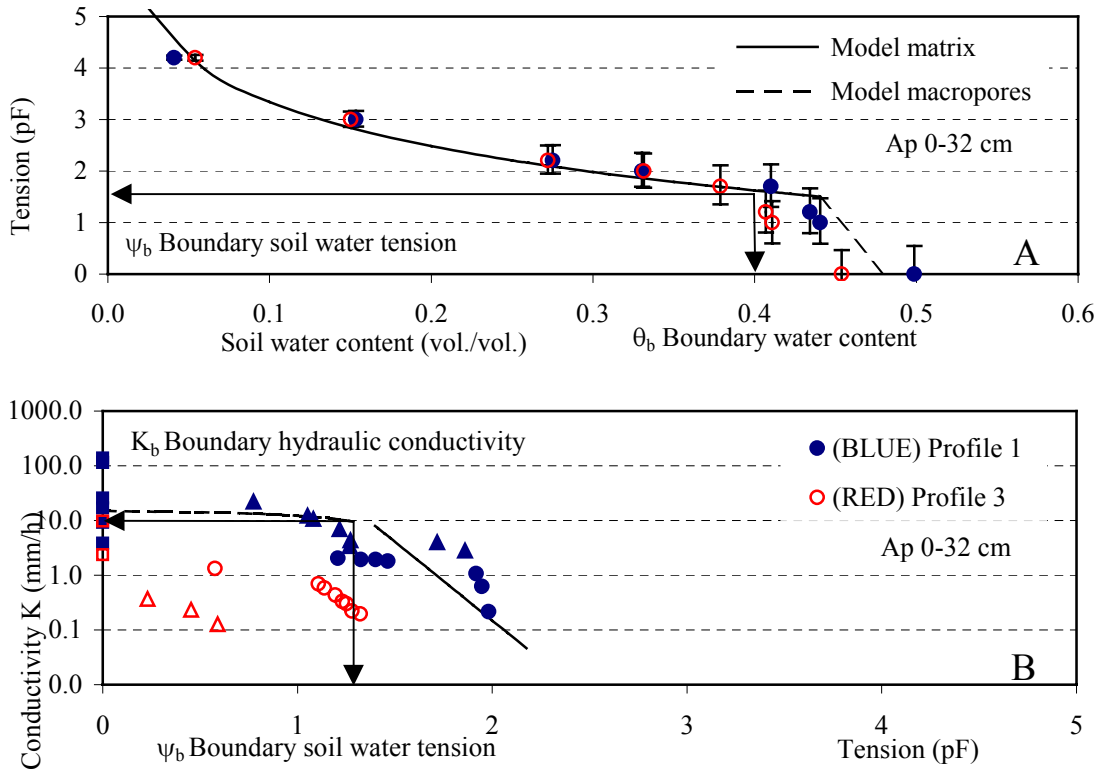

Figure A5.1 Measured and modelled soil hydraulic conductivity and retention curves at Tylstrup.

The experimental data indicated that preferential flow was virtually absent at the two sandy soils. The boundary hydraulic conductivity K_b was therefore assumed to be 50% of the measured saturated hydraulic conductivity K_s. The parameter α related to the water and

solute exchange between the matrix and the macropores was set to 1, which corresponds to a very rapid (equilibrium) exchange limiting the effect of macropore flow.

At the four clayey sites the boundary hydraulic conductivity K_b was identified as the point where the unsaturated hydraulic conductivity rose steeply towards the measured saturated conductivity K_s. The parameter α related to the water and solute exchange between the matrix and the macropores was set to 20 in all three horizons. This corresponds to the value suggested in the clay scenario (Langvad) used by the Danish EPA in their procedure for pesticide registration in Denmark.

The tortuosity factor n in the matrix is set to 0.5, as suggested by the Mualem (1976) approach of determining unsaturated hydraulic conductivity from the Brooks and Corey retention function. The tortuosity factor/pore size distribution index in the macropores n* varies from 6 at the sandy sites (representing a soil with a wide macropore size distribution and large tortuosity) to 3–4 at the clayey sites, which have larger and well-structured macropore/fracture systems.

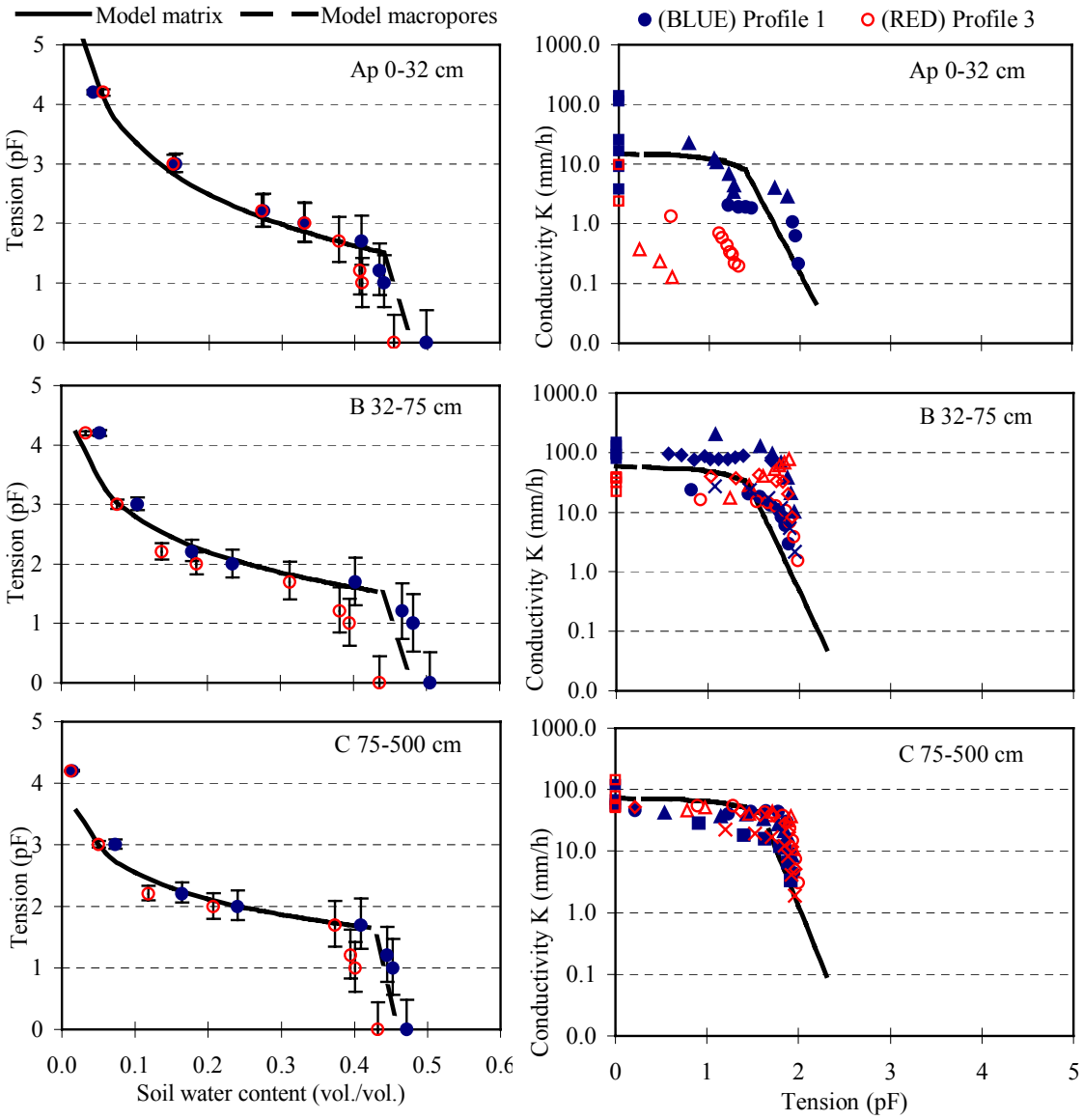

Figure A5.2 Measured (points) and fitted (solid line) retention and unsaturated conductivity curves in the A, B and C horizons at Tylstrup. The points represent data from two pedological profiles. Each point in the retention curve represents an average of 9 measurements. The bars indicate the standard deviation.

