

The Danish Pesticide Leaching Assessment Programme

Monitoring results May 1999 - July 2000

Jeanne Kjær, Preben Olsen, Pia Sjelborg, Inge Fomsgaard, Betty Mogensen, Finn Plauborg, Jørgen Ole Jørgensen and Bo Lindhardt.

Geological Survey of Denmark and Greenland
Ministry of Environment and Energy

Danish Institute of Agricultural Sciences
Ministry of Food, Agriculture and Fisheries

National Environmental Research Institute
Ministry of Environment and Energy



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Thoravej 8, DK-2400 Copenhagen, Denmark

Phone: +45 38 14 20 00, fax +45 38 20 50, e-mail: geus@geus.dk

www.geus.dk

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Preface

This report presents the first monitoring results from the Danish Pesticide Leaching Assessment Programme (PLAP), an intensive monitoring programme aimed at evaluating the leaching risk of pesticides under field conditions. PLAP was funded by the Danish Government, and 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:

Bo Lindhardt, GEUS

Jeanne Kjær, GEUS (replaced Peter Gravesen per 1 August 2000)

Svend Elsnab Olesen, DIAS

Arne Helweg, DIAS

Ruth Grant, NERI

Betty Bügel Mogensen, NERI

Christian Ammitsøe, Danish Environmental Protection Agency

Christian Deibjerg Hansen, Danish Environmental Protection Agency

Jeanne Kjær

August 2001

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 assessment of pesticides for registration 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.

Under the PLAP, the leaching risk of 24 pesticides was evaluated at six agricultural sites (ranging from 1.1 to 2.4 ha) representing a wide range of Danish soil and climate conditions. The pesticides were all applied using the maximum permitted dosage. Bromide tracer was applied concomitantly with the pesticides and the concentrations of the bromide and pesticides measured monthly in both the unsaturated and the saturated zone. This report presents the monitoring results for three of the six agricultural sites during the first monitoring period (May 1999 to June 2000).

The findings indicate that transport of the bromide tracer will continue throughout the subsequent monitoring period. Although no final conclusion can thus be drawn concerning bromide transport and pesticide leaching risk until the results of the subsequent monitoring period are available, the findings hitherto suggest that:

- The monitoring system in terms of instrumentation, sampling procedure etc. is suitable for describing the transport of pesticides through the root zone down to the upper aquifer. The tracer application studies thus provide a good indication of the water transport occurring during the monitoring period and revealed a marked breakthrough of bromide in various parts of the hydrological cycle. In addition, they provide a good indication of the heterogeneity occurring at field level.
- The leaching risk could not yet be evaluated for linuron, glyphosate, fenpropimorph, propiconazol, pirimicarb, fluroxypyr and tribenuron-methyl since the monitoring period did not fully cover the potential leaching period. The results obtained so far provide no evidence that these pesticides or their degradation products AMPA, fenpropimorphic acid and triazinamin-methyl leach out of the topsoil.
- With ioxynil, bromoxynil and ETU (degradation product of mancozeb) the leaching risk was found to be negligible – none of the substances were detected in the analysed water samples, thus suggesting that they had already degraded.
- Two degradation products of metribuzin (desamino-diketo-metribuzin and diketo-metribuzin) were found to leach from the root zone in concentrations exceeding the maximum permitted concentration of 0.1 µg/l. Leaching was most pronounced with desamino-diketo-metribuzin, which was detected in concentrations as high as 2.1 µg/l 1 m b.g.s. and 1.4 µg/l 2 m b.g.s. As these degradation products have not yet

reached the downstream monitoring wells, their impact on groundwater quality cannot yet be assessed.

- At the two sandy sites, previous application of pesticides has caused marked groundwater contamination with the degradation products of metribuzin, particularly diketo-metribuzin, which was detected at a maximum concentration of 0.33 µg/l at the Tylstrup site and 0.5 µg/l at the Jyndevad site.

The field monitoring was supported by site-specific determination of sorption and degradation parameters. These determinations were performed on various combinations of pesticides and soil types representative of the PLAP programme. The results verified the low microbial activity, sorption and degradation rates that are generally found in subsoil. The findings also demonstrated the importance of the availability of site-specific parameters when carrying out root zone modelling. Thus, the determined sorption and degradation parameters (DT_{50} values) were all in the lower end of the literature values, particularly in the case of bromoxynil, the DT_{50} of which was remarkably low, ranging from <1 day in the plough layer to <5 days in the subsoil. Ioxynil also degraded very fast, DT_{50} ranging from <1 day in the plough layer to 12 days in the subsoil. Finally, the K_{oc} of bromoxynil and ioxynil only reached 85 ml/g in the plough layer and 52 ml/g in the subsoil.

The quality of the pesticide analyses was evaluated continuously using an intensive quality assurance (QA) system consisting 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, the QA system showing that:

- Reproducibility of all the analyses was good and the internal control samples were acceptably close to the nominal concentrations.
- No contamination of the samples took place at the laboratories.
- All the pesticides in the spiked samples were detected, although the observed concentrations were low compared to the nominal concentrations, with recovery ranging from 25–85%. It is difficult to find an unambiguous explanation for the low recovery rate, which is most likely due to uncertainty in the spiking procedure in the field. A new spiking procedure has already been introduced that is expected to improve the results.

1 Introduction

There is a growing public concern in Denmark about pesticide contamination of our groundwater and surface waters. 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 (GEUS, 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 might occur under actual field conditions. A major limitation is that the laboratory and lysimeter studies provide little if any information concerning the spatial variability of the soil parameters (hydraulic, chemical and microbiological soil properties) that affect pesticide leaching. This is of particular importance for silty and loamy soils, where preferential transport might 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. The US Environmental Protection Agency (US-EPA) has included field-scale studies in its risk assessments since 1987, for example. Pesticides that could potentially leach to the groundwater are required to be subject to 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, Annex 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 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 assessment of pesticides for registration 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.

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 are 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.

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, Jynde vad 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). The present report presents the results of the first monitoring period – May 1999 to July 2000. As the transport of pesticides from the soil surface to the groundwater can easily take 1–3 years and the available monitoring data only cover 9–13 months, the present report must be considered preliminary. A more complete interpretation of the data, including model simulation of the transport and transformation processes, will be made once a more comprehensive data set covering the entire leaching period becomes available.

It should be noted, that the present report only encompasses monitoring data from three of the six sites (Tylstrup, Jynde vad and Faardrup) as data are as yet only available for the period April–July 2000 for the other three sites (Estrup, Silstrup and Slaeggerup). The data for the latter three sites will therefore be presented in the 2002 PLAP report.

The risk of pesticide leaching is highly dependent on the degradation and sorption processes occurring in the root zone. To improve interpretation of the data, sorption and degradation studies have therefore been conducted on selected combinations of pesticides and soil types representative of the PLAP programme. The methodology and initial results are presented in Section 5.

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 6.

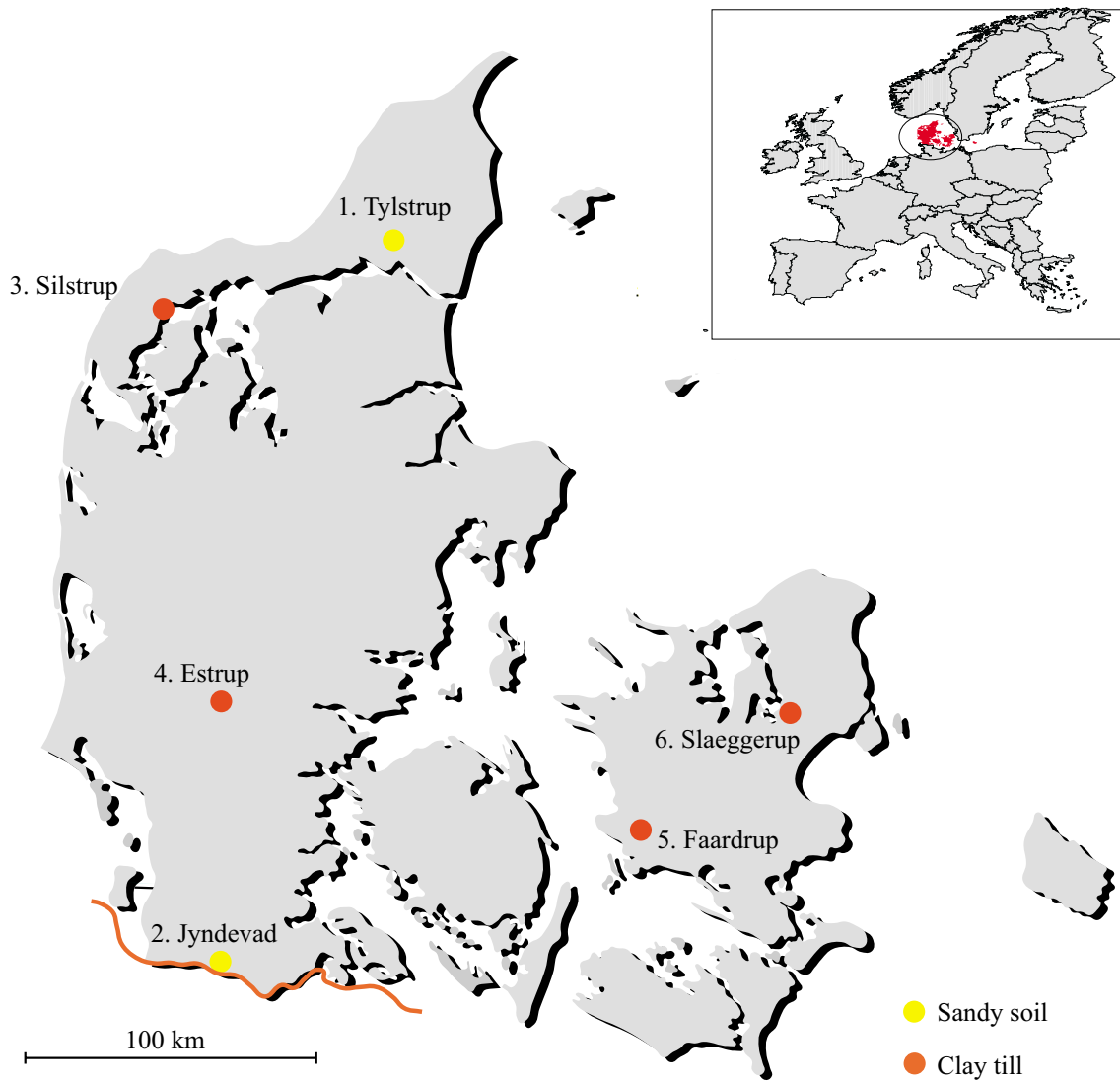


Figure 1. Location of the six PLAP sites Tylstrup, Jyndevad, Silstrup, Estrup, Faardrup and Slaeggerup.

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

	Tylstrup	Jydevad	Silstrup	Estrup	Faarstrup	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
B 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 at 3–4 m depth (fractures m ⁻¹)	-	-	<1	11	4	11
– Ks in C-horizon (m/s)	2.0·10 ⁻⁵	1.3·10 ⁻⁴	3.4·10 ⁻⁶	8.0·10 ⁻⁸	7.2·10 ⁻⁶	3.1·10 ⁻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

2) Large variation within the field

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

2 Pesticide leaching at Tylstrup

2.1 Materials and methods

2.1.1 Site description

Tylstrup is situated in northern Jutland (Figure 1). The test field covers a cultivated area of 1.1 ha (70x166 m) and is practically flat, with a windbreak bordering the eastern and western sides. The soil is a Typibrunsols (DK-classification) and 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 m b.g.s. Overall groundwater flow was towards the west (Figure 2 and Figure 4).

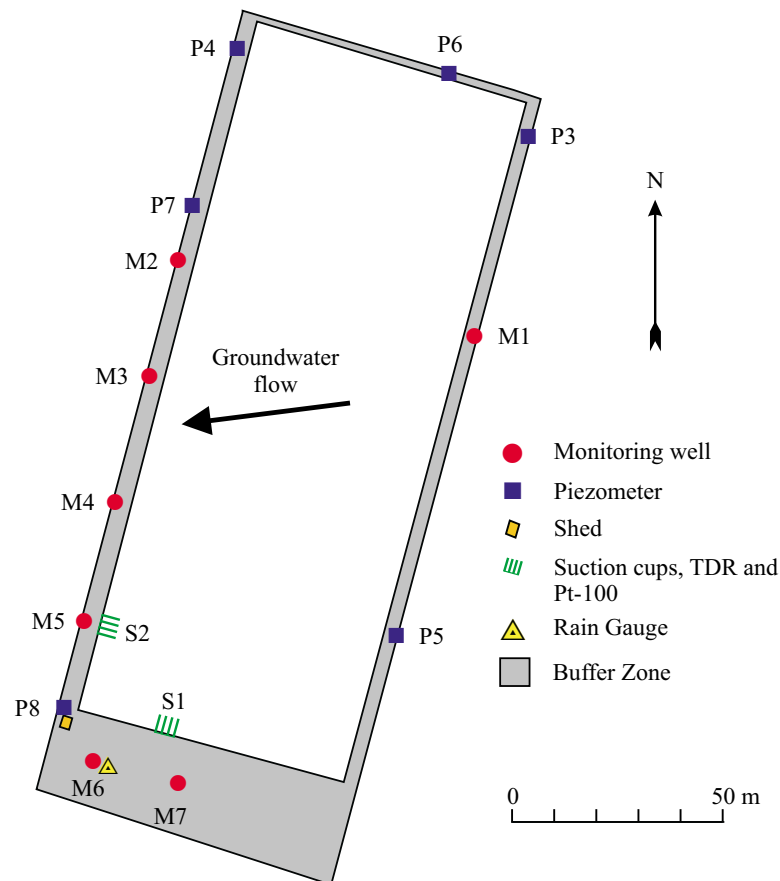


Figure 2. Overview of the Tylstrup test site. The innermost white area indicates the cultivated land, while the grey area indicates the surrounding buffer zone. The positions of the various installations are indicated, as is the direction of groundwater flow.

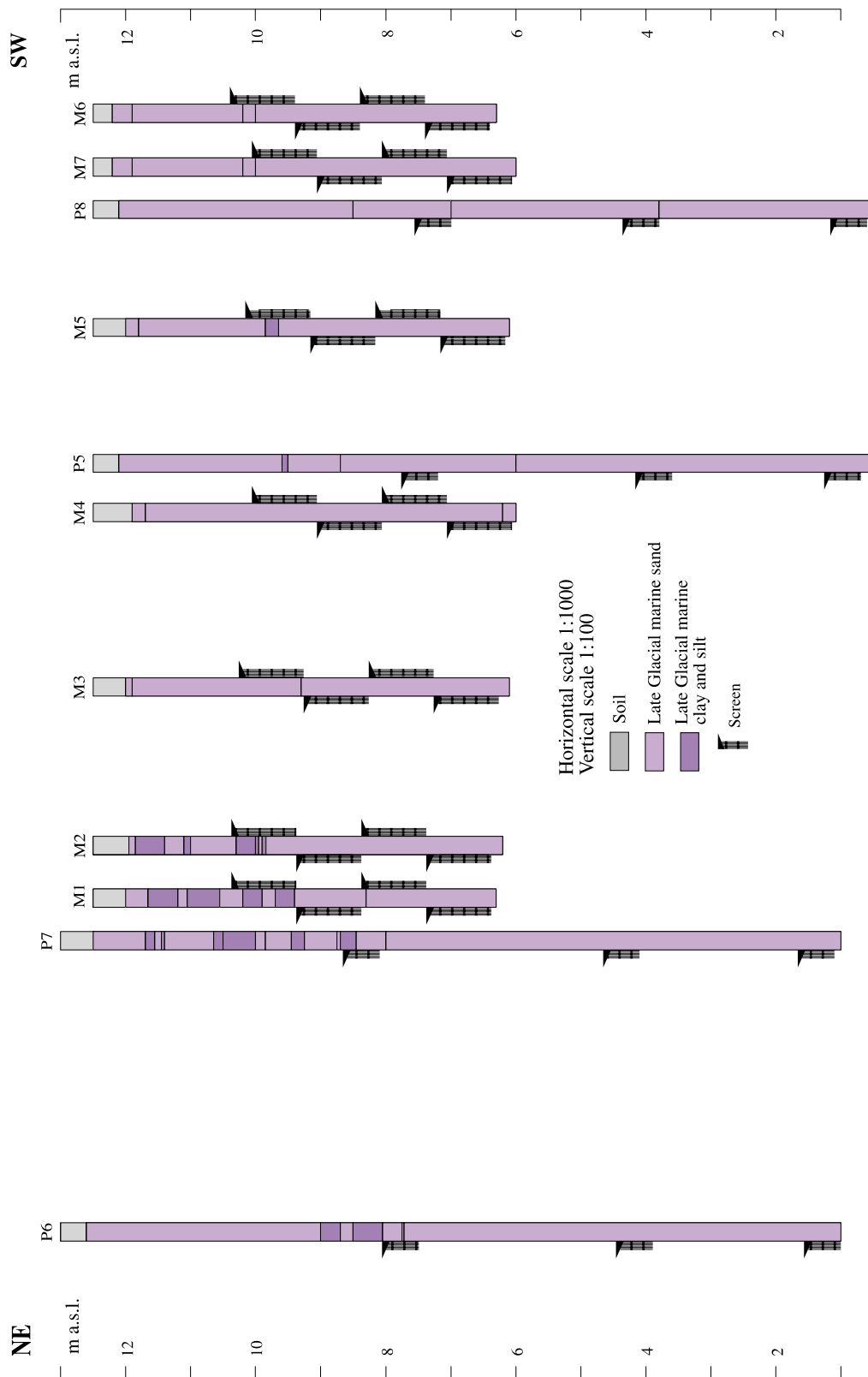


Figure 3. NE-SW cross sections based on wells at the Tylstrup site (Lindhardt *et al.* 2001). The location of the wells is indicated in Figure 2.

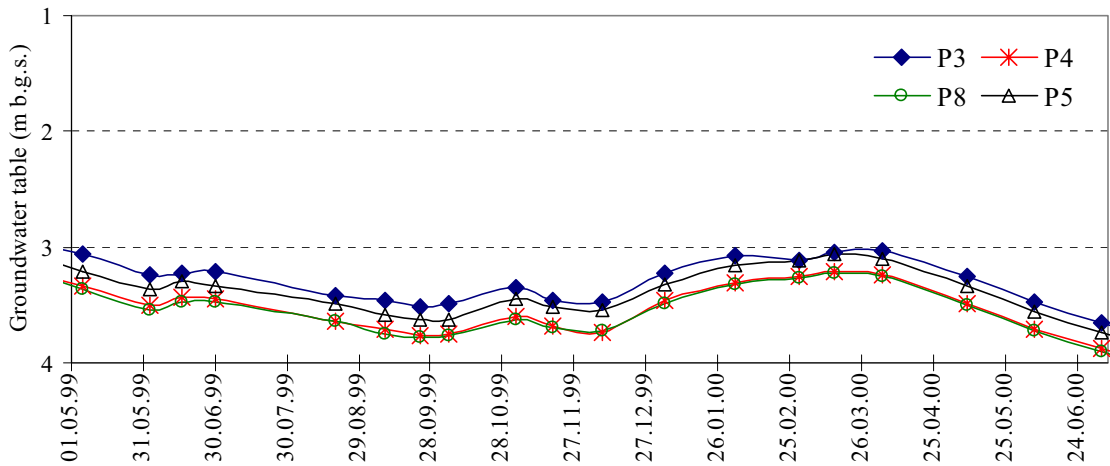


Figure 4. Temporal variation in the groundwater table at Tylstrup. The data derive from piezometers P1–P4.

2.1.2 Agricultural management

The PLAP fields are cultivated in the same manner as conventional fields in the vicinity. However, the pesticides are applied in the maximum permitted dosage. At Tylstrup the 1999 crop was potatoes for starch production. The cultivare used was Dianella, which is a commonly used variety. Due to the fact that the growing season was wet, irrigation was only carried out once during the monitoring period (33 mm/ha on September 12). The yield of tubers was 4.75 tonnes per ha, which is somewhat less than the average for the location. Likely explanations for the low yield are very uneven emergence attributable to the quality of the seed potatoes and the potato planter used, that the month of June was very wet, and that the field appeared to have been infected with nematodes. In spite of the intense spraying, moreover, potato blight halted the growth of the potatoes in the autumn. Tick attacks necessitated the application of a pyrethroid, Karate (lambda-cyhalothrin). However, this was not included in the monitoring programme.