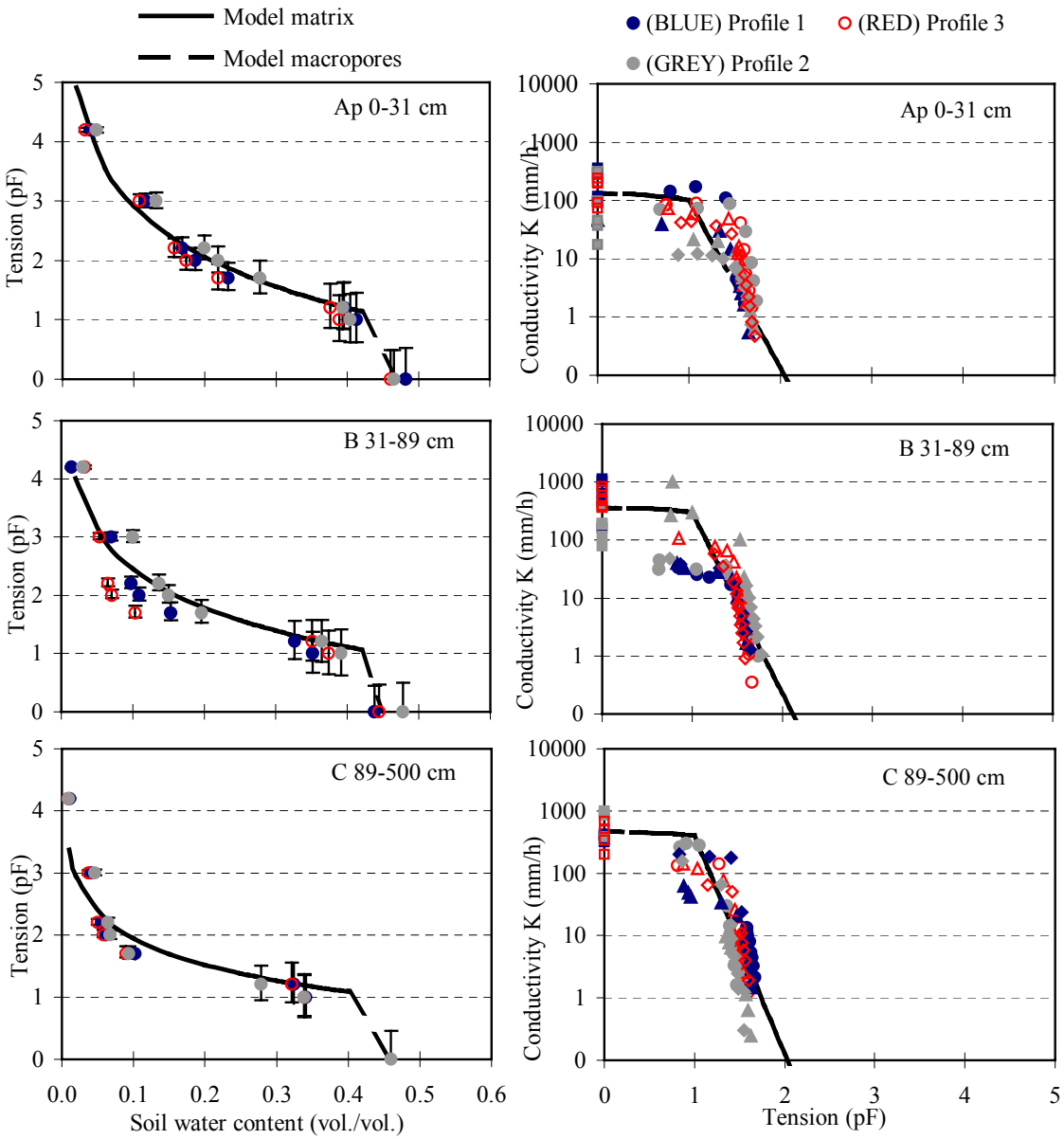

Figure A5.3 Measured (points) and fitted (lines) retention (left) and unsaturated conductivity curves (right) in the A, B and C horizons at Jyndevad. The points represent data from three pedological profiles. Each point in the retention curve represents an average of 9 measurements. The bars indicate the standard deviation.

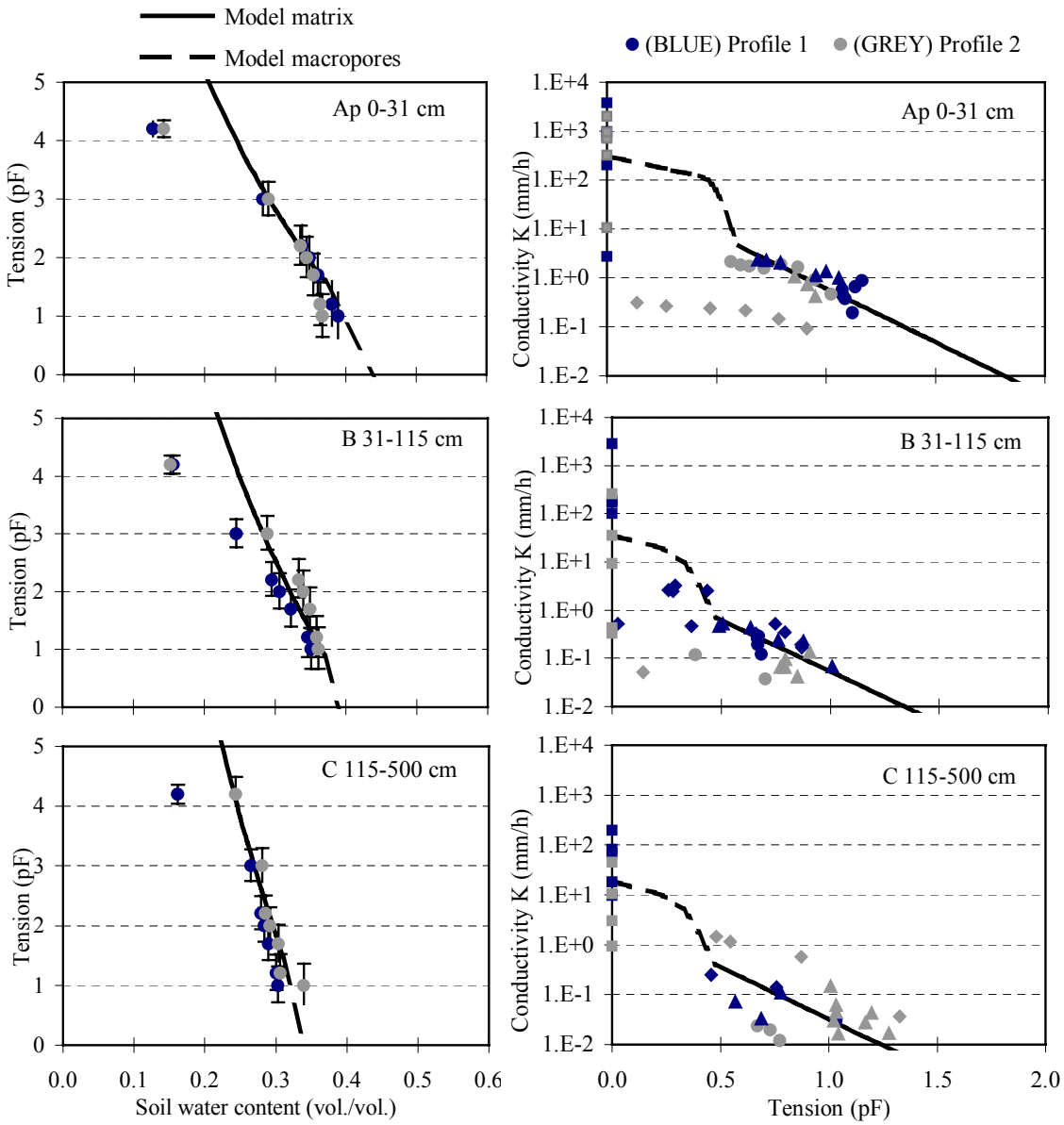

Figure A5.4 Measured (points) and fitted (lines) retention (left) and unsaturated conductivity curves (right) in the A, B and C horizons at Silstrup. The points represent data from two pedological profiles. Each point in the retention curve represents an average of 9 measurements. The bars indicate the standard deviation.