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

Date	Management practice
19.11.1998	Ploughing – 20 cm depth
15.03.1999	Rolled with a concrete roller
22.04.1999	1 st seed bed preparation – 10 cm depth
23.04.1999	Fertilization – 121 kg N/ha and 8 kg P/ha
27.04.1999	Fertilization – 63 kg K/ha
03.05.1999	2 nd seed bed preparation – 10 cm depth
04.05.1999	Potatoes planted – cultivare Dianella, 2,200 kg/ha, planting depth 5 cm, row distance 75 cm
25.05.1999	Herbicide application – 1.0 l/ha Afalon (linuron)
25.05.1999	Herbicide application – 0.2 kg/ha Sencor WG (metribuzin)
27.05.1999	Tracer application – 30 kg/ha potassium bromide
07.06.1999	Herbicide application – 0.15 kg/ha Sencor WG (metribuzin)
11.06.1999	Insecticide application – 0.3 l/ha Karate (lambda-cyhalothrin)
15.06.1999	85% emergence – very uneven
22.06.1999	Fungicide application – 2.0 kg/ha Dithane DG (mancozeb)
02.07.1999	Fungicide application – 2.0 kg/ha Dithane DG (mancozeb)
07.07.1999	Fungicide application – 2.0 kg/ha Dithane DG (mancozeb)
16.07.1999	Fungicide application – 2.0 kg/ha Dithane DG (mancozeb)
22.07.1999	Fungicide application – 2.0 kg/ha Dithane DG (mancozeb)
03.08.1999	Fungicide application – 2.0 kg/ha Dithane DG (mancozeb)
20.08.1999	Fungicide application – 2.0 kg/ha Dithane DG (mancozeb)
30.08.1999	Fungicide application – 2.0 kg/ha Dithane DG (mancozeb)
09.09.1999	Fungicide application – 2.0 kg/ha Dithane DG (mancozeb)
12.09.1999	Irrigation – 33 mm/ha
14.09.1999	Fungicide application – 2.0 kg/ha Dithane DG (mancozeb)
20.10.1999	Potato harvest (tuber yield was 4.75 tonnes/ha and dry matter yield was 1.164 tonnes/ha)
22.10.1999	Disc harrowed – 6 cm depth
01.11.1999	Harrowed – 3 cm depth
11.11.1999	Harrowed – 5 cm depth
25.11.1999	Harrowed – 7 cm depth
17.03.2000	Ploughed – 20 cm depth
24.03.2000	Rolled with a concrete roller
28.03.2000	Fertilization – 124 kg N/ha, 18 kg P/ha and 59 kg K/ha
28.03.2000	Seed bed preparation – 5 cm depth
29.03.2000	Spring barley sown – cultivare Bartok, 145 kg/ha, sowing depth 4 cm and row distance 12 cm.
20.04.2000	BBCH stage 09 – emergence
25.04.2000	BBCH stage 11 – first leaf unfolded – plant density 350/m ²
13.05.2000	BBCH stage 23 – 3 tillers visible
13.05.2000	Herbicide application – 0.02 kg/ha Logran 20 WG (triasulfuron)
16.05.2000	BBCH stage 31 – first node detectable, biomass measured
30.05.2000	BBCH stage 37 – tip of flag leaf visible
15.06.2000	BBCH stage 53 – headed 1/3, biomass measured
19.06.2000	BBCH stage 55 – headed 1/2
19.06.2000	Fungicide application – 1.0 l/ha Tilt Top (propiconazol + fenpropimorph)
19.06.2000	Insecticide application – 0.25 l/ha Pirimor G (pirimicarb)

2.1.3 Monitoring strategy

The bromide and the pesticide concentrations were measured monthly in both groundwater and the unsaturated zone. The groundwater monitoring was carried out by means of seven monitoring wells installed in the surrounding buffer zone. Each monitoring well consists of four 1 m screens covering the upper approx. 4 m of the saturated zone (Figure 5). Monitoring of the unsaturated zone was carried out using groups of teflon suction cups 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 (Figure 2 and Figure 5).

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

- Analysis of the inorganic parameters is performed each month on water samples deriving from all monitoring wells (M1–M7) 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.
- 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. and from two of the downstream monitoring wells. In addition, more intensive monitoring encompassing all suction cups and all monitoring wells except M7 and M2 is performed every fourth month (Table 4).

A brief description of the sampling procedure and analysis methods is provided in Appendixes 1–3. Monitoring design is described in detail in Lindhardt *et al.* (2001).

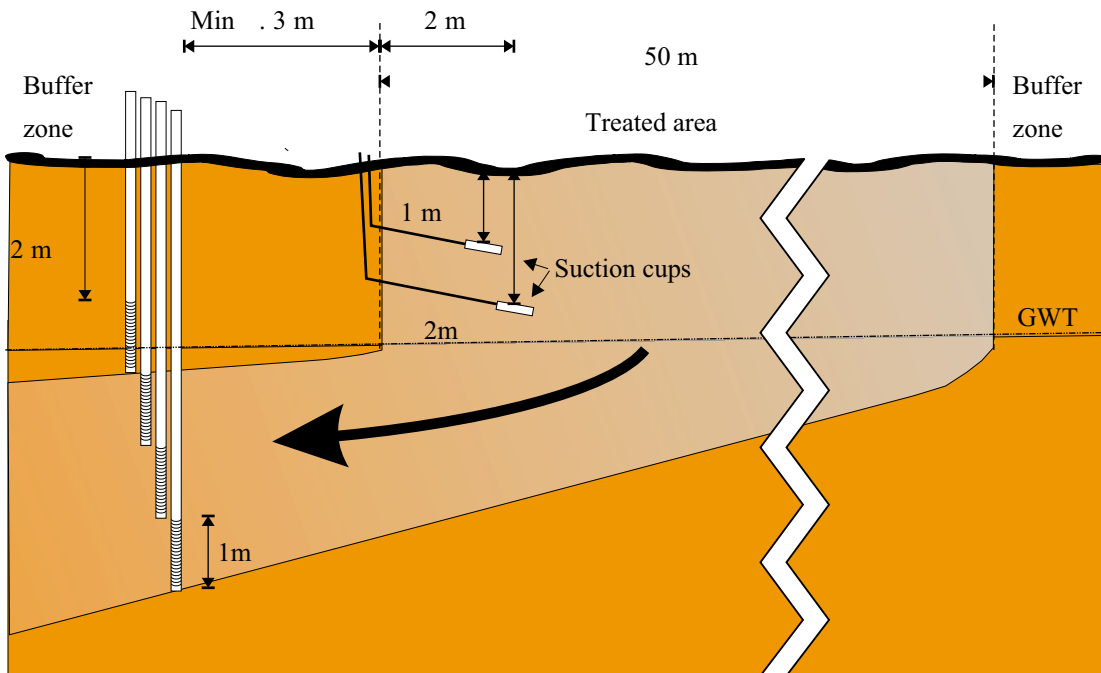


Figure 5. Illustration of the monitoring design at the PLAP test fields.

Table 4. Pesticide monitoring programme at Tylstrup.

	Measured every month	Measured every fourth month	Not measured
Suction cups	S1 – 1 m b.g.s. S2 – 1 m b.g.s.	S1 – 2 m b.g.s. S2 – 2 m b.g.s.	- -
Monitoring wells	M5, M6	M1, M3, M4	M7, M2

2.1.4 Climate

The present brief description of the main climatic elements during the period May 1999 to June 2000 is based on data from the DIAS meteorological station located less than 1 km from the Tylstrup test site. The potential water balance in terms of accumulated potential evapotranspiration and precipitation is illustrated in Figure 6. Table 5 compares the actual climatic conditions to the monthly normal for the period 1961–90. It should be noted that the precipitation was monitored at 1.5 m above ground, and that the potential evapotranspiration is defined as the evapotranspiration from well-growing short grass adequately supplied with water as calculated using a modified Makkink equation (Aslyng and Hansen, 1982).

The monitoring period (May 1999–June 2000) was very wet at Tylstrup, sum precipitation being about 1,047 mm, which is 35% more than normal (Table 5). Precipitation was particularly high in June, August and December.

During the summer months the precipitation input was counterbalanced by the potential evapotranspiration. During the winter period, in contrast, a large precipitation surplus accumulated (Figure 6). The monitoring period was thus characterized by a large overall precipitation surplus of 293 mm, which considerably exceeds the yearly normal (Table 5).

Table 5. Monthly precipitation (Precip.) and potential evapotranspiration (Pot. evap.) at Tylstrup in mm/month. The normal values based on time series for 1961–90 are shown in parentheses. The data derive from the DIAS Tylstrup meteorological station located less than 1 km from the test site.

	1999								2000						
	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Total
Precip.	53 (49)	148 (56)	84 (63)	106 (67)	79 (71)	79 (73)	23 (71)	99 (71)	71 (58)	60 (50)	60 (33)	71 (41)	50 (36)	64 (49)	1,047 (773)
Pot. Evap	89 (86)	88 (103)	112 (101)	90 (83)	48 (48)	23 (22)	8 (9)	5 (4)	6 (5)	12 (11)	32 (27)	54 (53)	98 (86)	89 (103)	754 (741)
Precip. surplus ¹⁾	-36 (-37)	60 (-47)	-28 (-38)	16 (-16)	31 (23)	56 (51)	15 (62)	94 (53)	65 (45)	48 (22)	28 (14)	17 (-17)	-48 (-37)	-25 (-47)	

¹⁾ The potential evapotranspiration (Pot. Evap) is calculated using a modified Makkink equation (Aslyng and Hansen, 1982)

²⁾ Precipitation surplus (Precip. surplus) is defined as the difference between the precipitation and the potential evapotranspiration

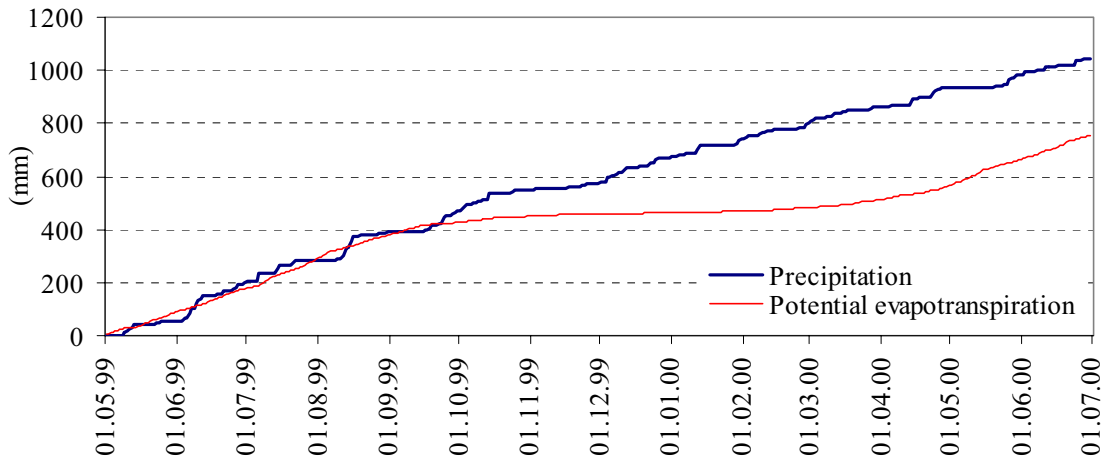


Figure 6. Accumulated precipitation and potential evapotranspiration at Tylstrup. The data derive from the DIAS Tylstrup meteorological station located less than 1 km from the test site.