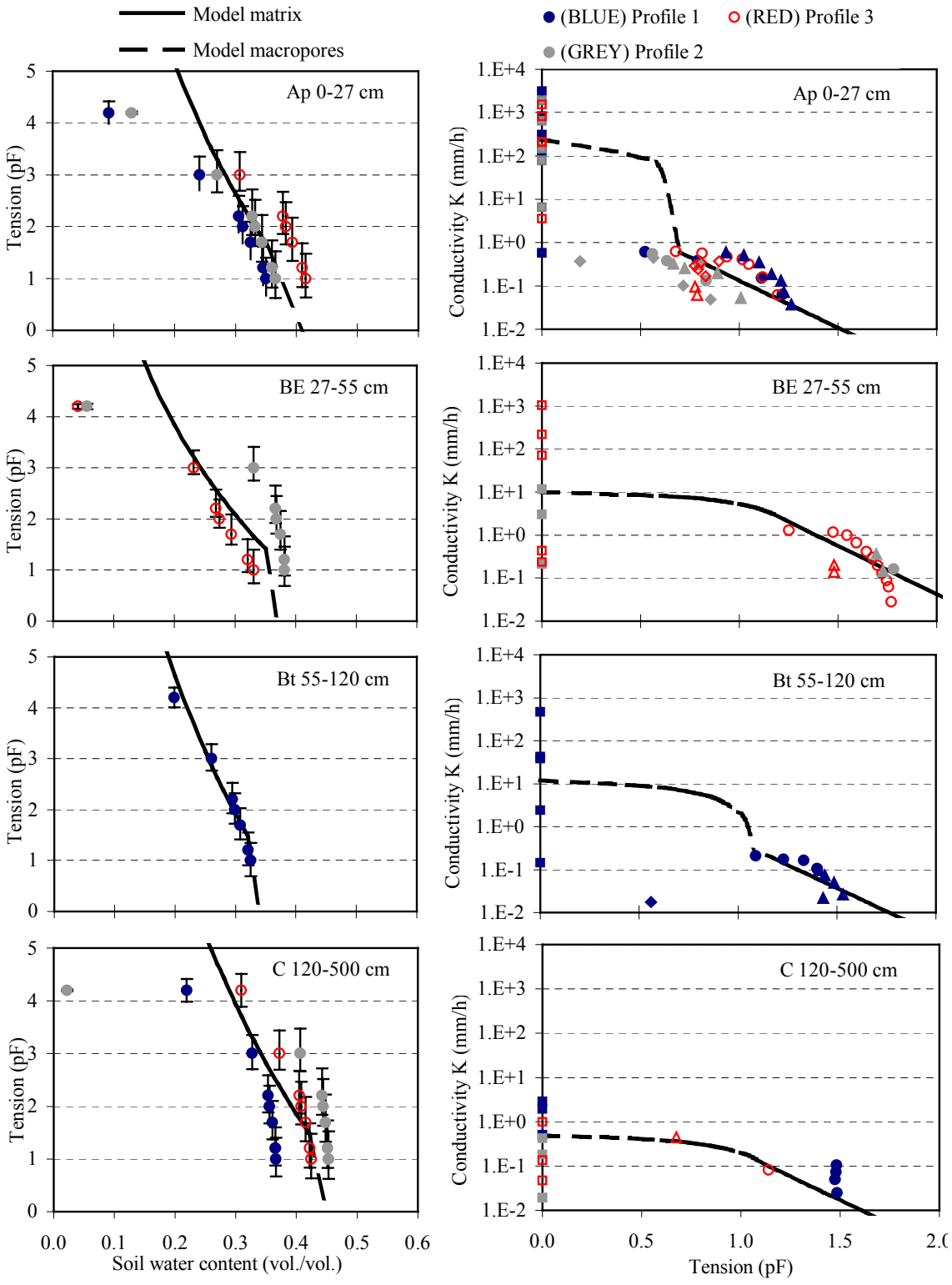

Figure A5.5 Measured (points) and fitted (lines) retention (left) and unsaturated conductivity curves (right) in the A, BE-, Bt- and C horizons at Estrup. The points represent data from three pedological profiles. Each point in the retention curve represents an average of 9 measurements. The bars indicate the standard deviation.

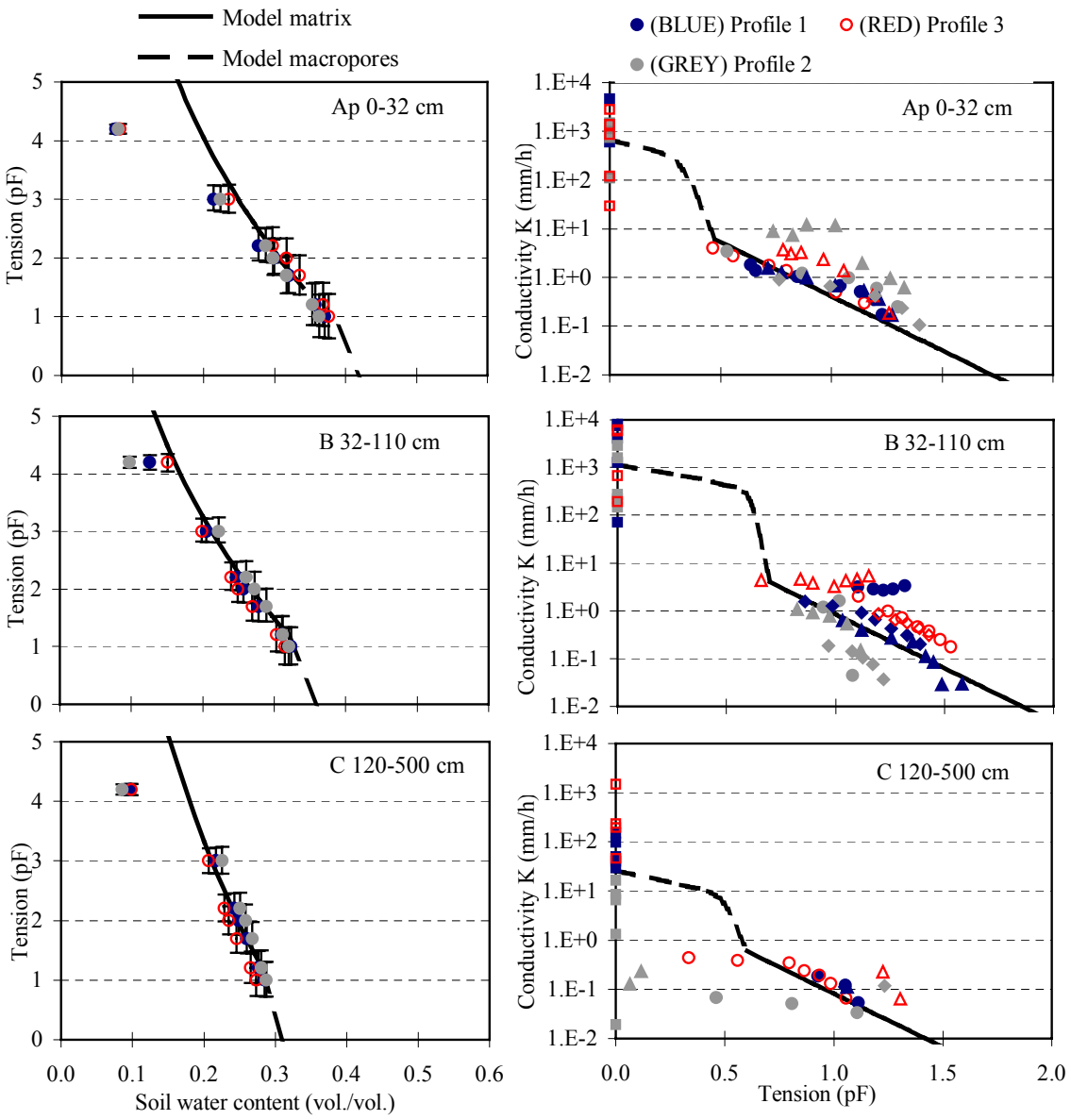

Figure A5.6 Measured (points) and fitted (lines) retention (left) and unsaturated conductivity curves (right) in the A, B and C horizons at Faardrup. The points represent data from three pedological profiles. Each point in the retention curve represents an average of 9 measurements. The bars indicate the standard deviation.

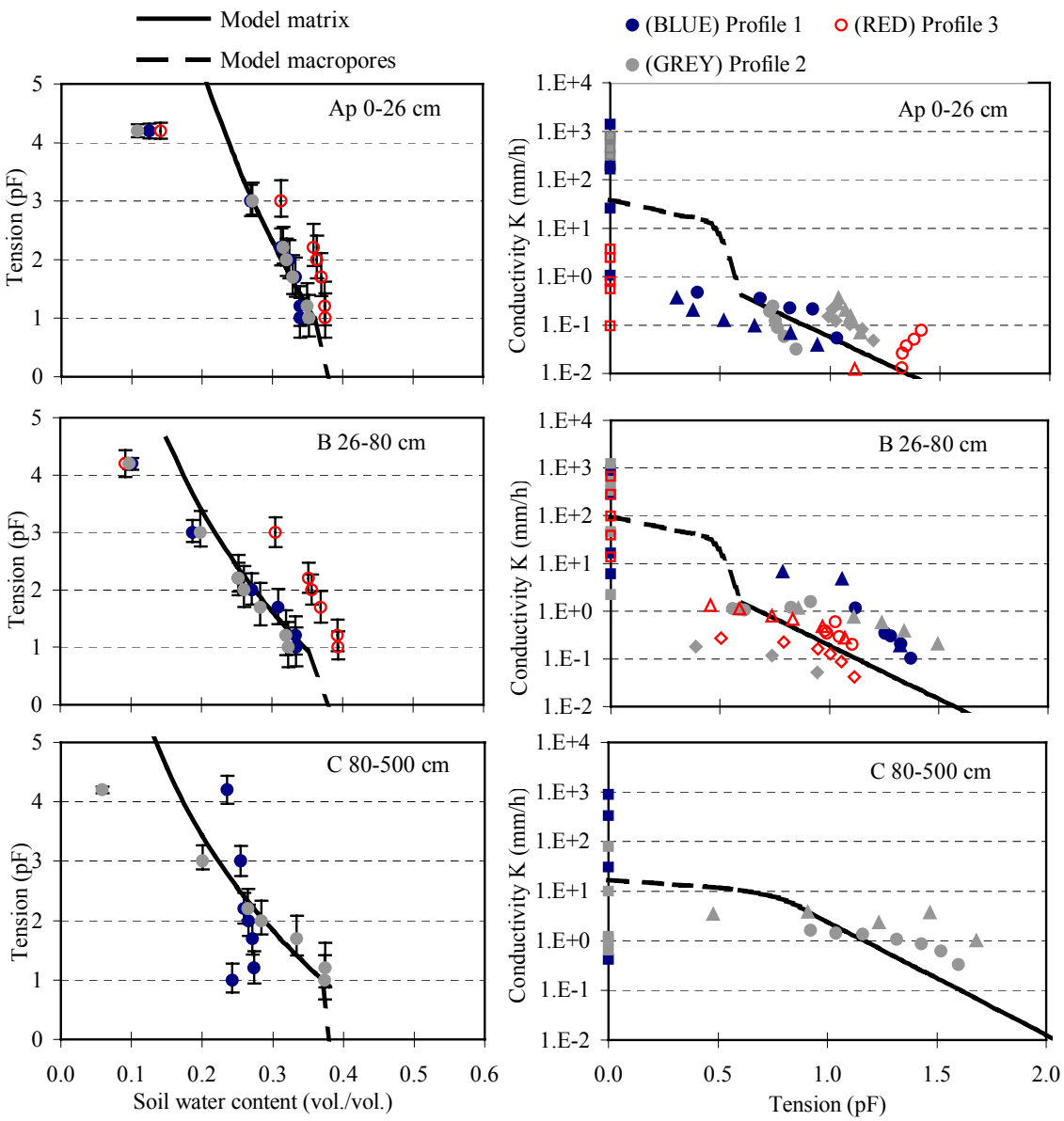

Figure A5.7 Measured (points) and fitted (lines) retention (left) and unsaturated conductivity curves (right) in the A, B and C horizons at Slaeggerup. The points represent data from three pedological profiles. Each point in the retention curve represents an average of 9 measurements. The bars indicate the standard deviation.