2.2 Results and discussion

2.2.1 Bromide leaching

Marked breakthrough of the bromide curves occurred in both the saturated and the unsaturated zone indicative of water transport occurring during the monitoring period:

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 7). As expected, the breakthrough of bromide at 2 m b.g.s. was delayed by a few months and the concentration profile in this depth was somewhat wider due to hydrodynamic dispersion. The bromide concentration peaked in February and the majority of the bromide seems to have leached out by June 2000. The results clearly illustrate the spatial variability of the infiltration pattern within the field. Thus, at 1 m b.g.s. the bromide concentration in S2 peaked at a level about three times that in S1.

In the saturated zone the hydrological conditions varied considerably within the field. A marked breakthrough of bromide was only seen in one monitoring well (M4), while slightly elevated concentrations (up to 1 mg/l) were observed in very few of the other screens (Figure 8). It should be noted that a bromide concentration below 0.4 mg/l cannot be distinguished from the background concentration, which was 0.23 ± 0.06 mg/l at Tylstrup.

Compared to the suction cups located at 2 m b.g.s. the breakthrough of bromide in M4 is remarkably rapid, possibly indicating preferential flow in the unsaturated zone in parts of the field upstream of M4. The remarkable difference between the various monitoring wells demonstrates the marked heterogeneity within the test field, where the hydrological conditions upstream of M4 differ from those elsewhere. Silt lenses have also been

identified in the northern part of the area that probably cause heterogeneous water flow (Figure 3).

Slightly elevated bromide concentrations were detected in monitoring well M1 shortly after bromide application. As M1 is located upstream of the field site, the tracer bromide should not reach it. However, the silt lenses present might have deflected the vertical transport through the unsaturated zone, enabling bromide to be transported to the up-stream monitoring well M1.

The results indicate that bromide transport to the monitoring well will continue during the subsequent monitoring period and no final conclusion can be drawn until the data from 2001 have become available.

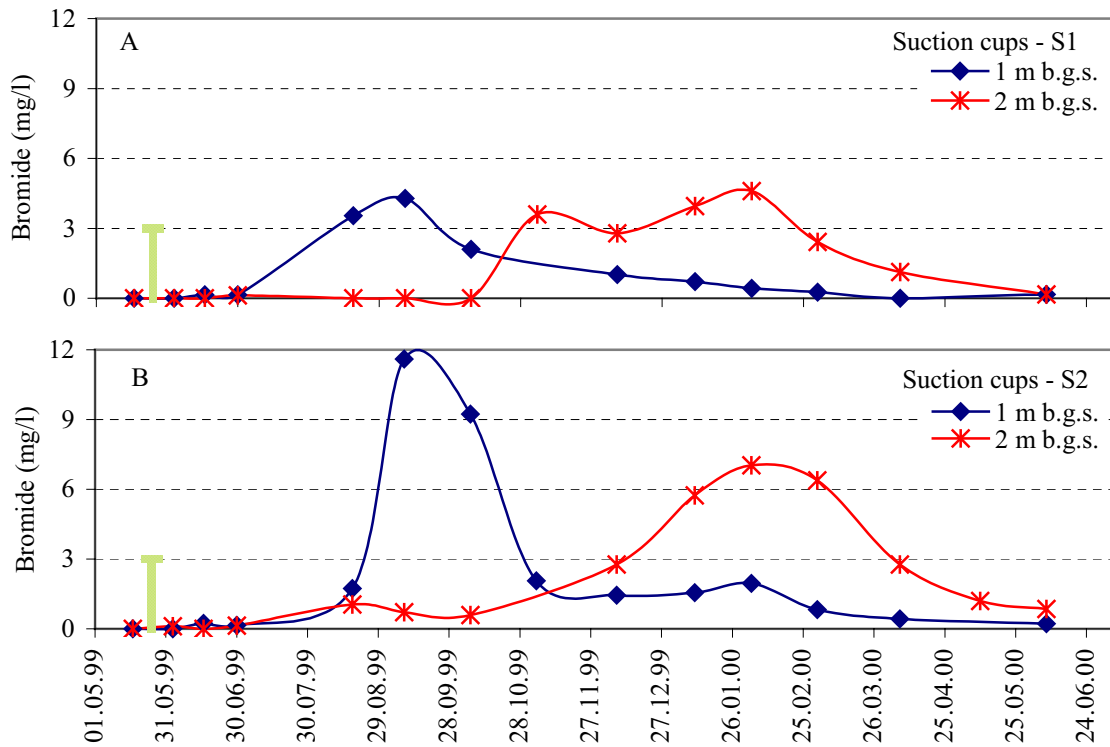


Figure 7. Bromide concentration in the unsaturated zone at Tylstrup (suction cups S1 and S2) at 1 m b.g.s. and 2 m b.g.s. The green vertical line indicates the date of bromide application.

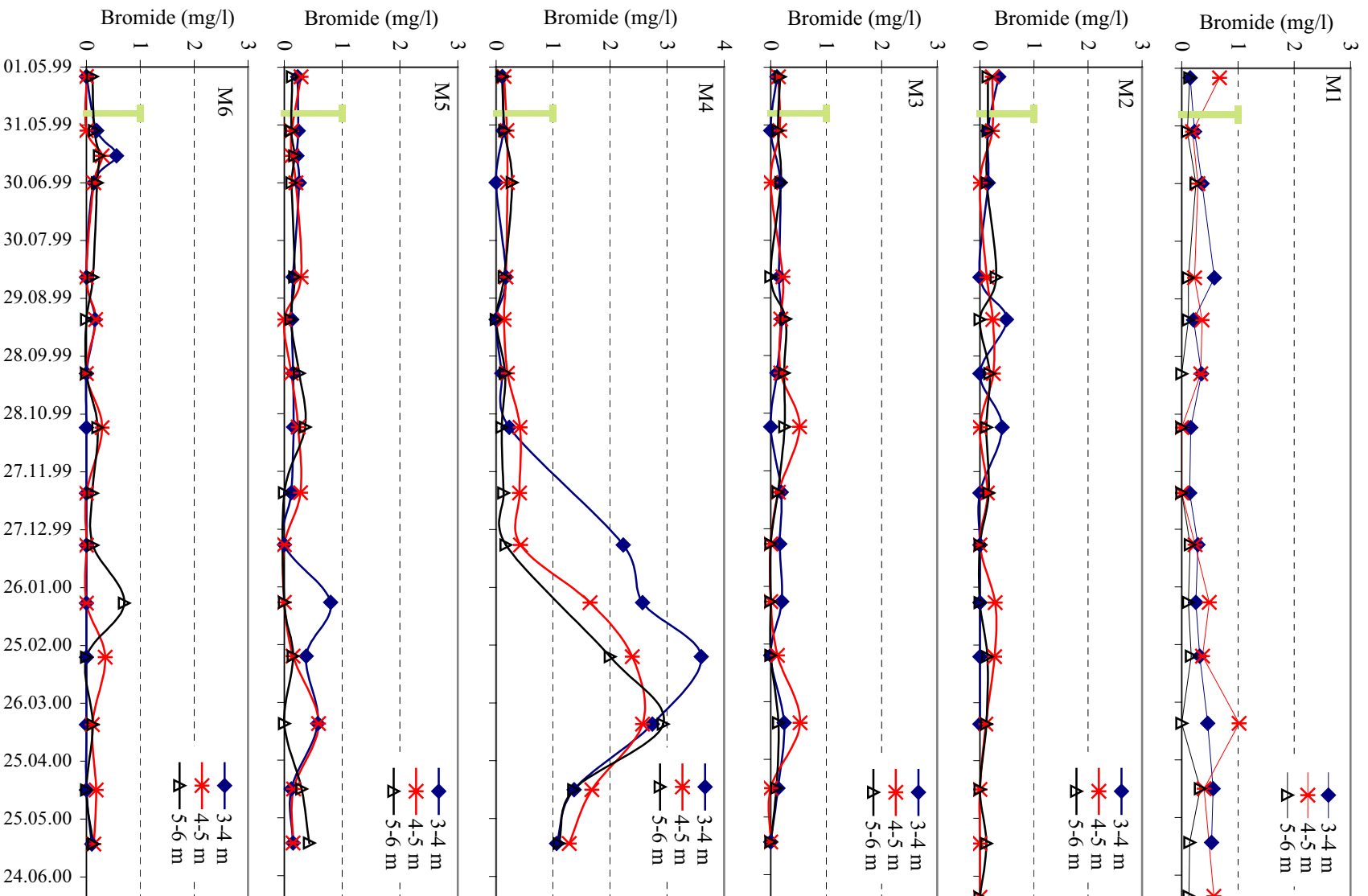


Figure 8. Bromide concentration in the groundwater at Tystrup. The data derive from monitoring wells M1–M7. The screen depths are in m b.g.s. and the green line indicates the date of bromide application

2.2.2 Pesticide leaching

The leaching risk of mancozeb, linuron and metribuzin was assessed at the Tylstrup site during the monitoring period.

Linuron – the active ingredient in Afalon – was not detected in any of the water samples. Linuron has a high sorption capacity towards soil and groundwater sediments. A considerable delay is therefore to be expected relative to bromide transport and a final conclusion concerning the leaching risk must await the results of the subsequent monitoring period.

Mancozeb – the active ingredient in Dithane DG – hydrolyzes rapidly in the environment. The leaching risk is therefore more associated with its degradation product ethylenethiourea (ETU). ETU was only detected in few of the water samples in the unsaturated zone in concentration levels of approx. 0.03 µg/l. ETU is considered to be extremely mobile, and no delay is therefore to be expected relative to bromide transport. The leaching risk associated with mancozeb and ETU is therefore considered to be negligible.

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, degradation products of metribuzin leached from the root zone in concentrations considerably exceeding 0.1 µg/l (Figure 9 and Figure 10).