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.*

Table A6.1 Estimated percolation rate (Perc.) and measured concentration of metribuzin-diketo (MD) and metribuzin-desamino-diketo (MDD). 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	MDD (µg/l) C_i	MD (µg/l) C_i	Date t_i	Perc. (mm) P_i	MDD (µg/l) C_i	MD (µg/l) C_i
23.08.99	86	na	na	23.08.99	86	na	na
09.09.99	44	*	*	09.09.99	44	*	<0.2
04.11.99	87	*	<0.2	04.11.99	117	*	<0.2
08.12.99	82	0.25	0.22	10.01.00	138	0.25	0.08
10.01.00	87	0.72	0.62	03.02.00	49	0.23	0.11
03.02.00	47	2.05	0.39	02.03.00	57	0.23	0.07
02.03.00	57	2.10	0.17	06.04.00	43	0.20	0.14
06.04.00	43	1.96	0.50	10.05.00	11	0.21	0.09
10.05.00	11	1.39	na	07.06.00	11	0.21	<0.02
07.06.00	11	1.06	0.48	03.10.00	34	0.11	0.09
03.10.00	1	0.28	0.15	05.12.00	149	0.30	0.12
31.10.00	87	0.10	0.17	04.01.01	60	0.24	0.08
05.12.00	188	0.11	0.01	07.02.01	36	0.37	0.10
30.04.01	73	0.74	0.20	06.03.01	14	0.30	0.11
30.05.01	14	0.56	0.18	03.04.01	13	0.42	0.12
				30.04.01	56	0.66	0.23
1.7.99–30.6.00		**0.91–1.0**	**0.25–0.35**	**1.7.99–1.7.00**		**0.14–0.27**	**0.05–0.11**
1.7.00–30.6.01		**0.28**	**0.11**	**1.7.00–1.7.01**		**0.34**	**0.12**

**) Degradation product detected in the range of 0.05–0.5 µg/l; [na)] not analysed*

The methods of analysis for these degradation products were developed during the present project. Results are consequently 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 from 1.6.99–23.8.99. The first analyses (October and November) were also subject to some uncertainty due to the high detection limit of 0.2 µg/l. The average concentration for 1999/2000 is therefore given as a range representing the maximum and minimum concentration estimated by applying a concentration equal to either zero or the detection limit.

Table A7.1 Measured pesticide concentrations of metribuzin-desamino-diketo and metribuzin-diketo in the groundwater at Tylstrup.

Monitoring well	M1			M3			M4			M5			M6		
Screen depth (m b.g.s.)	3–4	4–5	5–6	3–4	4–5	5–6	3–4	4–5	5–6	3–4	4–5	5–6	3–4	4–5	5–6
Metribuzin-desamino-diketo															
Apr-99	*	*	***	*						*	*	***	*		
08.12.99										0.08	0.04	0.04	0.07	0.07	0.05
04.01.00										0.06	0.02		0.05	0.06	0.06
03.02.00	0.04	0.03	0.09	0.04	0.03	<	0.03	0.04		0.02	<	<	0.02	0.02	0.02
02.03.00										<	0.02	0.02	0.04	0.05	0.03
06.04.00										<	<	<	0.03	0.02	0.02
10.05.00	0.05	0.02	0.08	<	<	<	0.04	0.04	0.03	<	<	<	<	0.02	0.03
07.06.00										<	<	<	<	0.05	<
01.08.00		0.07	0.06		<	<		0.02	0.02		<	<		<	<
05.09.00								<	<			<			
03.10.00								0.04	0.04		0.06	<		0.05	
31.10.00		0.02	0.03		<	<		<	0.02		0.03	<		0.02	0.03
05.12.00								0.04	0.03		<	0.02		<	0.03
04.01.01							0.02	0.02	0.04	0.04	<	<	<	0.02	0.02
07.02.01	0.03	0.04	0.04	<	<	0.03	<	0.02	0.05	0.02	0.03	<	<	<	0.04
06.03.01							0.02	<	0.03	<	0.02	<	0.03	0.02	0.02
03.04.01							<	<	<		<	<			0.03
30.04.01	0.04	0.06	0.06	<	<	<	0.03	0.03	0.03	<	<	<	0.02	<	0.02
30.05.01							0.03	0.03	0.03	<	<	<	0.02	0.02	0.02
Average	**0.04**	**0.04**	**0.06**	–	–	–	**0.02**	**0.02**	**0.03**	–	–	–	**0.03**	**0.03**	**0.03**
Median	**0.04**	**0.03**	**0.06**	–	–	–	**0.02**	**0.02**	**0.03**	–	–	–	**0.02**	**0.02**	**0.02**
Metribuzin-diketo															
Apr-99	*	*	***	***						*	*	*	*		
08.12.99										<	0.06	0.23	0.33	0.32	0.33
04.01.00										<	<		<	0.13	0.06
03.02.00	0.10	0.07	0.19	0.09	0.12	0.14	0.14	0.17		0.06	0.07	0.10	0.19	0.19	0.20
02.03.00										<	0.03	0.07	0.10	0.10	0.16
06.04.00										<	0.04	0.06	0.10	0.17	0.20
10.05.00	0.06	0.04	0.08	0.08	<	<	0.11	0.08	0.12	<	<	0.08	0.10	0.13	0.09
07.06.00										<	<	<	0.09	0.06	
05.07.00											<	0.07		0.17	0.31
01.08.00		<	0.09		0.09	0.14		<	0.07		0.07	0.08		0.15	0.35
05.09.00											0.06	0.11			0.23
03.10.00								0.13	0.15		0.06	<		0.11	
31.10.00		0.10	0.10		0.11	0.10		0.21	0.20		0.11	0.06		0.14	0.20
05.12.00								0.19	0.55		0.10	0.19		0.39	0.22
04.01.01							0.22	0.25	0.36	0.08	0.10	0.14	0.15	0.19	0.31
07.02.01	0.07	0.13	0.15	0.09	0.10	0.11	0.15	0.16	0.22	0.10	0.07	0.07	0.09	0.15	0.18
06.03.01							0.15	0.14	0.16	<	0.06	0.09	0.06	0.12	0.20
03.04.01							0.14	0.10	0.21		0.07	0.05			0.06
30.04.01	0.16	0.17	0.18	0.17	0.13	0.20	0.22	0.25	0.35	0.10	0.07	0.13	0.08	0.12	0.26
30.05.01							0.09	0.13	0.24	<	0.04	0.08	0.04	0.07	0.14
30.04.01	0.16	0.17	0.18	0.17	0.13	0.20	0.22	0.25	0.35	0.10	0.07	0.13	0.08	0.12	0.26
30.05.01							0.09	0.13	0.24	<	0.04	0.08	0.04	0.07	0.14
Average	**0.11**	**0.10**	**0.14**	**0.12**	**0.10**	**0.13**	**0.15**	**0.16**	**0.25**	**0.04**	**0.06**	**0.09**	**0.10**	**0.15**	**0.20**
Median	**0.10**	**0.10**	**0.15**	**0.09**	**0.11**	**0.14**	**0.14**	**0.15**	**0.22**	**0.01**	**0.06**	**0.08**	**0.09**	**0.13**	**0.20**

*<) Below the detection limit of 0.02 µg/l *) Degradation product was detected in the range 0.05–0.5 µg/l ***) Degradation product was detected in the range 0.1–0.5 µg/l*

The average and median 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). Results from April 1999 refer to an initial screening analysis carried out before PLAP monitoring started.

Appendix 8. Sencor application at Tylstrup

Table A8.1 Sencor application on the Tylstrup test site and neighbouring upstream fields. The positions of the various fields are indicated in the figure below. The direction of groundwater flow is indicated by a red arrow.