Leaching was most pronounced with desamino-diketo-metribuzin. In S1, the concentration of desamino-diketo-metribuzin reached 2.1 µg/l at 1 m b.g.s. and 1.5 µg/l at 2 m b.g.s. (Appendix 4, Figure 10A and B). In S2 leaching was less pronounced, although the concentration level exceeded the maximum level of 0.1 µg/l throughout the winter period (Appendix 4, Figure 10C and D).

The intermediate degradation product diketo-metribuzin also leached from the root zone, the maximum concentration reached being 0.62 µg/l at 1 m b.g.s. and 0.20 µg/l at 2 m b.g.s. (Appendix 4).

Monitoring also revealed marked groundwater contamination with degradation products of metribuzin. Desamino-diketo-metribuzin and diketo-metribuzin were detected in a large number of the groundwater samples, although the spatial and temporal distribution of the concentration levels varied throughout the monitoring period (See Table 6). The highest concentration of diketo-metribuzin detected was 0.33 µg/l, and the maximum allowable concentration of 0.1 µg/l was exceeded in 36% of the samples. Desamino-diketo-metribuzin was also detected in a large number of groundwater samples, although the concentrations never exceeded 0.1 µg/l. It should be noted, however, that the methods of analysis for these degradation products were developed during the project. The 1999 analyses are therefore subject to some uncertainty due to the high detection limit of 0.2 µg/l (Table 6).

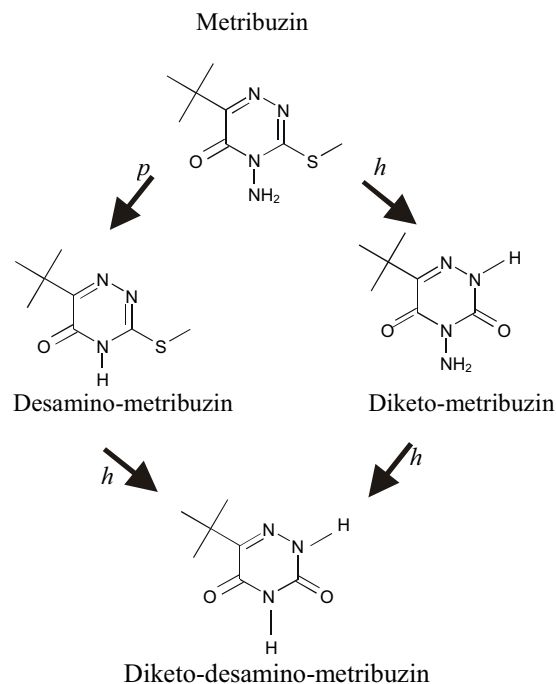


Figure 9. Degradation pathways for metribuzin involving hydrolysis (*h*) and photodegradation (*p*).

The occurrence of these degradation products in the groundwater is presumably due to prior application of metribuzin. According to the initial screening analysis, the degradation products were already present in the groundwater before monitoring started in September 1999 (Table 6). Moreover, the highest concentration of diketo-metribuzin was detected in the deepest screen of monitoring well M6, which the bromide tracer had not yet reached. Metribuzin had been applied to the field several times during the past decade, most recently in 1994 (Table 7). Metribuzin is in widespread use and has frequently been applied to the neighbouring fields located upstream of the test site (Table 7). The concentration in the deeper groundwater might thus be influenced by its “upstream” use. From the bromide transport it is unlikely that the metribuzin applied in 1999 would have reached any of the monitoring wells other than M4. The impact of the metribuzin applied during the PLAP programme on the quality of the groundwater will therefore be assessed when the monitoring results from 2001 become available.

It should be noted that only two of the known degradation products were detected at Tylstrup, whereas the third degradation product desamino-metribuzin was not detected in any of the water samples. A likely explanation is that desamino-metribuzin is unstable and degrades forming diketo-desamino-metribuzin, or that hydrolysis is the predominant degradation pathway at Tylstrup (Figure 9).

No evidence was found of groundwater contamination deriving from earlier pesticide application apart from metribuzin. Thus, the initial screening analysis determining the background concentration of 42 pesticides revealed no sign of other pesticides in the groundwater (Appendix 5).

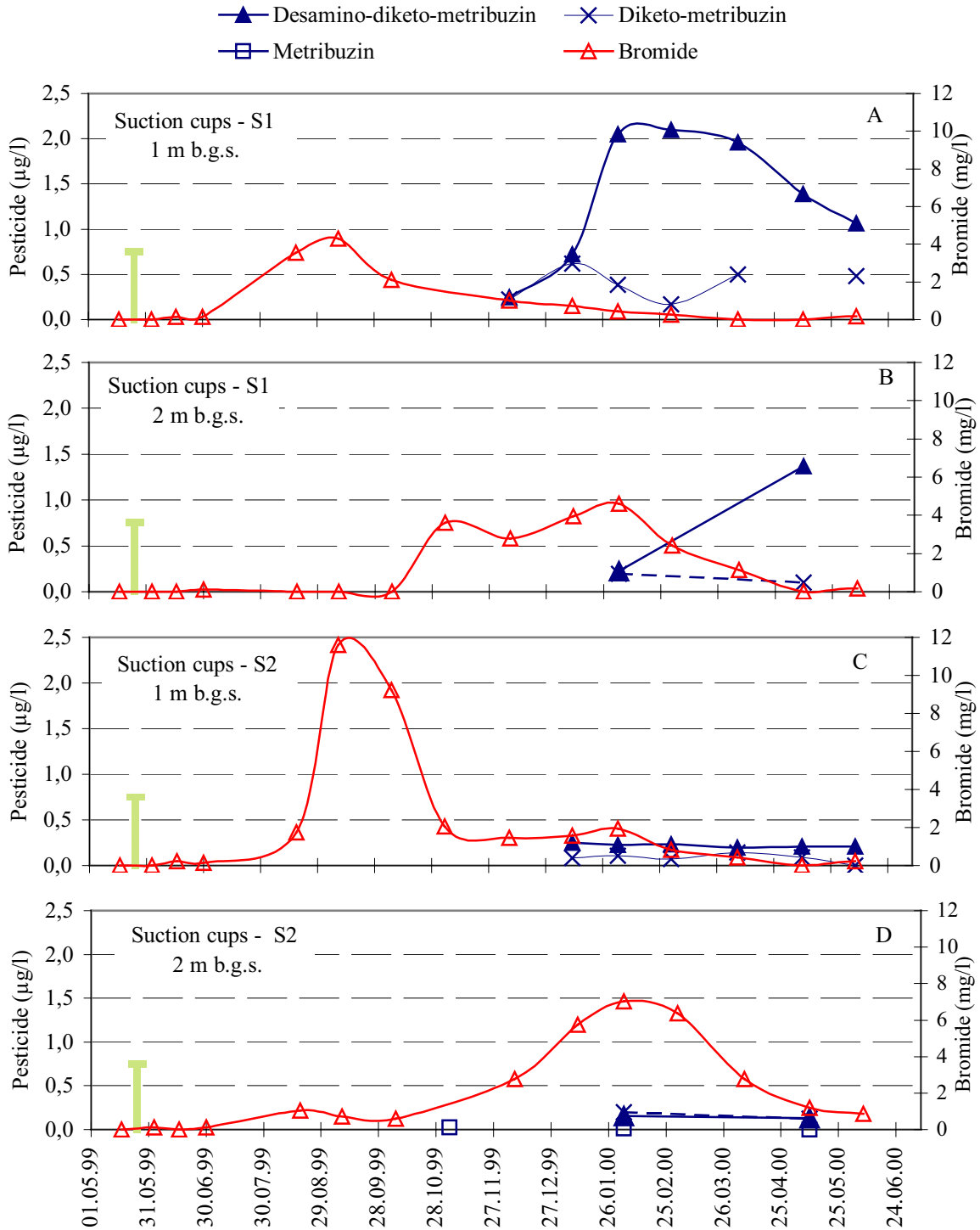


Figure 10. Bromide and pesticide concentration in the unsaturated zone at Tylstrup. The data derive from suction cups installed 1 m b.g.s. and 2 m b.g.s. at locations S1 and S2 indicated in Figure 2. The green vertical line indicates the date of bromide application.

Table 6. Concentration of desamino-diketo-metribuzin and diketo-metribuzin in the groundwater at Tylstrup ($\mu\text{g/l}$).

Monitoring well/ Screen depth (m b.g.s.)	M1			M3			M4			M5			M6		
	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
Desamino-diketo-metribuzin															
Apr-99	*	*	***	*						*	*	***	*		
09.09.99										<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
04.11.99	<0.2	<0.2	*	<0.2	*	<0.2	<0.2	<0.2	*	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
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	<
05.07.00										<	<	<	<	<	<
Diketo-metribuzin															
Apr-99	*	*	***	***						*	*	*	*		
09.09.99										<0.2	<0.2	<0.2	<0.2	*	*
04.11.99	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	*	<0.2
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

) Below the detection limit of 0.01 $\mu\text{g/l}$.

*) Degradation product was detected in the range of 0.05–0.5 $\mu\text{g/l}$;

***) Degradation product was detected in the range of 0.1–0.5 $\mu\text{g/l}$

Table 7. Previous application of metribuzin at Tylstrup and the neighbouring fields.

	Year	Product	Dosage ¹⁾ (kg/ha/y)
Tylstrup	1990	Sencor WG	0.70
	1992	Sencor WG	0.50
	1994	Sencor WG	0.30
	1999	Sencor WG	0.35
Neighbouring field situated southeast of Tylstrup	1989	Sencor WG	0.70
Neighbouring field situated east of Tylstrup	1999	Sencor WG	0.35

1) The maximum permitted dosage was reduced from 0.7 kg/ha/y to 0.35 kg/ha/y in 1994.

2.3 Summary

The results of the monitoring hitherto undertaken at the Tylstrup test field can be summarized as follows:

- The tracer study provided a good indication of the water transport occurring during the monitoring period. Marked breakthrough of bromide was detected in the unsaturated zone, indicating that the predominant part of the applied bromide had leached from a depth of 2 m. In the saturated zone the hydrological conditions within the field site varied considerably. Marked breakthrough of bromide only occurred in one of the monitoring wells, only low or background concentrations being detected in the other monitoring wells.
- With metribuzin, ETU (degradation product of mancozeb) and linuron the leaching risk was found to be negligible. It should be noted, however, that the current monitoring period did not fully cover the potential leaching period and a final conclusion concerning the leaching risk of linuron must await the results of the subsequent monitoring period.
- Two degradation products of metribuzin (desamino-diketo-metribuzin and diketo-metribuzin) were found to leach from the root zone in concentrations considerably exceeding 0.1 µg/l. Leaching was most pronounced with desamino-diketo-metribuzin, which was detected in concentrations as high as 2.1 µg/l at 1 m b.g.s. and 1.5 µg/l at 2 m b.g.s. As these degradation products have not yet reached the downstream monitoring wells, their impact on groundwater quality cannot be assessed from this current monitoring period.
- Pesticide application prior to the monitoring period has resulted in marked groundwater contamination with degradation products of metribuzin. Diketo-metribuzin was detected in particularly high concentrations of 0.33 µg/l and the maximum allowable concentration of 0.1 µg/l was exceeded in 36% of the samples analysed. Desamino-diketo-metribuzin was also detected in a large number of groundwater samples, although the concentrations never exceeded 0.1 µg/l.

3 Pesticide leaching at Jynde vad

3.1 Materials and methods

3.1.1 Site description

Jynde vad is situated 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 windbreak bordering the eastern side. The soil is a Typipodzols (DK-classification) and the top soil is characterized as sand with 5% clay and 1.8% total organic carbon (Table 1). The geological description points to a rather homogeneous aquifer of meltwater sand, with local occurrence of thin clay and silt beds. The area is characterized by a shallow groundwater table located 1–2 m b.g.s. The overall direction of groundwater flow is towards the northwest (Figure 11, Figure 12 and Figure 13).

3.1.2 Agricultural management

The crop during the monitoring period was winter rye (cultivare Dominator). Due to large amounts of common bearded couch grass (*Agropyron repens L.*), the field had to be sprayed with glyphosate, which was not part of the original plan. The glyphosate was applied to the field on 22 September, three weeks before sowing of the winter rye (Table 8).

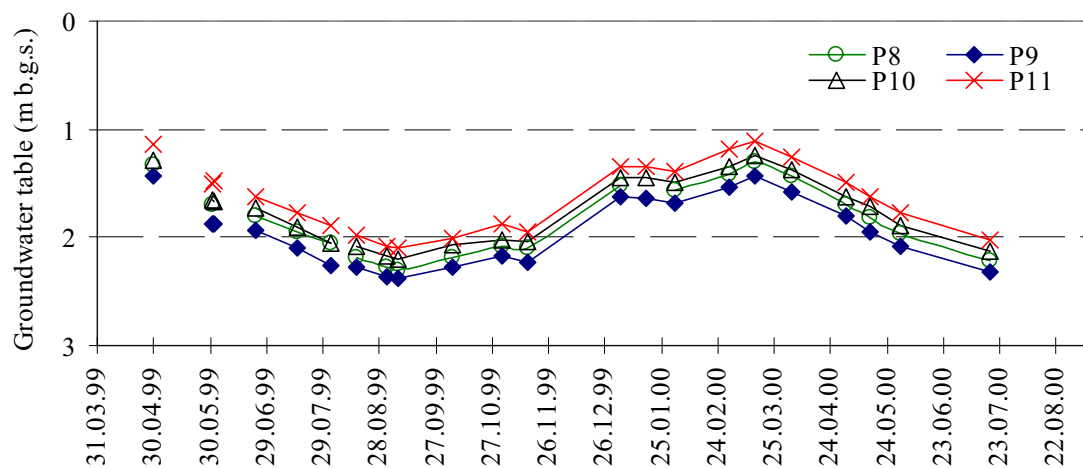


Figure 11. Temporal variation of the groundwater table at Jynde vad. The data derive from piezometers P8–P11 indicated in Figure 12.

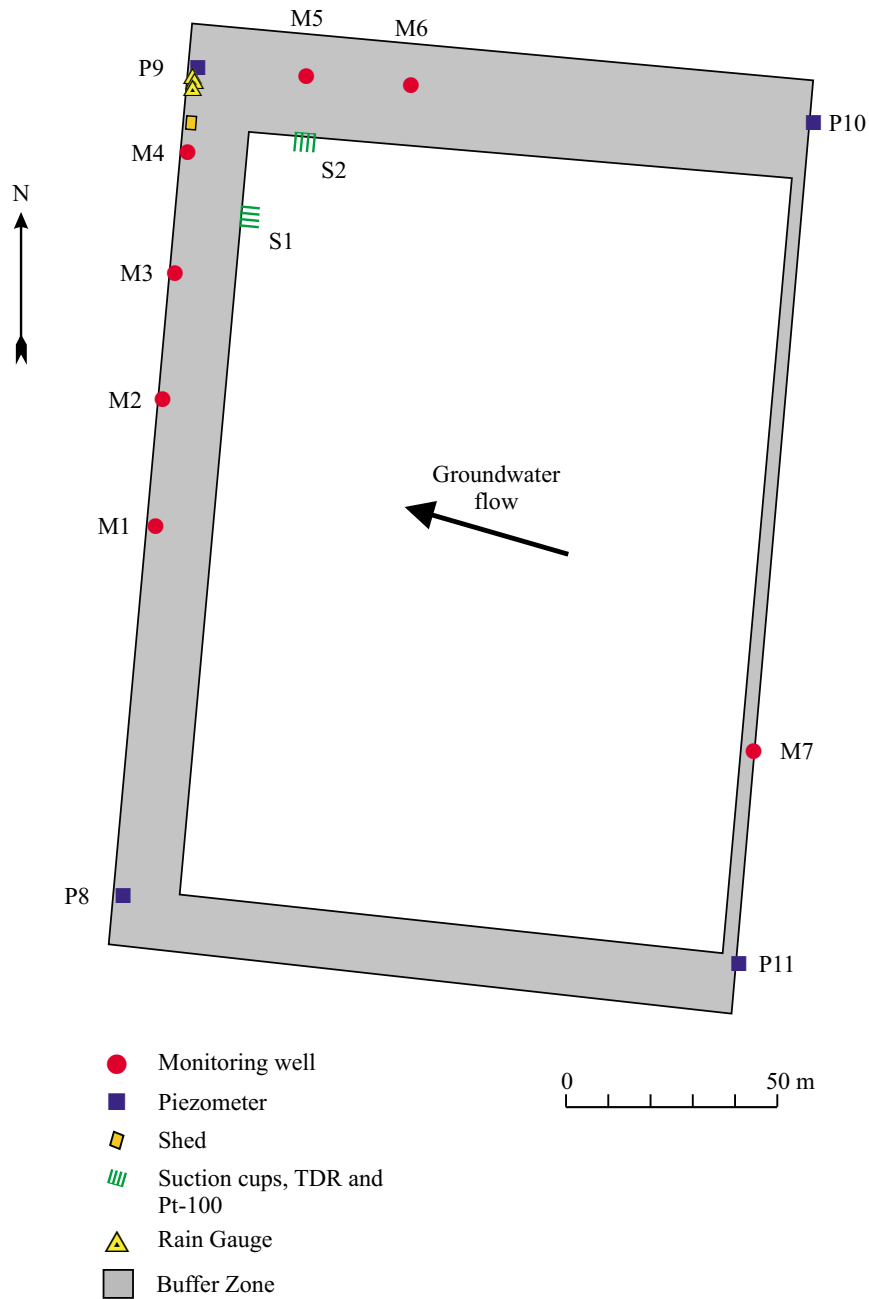


Figure 12. Overview of the Jydevad test site. The innermost white area indicates the cultivated land, while the grey area indicates the surrounding buffer zone. The positions of the various installations are indicated, as is the direction of groundwater flow

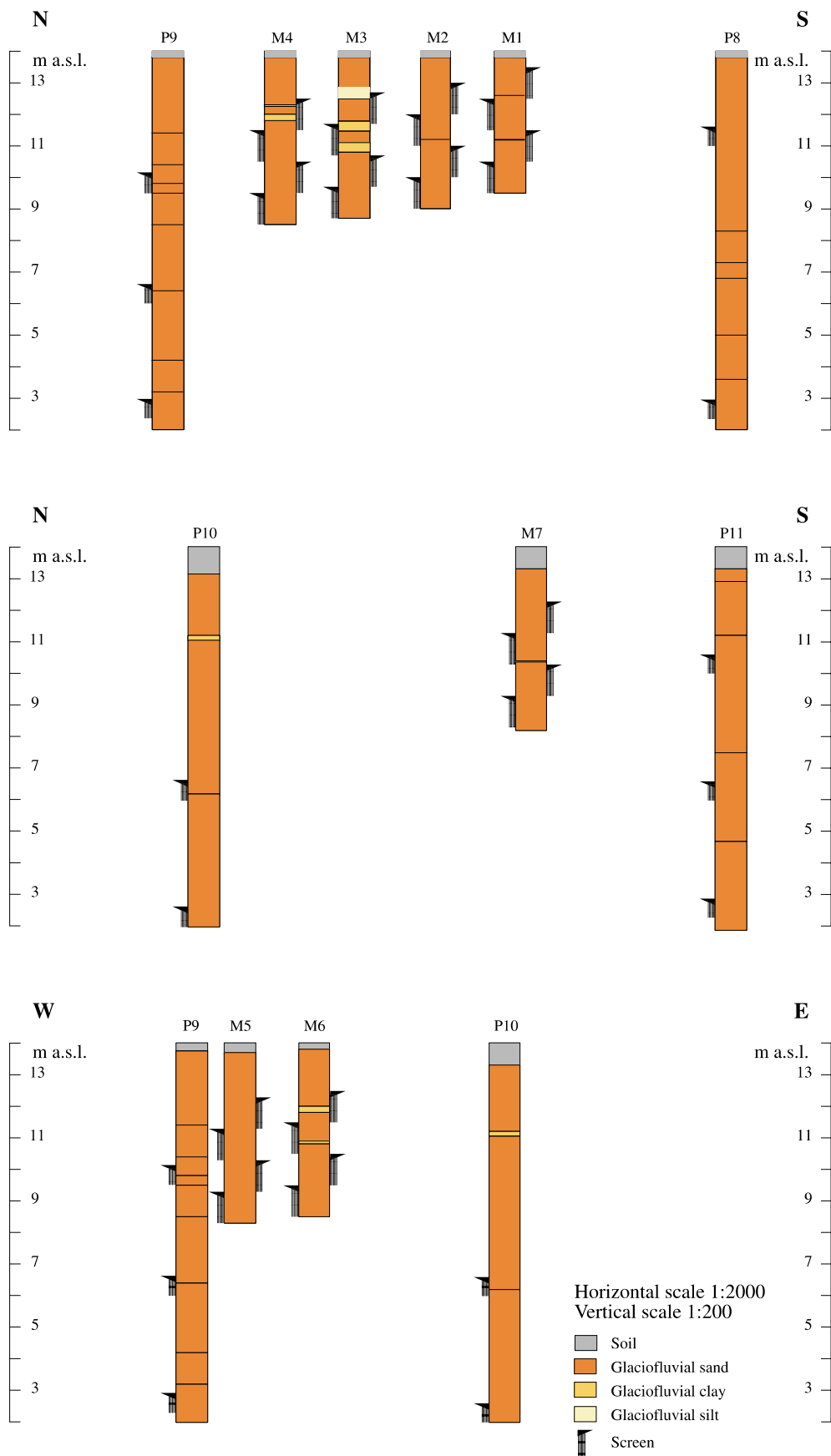


Figure 13. Cross sections based on wells at the Jyndevad site (Lindhardt *et al.*, 2001). The location of the wells is indicated in Figure 12.