Field ID	Year of application	Dosage[1)] (kg Sencor /ha/y)
Tylstrup test site (red field)		
	1990	0.70
	1992	0.50
	1994	0.30
Field 1 [2)]		
	1989	0.70
	1992	0.50
	1994	0.30
	1999	0.35
Field 2	1999	0.35
Field 3	1996	0.50
	2000	0.35
Field 4		No Sencor application
Field 5	1997	0.50
	2001	0.35
Field 6	1998	0.25

[1)] *The maximum permitted dosage was reduced from 0.7 kg/ha/y to 0.35 kg/ha/y in 1994*
[2)] *M6 and M7 are located in this field*

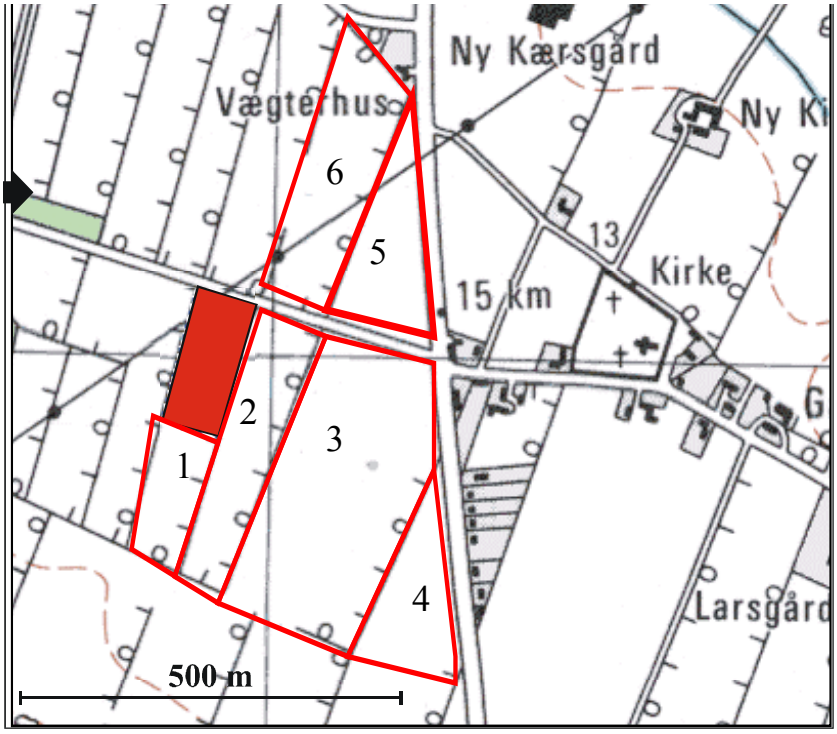

Table A9.1. Sencor application on the Jyndevad test site and neighbouring upstream fields. The positions of the various fields are indicated in the figure below. The direction of groundwater flow is indicated by a red arrow.

Field-ID	Year of application	Dosage (kg Sencor/ha)
N-W	2001	0.35
N-E	2000	0.35
F1	1999	0.35
F2	1998	0.20
F5	1998	0.20
D2	1998	0.20
S2	1998	0.20
Jyndevad PLAP site	1998	0.20
Jyndevad PLAP site	1997	0.30
S1	1997	0.20
S3	1995	0.30
S4	1996	0.35
K-N	1997	0.20

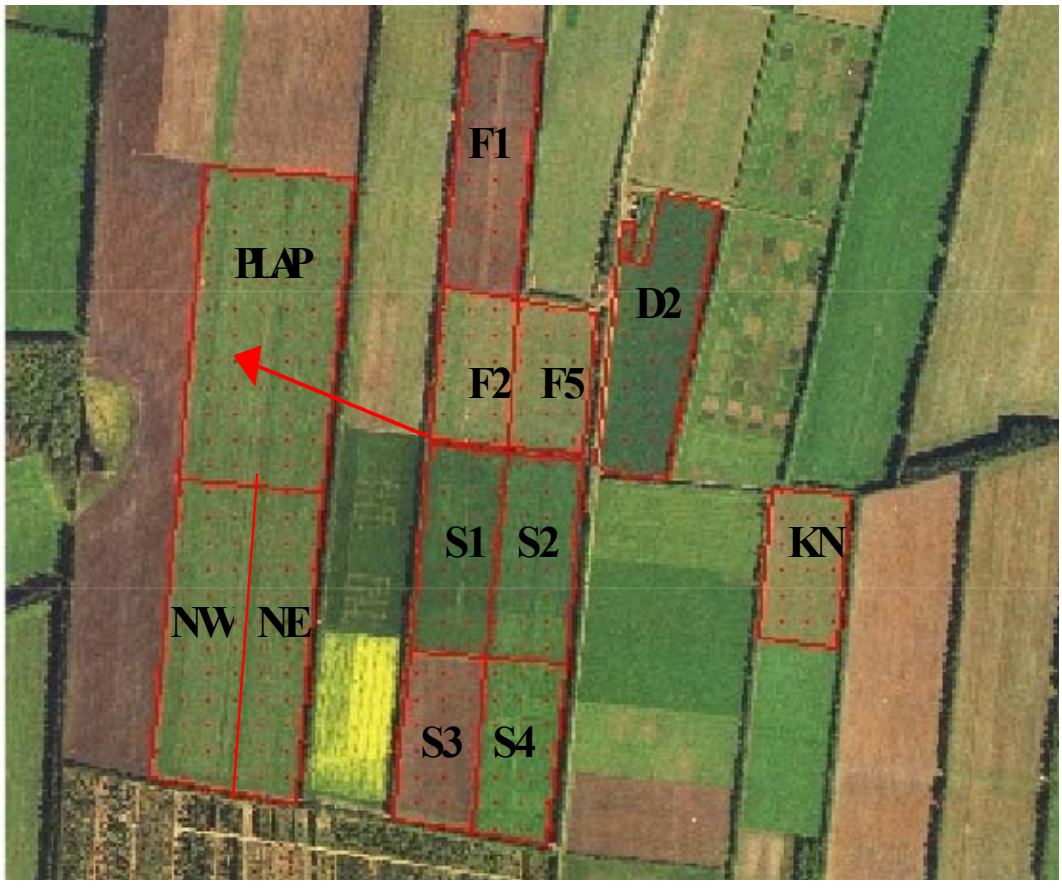

Table A10.1 Concentration of metamitron and metamitron-desamino (µg/l) in the vertical monitoring wells at Silstrup.

Monitoring well		M12				M13			M5				M6				M9			
Screen number		1	2	3	4	1	2	3	1	2	3	4	1	2	3	4	1	2	3	4
Metamitron	06.04.00		<	<	<				<	<	<		<	<	<		<	<	<	
	03.05.00								<	<	<			<	<	<				
	07.06.00								0.17	0.11	<		0.02	<	<					
	04.07.00		<	<	<	<	<	<	0.07	0.02	<		<	<	<		0.06	<	<	
	01.08.00								0.03	<	<			<	<	<				
	05.09.00									<	<	<		<	<	<				
	03.10.00			<	<	<		<		0.01	<	<			<	<			0.01	<
	31.11.00								0.02	0.01	<		<	<	<					
	05.12.00								0.03	0.03	<		<	<	<					
	08.01.01	<	<	<		<	<	<	0.02	0.02	<		<	<	<		<	<	<	
	07.02.01								0.02	<	<		<	<	<					
	06.03.01								0.017	<	<		<	<	<					
	02.04.01	<	<	<		<	<	<	0.028	<			<	<	<		<	<	<	
	08.05.01								<	<	<		<		<	<				
	07.06.01								<	<	<		<	<	<					
Metamitron-desamino	06.04.00		<	<	<				<	<	<		<	<	<		<	<	<	
	03.05.00								<	<	<			<	<	<				
	07.06.00								0.05	0.08	<		<	<	<					
	04.07.00		<	<	<	<	<	<	<	0.04	<		<	<	<		<	<	<	
	01.08.00								<	0.02	<			<	<	0.09				
	05.09.00									<	<	<		<	<	<				
	03.10.00			<	<	0.19		<		<	<	<			<	<			<	<
	31.10.00								<	<	<		<	<	<					
	05.12.00								0.04	<	<		<	<	<					
	08.01.01	<	<	<		<	<	<	0.02	<	<		<	<	<		<	<	<	
	07.02.01								<	<	<		<	<	<					
	06.03.01								<	<		<	<	<	<					
	02.04.01	<	<	<		<	<	<	<	<	<		<	<	<		<	<	<	
	08.05.01								<	<	<		<		<	<				
	07.06.01								<	<	<		<	<	<					

**) 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 for metamitron and 0.02 µg/l for metamitron-desamino

Table A10.2. Concentration of metamitron and metamitron-desamino (µg/l) in the horizontal monitoring wells 3.5 m b.g.s. at Silstrup. The position of the horizontal wells is indicated in Figure 21.

		H1.1	H1.2	H1.3	H2.1	H2.2	H2.3
Metamitron							
	06.04.00	<	<	<	<	<	<
	03.05.00		<			<	
	07.06.00		0.037			<	
	04.07.00	0.028	0.019	<	<	<	<
	01.08.00		0.01			<	
	05.09.00		<			<	
	03.10.00	0.011	<	<	<	<	<
	31.10.00		0.013			<	
	05.12.00		0.02			<	
	08.01.01	<	<	0.018	<	<	<
	07.02.01		<			<	
	02.04.01	<	<	<			
	02.07.01	<	<	<			
Metamitron-desamino							
	06.04.00	<	<	<	<	<	<
	03.05.00		<			<	
	07.06.00		<			<	
	04.07.00	<	<	<	<	<	<
	01.08.00		0.126			0.111	
	05.09.00		<			<	
	03.10.00	<	0.019	<	<	<	<
	31.10.00		<			0.021	
	05.12.00		<			<	
	08.01.01	<	<	0.022	<	<	<
	07.02.01		<			<	
	02.04.01	<	<	<			
	02.07.01	<	<	<			

<) *Below the detection limit of 0.01 µg/l for metamitron and 0.02 µg/l for metamitron-desamino*

Table A10.3 Groundwater concentration (µg/l) of ethofumesate and pirimicarb at Silstrup.

Monitoring well		H1.2	M5	M5
Screen depth (m b.g.s.)		3.5	1.5–2.5	2.5–3.5
Ethofumesate				
	05.12.00		0.02	0.02
	08.01.01		0.01	
	11.09.01	0.02		
Pirimicarb				
	05.12.00		0.01	
	08.01.01		0.01	0.01

Appendix 11. Concentration of glyphosate and AMPA in drainage water at Estrup

Table A11.1 Measured concentration of AMPA and glyphosate in drainage water at Estrup. Drainage runoff refers to the accumulated runoff for each of the analysed samples.

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)
				31.10.00	1.90	0.24	20
08.11.00	0.70	0.11	28	03.11.00	1.80	0.28	14
15.11.00	1.00	0.15	33	12.11.00	1.80	0.35	13
21.11.00	0.17	0.07	27	21.11.00	2.10	0.73	15
28.11.00	0.10	0.04	9				
05.12.00	0.37	0.07	15	05.12.00	0.24	0.12	12
12.12.00	0.24	0.09	15				
19.12.00	0.48	0.20	36	15.12.00	0.92	0.44	21
27.12.00	0.04	0.02	6				
02.01.01	0.04	0.03	1				
09.01.01	0.32	0.20	25	08.01.01	0.44	0.29	13
16.01.01	0.04	0.02	5				
23.01.01	0.03	0.01	1				
30.01.01	0.13	0.08	14	26.01.01	0.43	0.27	7
06.02.01	0.02	0.02	3				
13.02.01	0.25	0.19	36	12.02.01	0.53	0.31	31
20.02.01	0.04	0.03	9				
27.02.01	0.02	0.02	2				
06.03.01	0.02	0.02	0				
13.03.01	0.13	0.10	11	12.03.01	0.19	0.16	9
20.03.01	0.08	0.05	12	20.03.01	0.10	0.08	13
27.03.01	0.01	0.01	3				
03.04.01	0.01	0.01	2				
10.04.01	0.01	0.01	4				
18.04.01	0.01	0.01	1				
24.04.01	0.01	0.01	1				
02.05.01	0.02	0.02	2				
08.05.01	0.01	0.01	1				

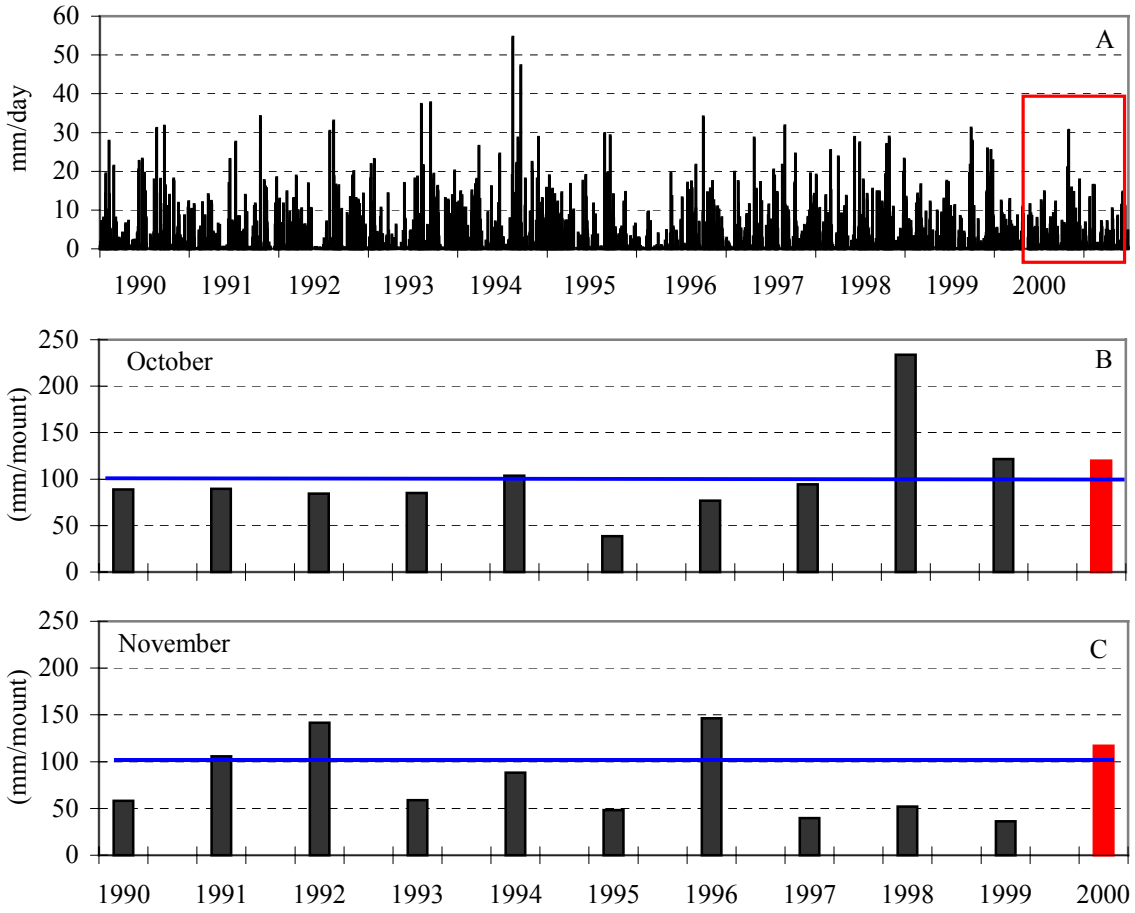

Figure A12.1 Comparison of the precipitation pattern for the current monitoring period (marked in red) and that for the preceding ten years (marked in black). The daily precipitation is compared in A, whereas the monthly precipitation in October and November is compared in B and C, respectively. Data from the monitoring period are marked in red, and the horizontal blue line indicates the monthly normal. Data from the current monitoring period derive from the Estrup test site, whereas data from the preceding ten years derives from the DIAS Askov meteorological station located less than 3 km from the test site. All data refer to precipitation measured at 1.5 m a.g.s.

Appendix 13. Primary data for degradation of fenpropimorph and propiconazole

Table A13.1. Degradation of fenpropimorph in the plough layer soil from Tylstrup, Jyndevad and Faardrup. Samples incubated for up to 240 days. Values are in mg/kg. Initial level 0.500 mg/kg.

Incubation(days)	1	20	30	40	60	80	100	120	180	240
Tylstrup	0.482	0.478	0.461	0.447	0.423	0.404	0.4	0.399	0.365	0.338
Jyndevad	0.484	0.408	0.356	0.329	0.293	0.242	0.23	0.237	0.23	0.235
Faardrup	0.45	0.175	0.13	0.108	0.07	0.05	0.034	0.028	0.024	0.02

Table A13.2. Degradation of fenpropimorph in the subsoil (80–100 cm) from Tylstrup, Jyndevad and Faardrup. Samples incubated for up to 300 days. Values are in mg/kg. Initial level 0.500 mg/kg.

Incubation (days)	6	100	150	200	300
Tylstrup	0.505	0.496	0.487	0.497	0.512
Jyndevad	0.51	0.498	0.504	0.506	0.502
Faardrup	0.5	0.489	0.5	0.504	0.479

Table A13.3. Degradation of propiconazole in the plough layer soil from Tylstrup, Jyndevad and Faardrup incubated for up to 360 days. Values are in mg/kg. Initial level 0.500 mg/kg.

Incubation (days)	2	30	45	60	90	120	150	180	270	360
Tylstrup	0.451	0.435	0.426	0.388	0.355	0.348	0.325	0.321	0.258	0.241
Jyndevad	0.477	0.421	0.389	0.358	0.302	0.282	0.252	0.225	0.194	0.178
Faardrup	0.471	0.372	0.354	0.303	0.255	0.215	0.188	0.15	0.102	0.045

Table A13.4. Degradation of propiconazole in the subsoil (80–100 cm) from Tylstrup, Jyndevad and Faardrup, incubated for up to 300 days. Values are in mg/kg. Initial level 0.500 mg/kg.

Incubation (days)	10	150	224	300
Tylstrup	0.49	0.467	0.463	0.454
Jyndevad	0.51	0.471	0.469	0.47
Faardrup	0.475	0.439	0.4	0.359