Table 8. Management practice at Jynde vad. The active ingredients in the various pesticides are indicated in parentheses.

Date	Management practice
09.08.1999	Spring barley harvested – grain yield 4.77 tonnes/ha with 85% dry matter, straw dry matter yield 4.03 tonnes/ha
22.09.1999	Herbicide application – 2.0 l/ha Roundup 2000 (glyphosate)
05.10.1999	Rotary cultivated – 5 cm depth
11.10.1999	Ploughed – 20 cm depth
11.10.1999	Rolled with a concrete roller
13.10.1999	Winter rye sown – cultivare Dominator, seeding rate 130 kg/ha, 8 cm depth, row distance 12 cm
20.10.2000	BBCH stage 09 – emergence
12.11.1999	Tracer application – 30.0 kg/ha potassium bromide
12.11.1999	Herbicide application – 0.0075 kg/ha Express (tribenuron-methyl)
30.03.2000	BBCH stage 21– biomass measured
04.04.2000	Fertilization – 115 kg N/ha, 16 kg P/ha and 55 kg K/ha
05.04.2000	Fungicide application – 0.5 l/ha Tilt Top (propiconazol + fenpropimorph)
18.04.2000	BBCH stage 30 – beginning of stem elongation
28.04.2000	BBCH stage 34 – 4 nodes detectable
03.05.2000	BBCH stage 41 – flag leaf sheath extending
05.05.2000	Irrigation – 29 mm/ha
11.05.2000	BBCH stage 51 – beginning of heading
16.05.2000	BBCH stage 59 – end of heading – biomass measured
22.05.2000	BBCH stage 61 – first flowers open
31.05.2000	BBCH stage 65 – full flowering
06.06.2000	BBCH stage 69 – end of flowering
15.06.2000	BBCH stage 71 – watery ripe
27.06.2000	BBCH stage 75 – milky ripe – biomass measured

3.1.3 Monitoring strategy

The bromide and pesticide concentrations were measured monthly in both the unsaturated and the saturated zone following the procedure already described in section 2.1.3. Thus, the monitoring programme for pesticides comprised monthly analysis of water from two monitoring wells, supplemented by quarterly analysis encompassing all monitoring wells except M6 and M3 (Table 9).

Table 9. Pesticide monitoring programme at Jynde vad.

	Measured monthly	Measured quarterly	Not measured
Suction cups	S1 – 1 m b.g.s. S2 – 1 m b.g.s.	S1 – 2 m b.g.s. S2 – 2 m b.g.s.	
Monitoring wells	M1, M4	M2, M5, M7	M6, M3

3.1.4 Climate

The period from May 1999 to June 2000 was rather wet at Jynde vad. Precipitation amounted to 1,148 mm which exceeds the normal by 17%, largely due to an unusually high precipitation in June, October and December 1999 (Table 10). Monitoring was initiated at Jynde vad in September 1999, when accumulated potential evapotranspiration exceeded the precipitation by approx. 100 mm. The high level of autumn precipitation reversed this situation, however, and a large precipitation surplus of 365 mm accumulated during the remainder of the monitoring period (Figure 14). The region around Jynde vad has one of the highest precipitation rates in Denmark (857 mm/year). During the fourteen-month monitoring period the accumulated precipitation surplus was 25% higher than at the Tylstrup test field.

Table 10. Monthly precipitation (Precip.) and potential evapotranspiration (Pot. evap.) at Jynde vad in mm/month. The normal values based on time series for 1961–90 are shown in parentheses. The data derive from the DIAS Jynde vad meteorological station located less than 1 km from the test site.

	1999								2000						Total
	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	
Precip.	53 (56)	127 (67)	48 (78)	62 (82)	66 (89)	160 (96)	41 (98)	188 (76)	65 (70)	75 (42)	90 (57)	40 (47)	51 (56)	82 (67)	1148 (981)
Pot. evap. ¹⁾	93 (88)	93 (99)	115 (96)	88 (84)	65 (49)	24 (25)	10 (9)	6 (5)	8 (6)	14 (12)	28 (28)	43 (54)	101 (88)	95 (99)	783 (742)
Precip. Surplus ²⁾	-40 (-32)	34 (-32)	-67 (-18)	-26 (-2)	1 (40)	136 (71)	31 (89)	182 (71)	57 (64)	61 (30)	62 (29)	-3 (-7)	-50 (-32)	-13 (-32)	

¹⁾ The potential evapotranspiration (Pot. Evap) is calculated using a modified Makkink equation (Aslyng and Hansen, 1982)

²⁾ Precipitation surplus (Precip. surplus) is defined as the difference between the precipitation and the potential evapotranspiration

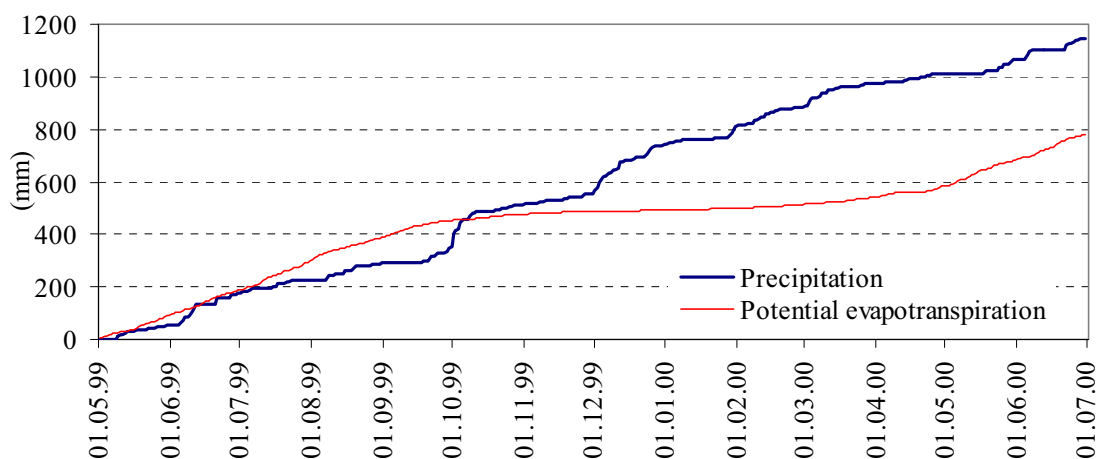


Figure 14. Accumulated precipitation and potential evapotranspiration at Jynde vad. The data derive from the DIAS Jynde vad meteorological station located less than 1 km from the test site.

3.2 Results and discussion

3.2.1 Bromide leaching

At Jyndevad the autumn application of bromide was followed by high autumn precipitation (Table 10), 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 and all the bromide had leached from the uppermost meter of the soil about four months after application (Figure 15). At 2 m b.g.s. the breakthrough of bromide occurred two months after application, and the bromide concentration remained elevated during much of the monitoring period. It should be noted that the suction cups located 2 m b.g.s. were below the groundwater table from December 1999 to July 2000 (Figure 11). Rather than indicating downward transport in the unsaturated zone, these concentration profiles describe the groundwater in the upper part of the saturated zone.

The results indicate rapid transport of bromide through the unsaturated zone followed by much slower transport in the saturated zone. Thus the bromide has not yet reached the downstream monitoring wells although elevated bromide concentrations were detected in M4 at the very end of the monitoring period (Figure 16).

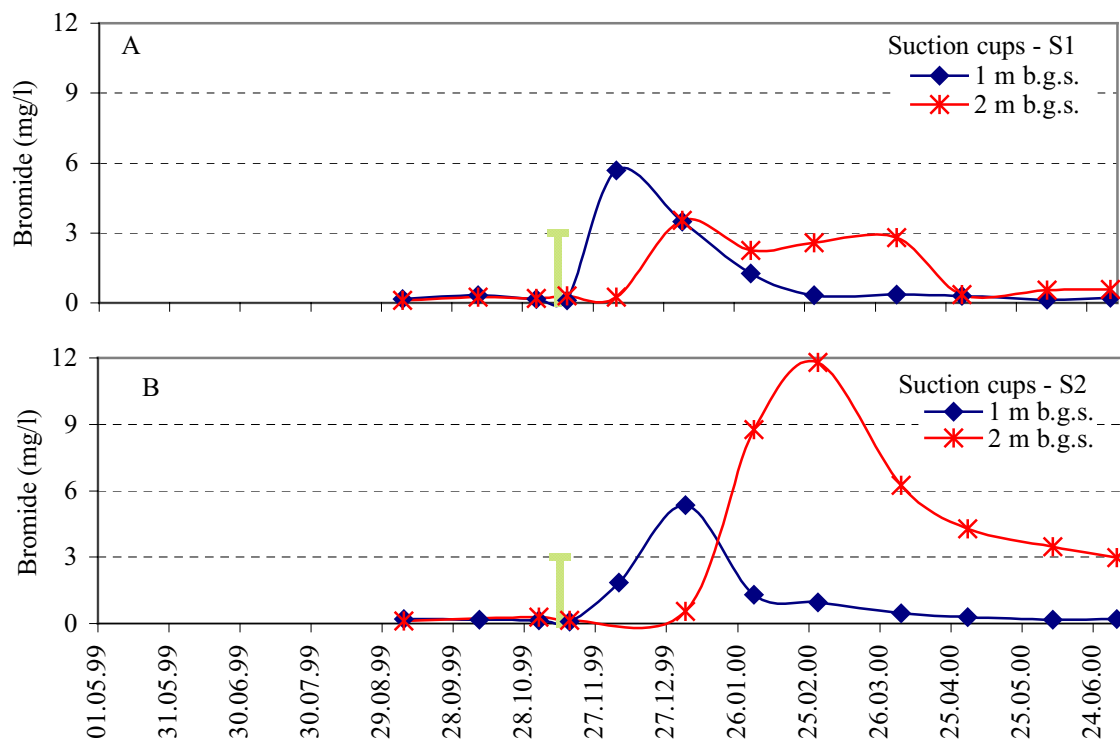


Figure 15. Bromide concentration at Jyndevad (suction cups S1 and S2) at 1 m b.g.s. and 2 m b.g.s. The green vertical line indicates the date of bromide application.