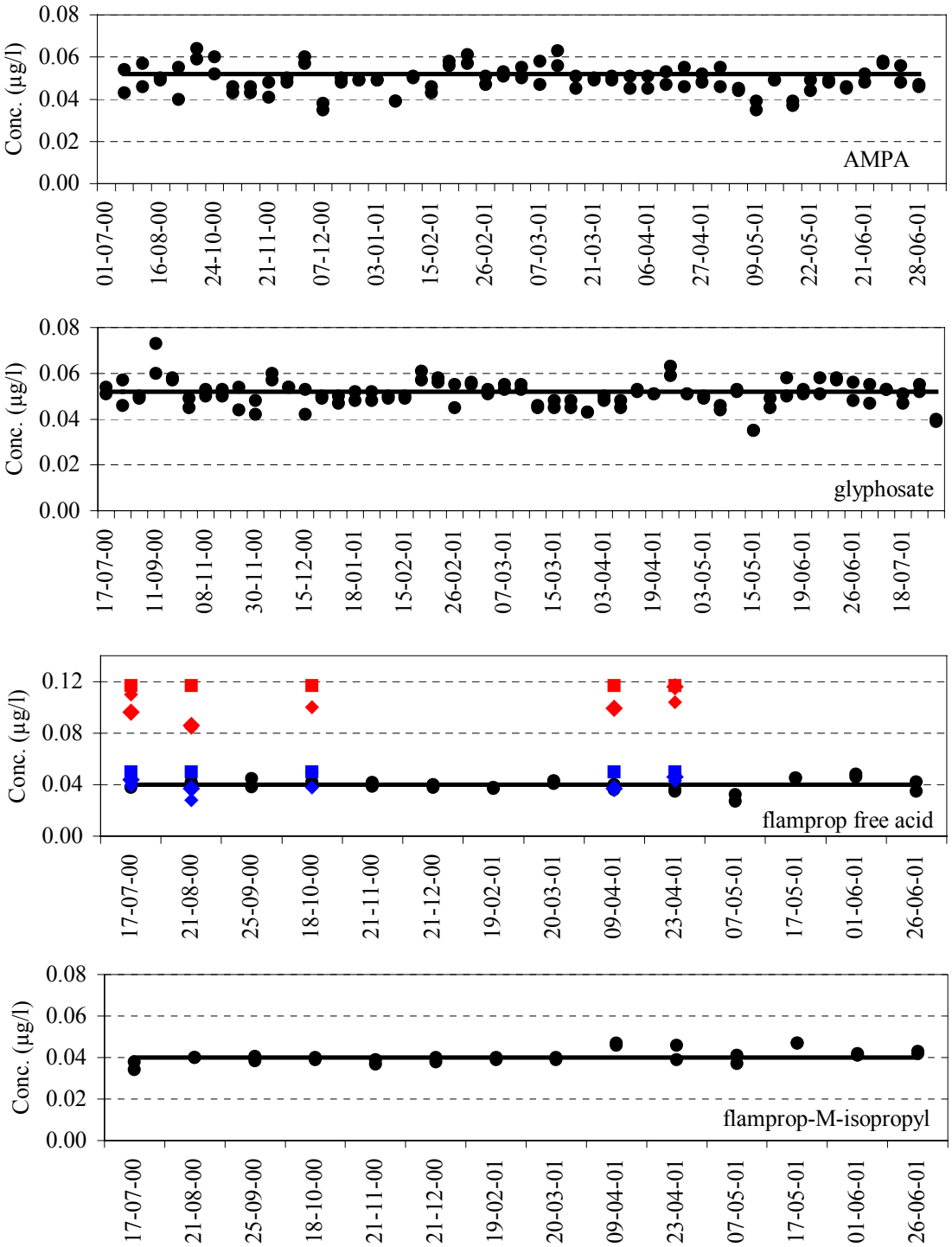

Figure A14.1 Pesticide concentrations in QA samples. The solid line and the closed circles indicate the nominal and observed concentrations, respectively, in internal laboratory controls. The closed red/blue squares indicate the nominal concentrations of the high-level/low-level external control samples. The red/blue diamonds indicate the observed concentrations of the high-level/low-level external control samples.

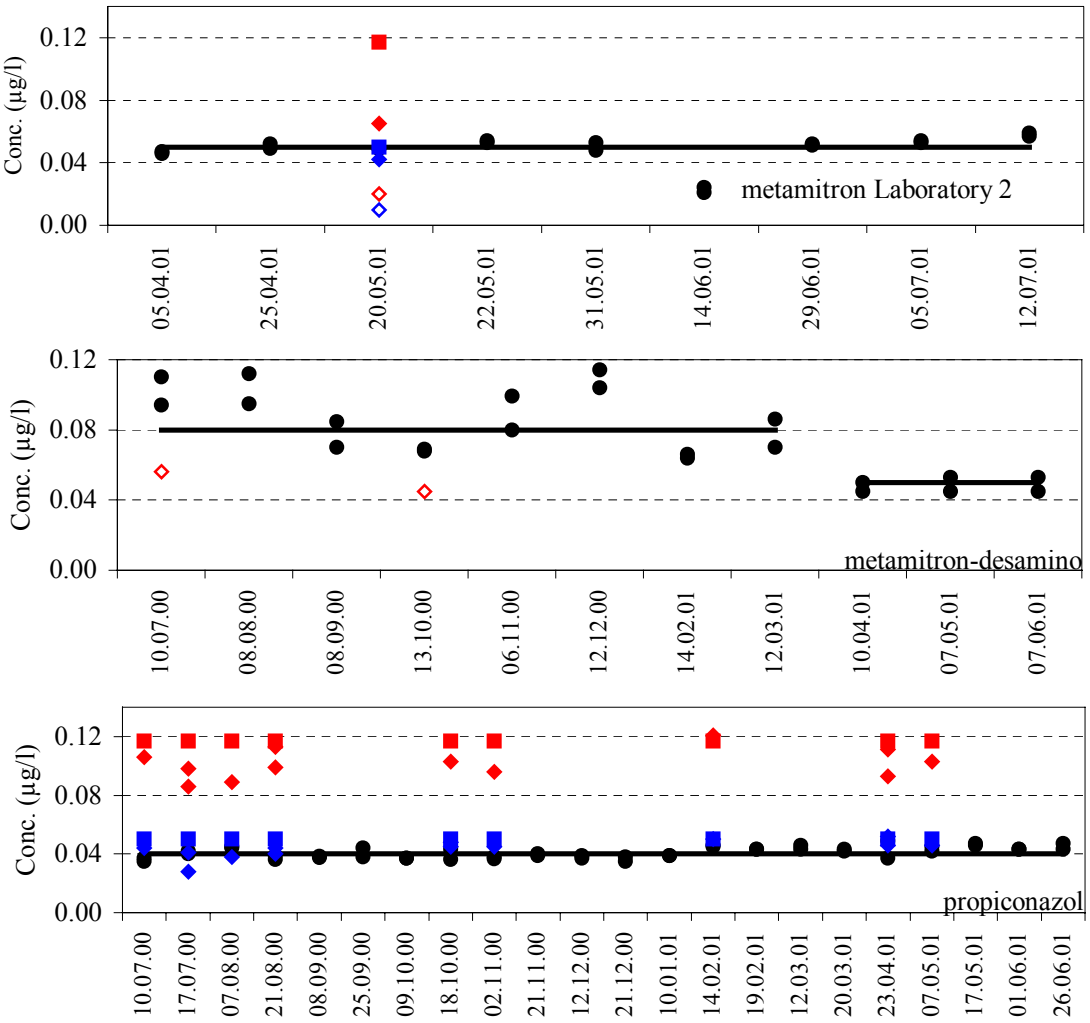

Figure A14.2 Pesticide concentrations in QA samples. The solid line and the closed circles indicate the nominal and observed concentrations, respectively, in internal laboratory controls. The closed red/blue squares indicate the nominal concentrations of the high-level/low-level external control samples. The red/blue diamonds indicate the observed concentrations of the high-level/low-level external control samples. Open diamonds indicate degradation products that are not present in the spike mixture.

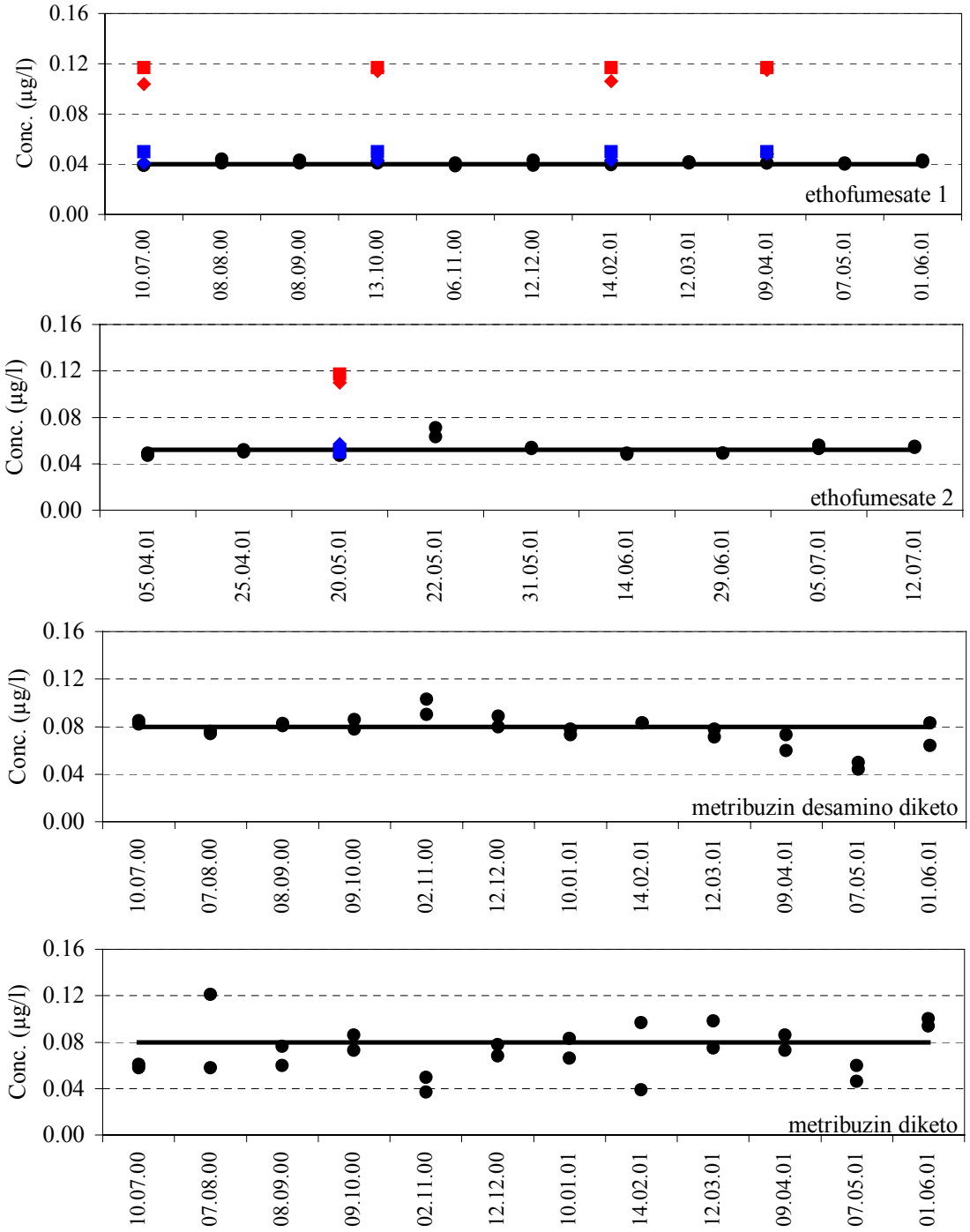

Figure A14.3 Pesticide concentrations in QA samples. The solid line and the closed circles indicate the nominal and observed concentrations, respectively, in internal laboratory controls. The closed red/blue squares indicate the nominal concentrations of the high-level/low-level external control samples. The red/blue diamonds indicate the observed concentrations of the high-level/low-level external control samples.

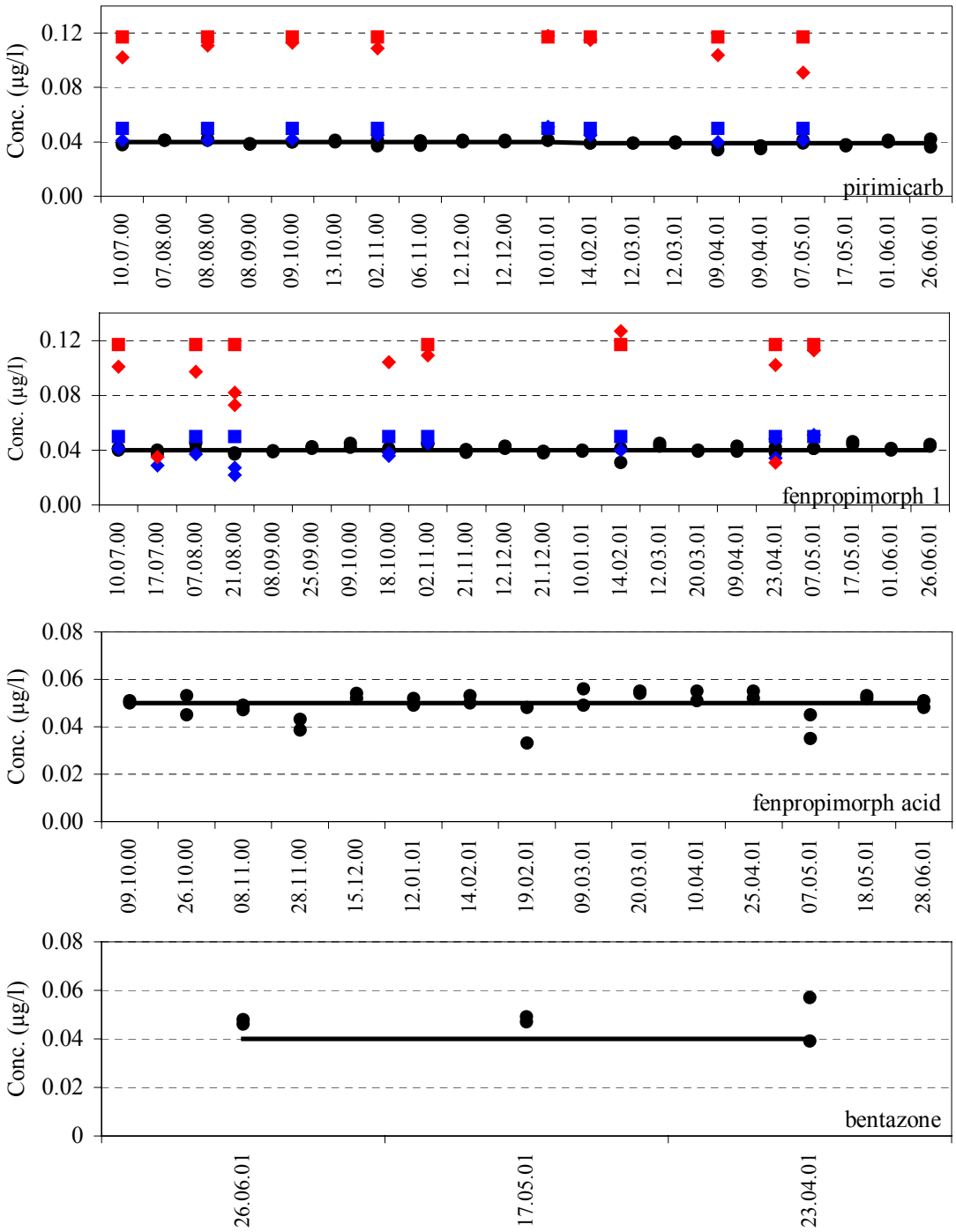

Figure A14.4 Pesticide concentrations in QA samples. The solid line and the closed circles indicate the nominal and observed concentrations, respectively, in internal laboratory controls. The closed red/blue squares indicate the nominal concentrations of the high-level/low-level external control samples. The red/blue diamonds indicate the observed concentrations of the high-level/low-level external control samples.

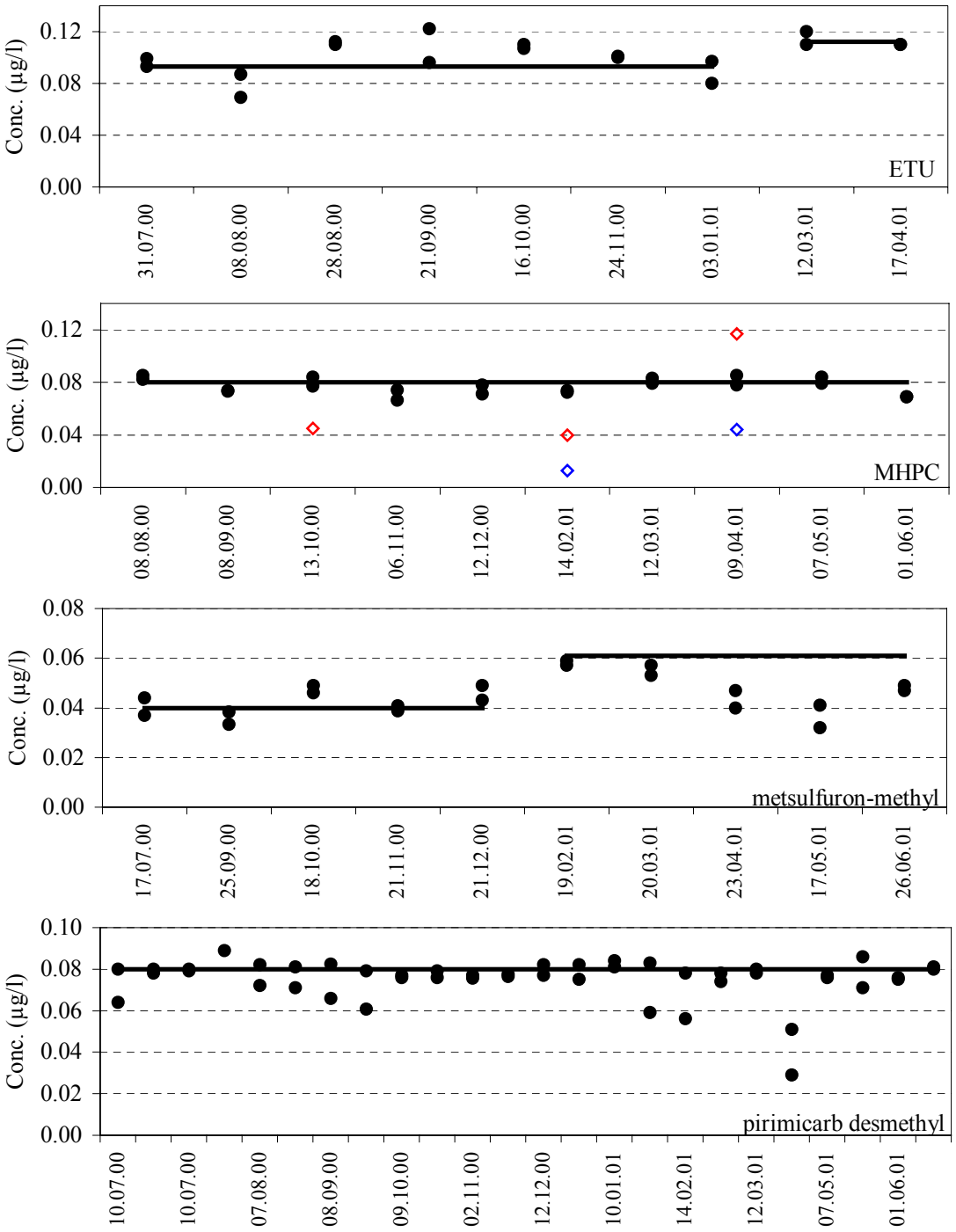

Figure A14.5 Pesticide concentrations in QA samples. The solid line and the closed circles indicate the nominal and observed concentrations, respectively, in internal laboratory controls. The closed red/blue squares indicate the nominal concentrations of the high-level/low-level external control samples. The red/blue diamonds indicate the observed concentrations of the high-level/low-level external control samples. Open diamonds indicate degradation products that are not present in the spike mixture.