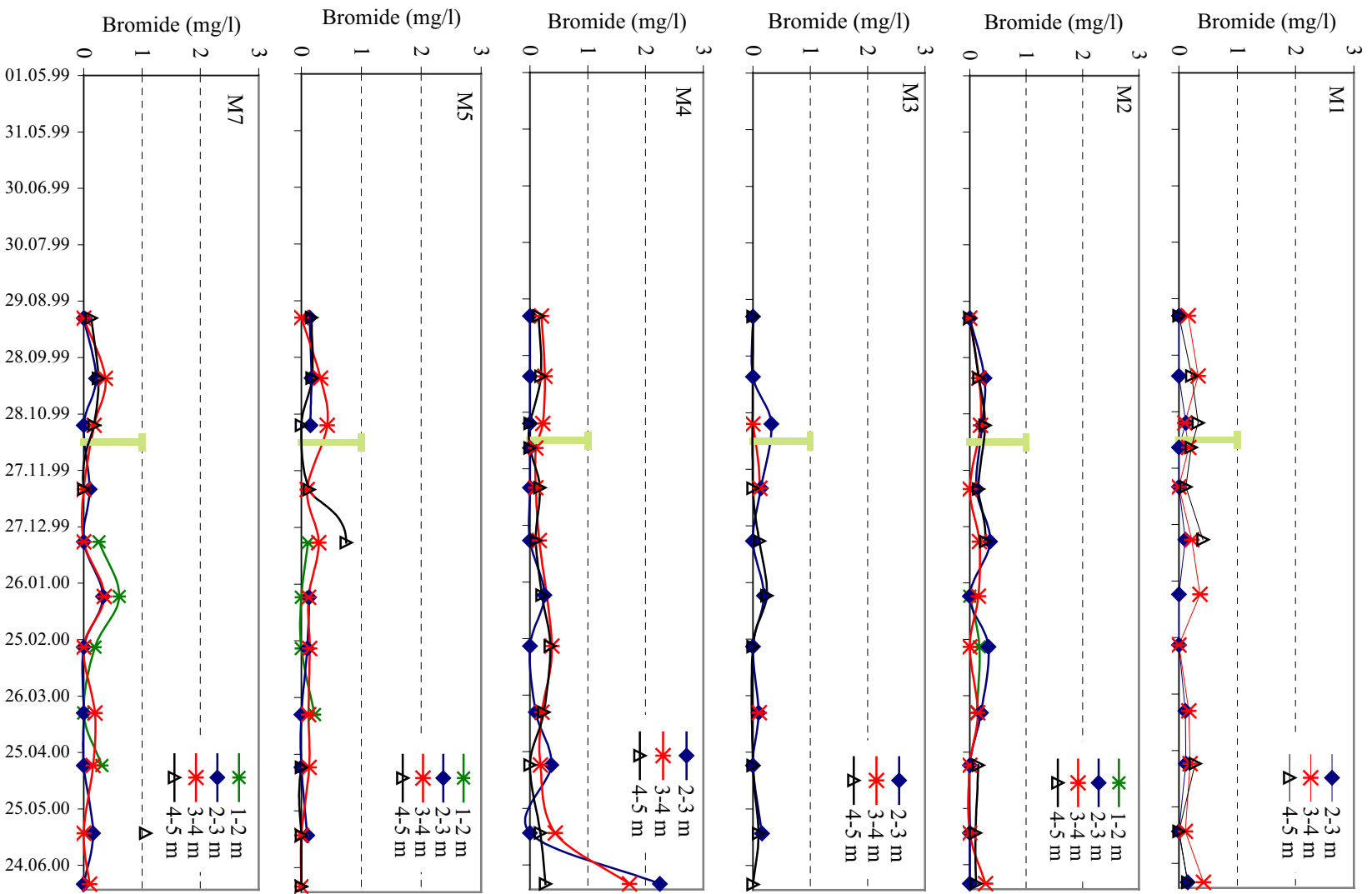


Figure 16. Bromide concentration in the groundwater at Jyndevad. The data derive from monitoring wells (M1–M7). The screen depths are in m b.g.s. and the green vertical line indicates the date of bromide application

3.2.2 Pesticide leaching

The leaching risk of tribenuron-methyl, glyphosate fenpropimorph and propiconazol was assessed at the Jynde vad site during the monitoring period:

Tribenuron-methyl – the active ingredient in Express – degrades rapidly in the soil, and the risk of leaching is therefore more associated with the degradation product triazinamin-methyl. As yet triazinamin-methyl has not been detected in any of the water samples. However, the mobility of triazinamin-methyl is considered to be very low due to its strong sorption capacity and it is therefore too early to assess the risk of leaching as the potential leaching period extends into the subsequent monitoring period.

Glyphosate – the active ingredient of Roundup – and the degradation product *AMPA* did not leach from the root zone during the monitoring period. Apart from two samples exhibiting AMPA concentrations of 0.02 µg/l, neither substance was detected in any of the other water samples. The mobility of both glyphosate and AMPA is considered to be very low due to their high sorption capacity towards soil and groundwater sediments. Again, it is too early to evaluate the leaching risk because the potential leaching period extends into the subsequent monitoring period.

Fenpropimorph and propiconazol – the active ingredients of Tilt Top – were applied to the field in April 2000, just two months before the end of the current monitoring period. It is consequently far too early to assess the leaching risk. Nevertheless, neither propiconazol nor fenpropimorph or its degradation product fenpropimorphic acid have been detected in any of the water samples so far analysed.

Previous application of pesticides has caused notable groundwater contamination with the degradation products of metribuzin. Evidence of such contamination was provided by supplementary analysis of eight groundwater samples for metribuzin and its degradation products (Table 11). The most prevalent contaminant was diketo-metribuzin, which was detected in all eight of the water samples. The highest concentration detected was 0.5 µg/l (monitoring well M2), and the maximum allowable concentration of 0.1 µg/l was exceeded in the downstream monitoring wells (M1, M2 and M5). Desamino-diketo-metribuzin was also detected in the downstream monitoring wells, the concentration again being high in M2 (1.1 µg/l), with concentrations below 0.1 g/l being detected in the other monitoring wells.

The occurrence of these degradation products appears to be attributable to regular use of the pesticide. Previous application of metribuzin at Jynde vad was carried out in accordance with current regulations, which permit a maximum dosage of 0.35 kg/ha/y (Table 12). The only other site in the vicinity of the Jynde vad test field where metribuzin has been applied is the neighbouring field located just south of the test site.

The results provided no evidence of groundwater contamination attributable to previous application of pesticides other than metribuzin. The initial screening analysis encompassing 42 pesticides thus revealed no sign of pesticides in the groundwater other than two samples containing desisopropylatrazine in concentrations of around 0.02 µg/l and one sample containing desethylatrazine in a concentration of 0.03 µg/l (Appendix 6).

Table 11. Groundwater concentration of desamino-diketo-metribuzin, diketo-metribuzin, desamino-metribuzin and metribuzin at Jynde vad ($\mu\text{g/l}$). The data derive from supplementary monitoring carried out in January 2001. Monitoring well M7 is situated upstream of the test site whereas M1, M2 and M5 are all situated downstream.

Monitoring well	M1		M2		M5	M7		
Screen depth (m b.g.s.)	1.6–2.6	2.0–3.0	3.0–4.0	4.0–5.0	3.7–4.7	2.6–3.6	3.6–4.6	4.6–5.6
Desamino-diketo-metribuzin	0.03	0.02	0.65	1.10	0.07	<	<	<
Diketo-metribuzin	0.10	0.07	0.54	0.53	0.30	0.06	0.05	0.05
Desamino-metribuzin	<	<	<	<	<	<	<	<
Metribuzin	<	<	<	<	<	<	<	<

<) Below the detection limit of $0.02 \mu\text{g/l}$

Table 12. Previous application of metribuzin at Jynde vad and the neighbouring field.

	Year	Crop	Product	Dosage ¹⁾ (kg/ha/y)
Jynde vad test site	1997	Potatoes	Sencor	0.30
	1998	Potatoes	Sencor	0.20
Neighbouring field located south of the Jynde vad test site	2000	Potatoes	Sencor	0.35

1) The maximum permitted dosage was reduced from 0.7 kg/ha/y to 0.35 kg/ha/y in 1994

3.3 Summary

The results of the monitoring hitherto undertaken at the Jydevad test field can be summarized as follows:

- The tracer studies provided a good indication of the water transport occurring during the monitoring period. Thus a large amount of the applied tracer leached from the unsaturated zone, although it has not yet reached the monitoring wells situated downstream of the test site.
- The leaching risk of the pesticides applied could not be assessed within the present monitoring period as it did not fully cover the potential leaching period. It should be noted, however, that no evidence was found of leaching by glyphosate, fenpropimorph, propiconazol, tribenuron-methyl or their degradation products AMPA, fenpropimorphic acid and triazinamin-methyl.
- Pesticide application prior to the monitoring period has resulted in marked groundwater contamination with degradation products of metribuzin. Diketo-metribuzin and desamino-diketo-metribuzin were detected in concentrations up to 0.5 µg/l and 1.1 µg/l, respectively.

4 Pesticide leaching at Faardrup

4.1 Materials and methods

4.1.1 Site description

Faardrup is situated in southern Zealand (Figure 1). The test field covers a cultivated area of 2.3 ha (150 x 160 m) and the terrain slopes 2%. The soil is a Pseudogleytypilessive (DK-classification) and the topsoil is characterized as sandy loam with 15% clay and 1.4% organic carbon (Table 1). The aquifer material contains glacial deposits dominated by clayey till. The geological description suggests that small channels or basins consisting of meltwater clay and sand occur in the clay till body. 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 area is characterized by a downward hydraulic gradient. The overall direction of groundwater flow is towards the west in the upper part of the aquifer. 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 (Figure 17, Figure 18 and Figure 19).

4.1.2 Agricultural management

The crop sown in 1999 was winter wheat (cultivar Stakado). The pesticides applied were glyphosate, ioxynil, bromoxynil and fluroxypyr (Table 13). The 1999 growing season was characterized by very good crop development with high expectations as to crop yield.

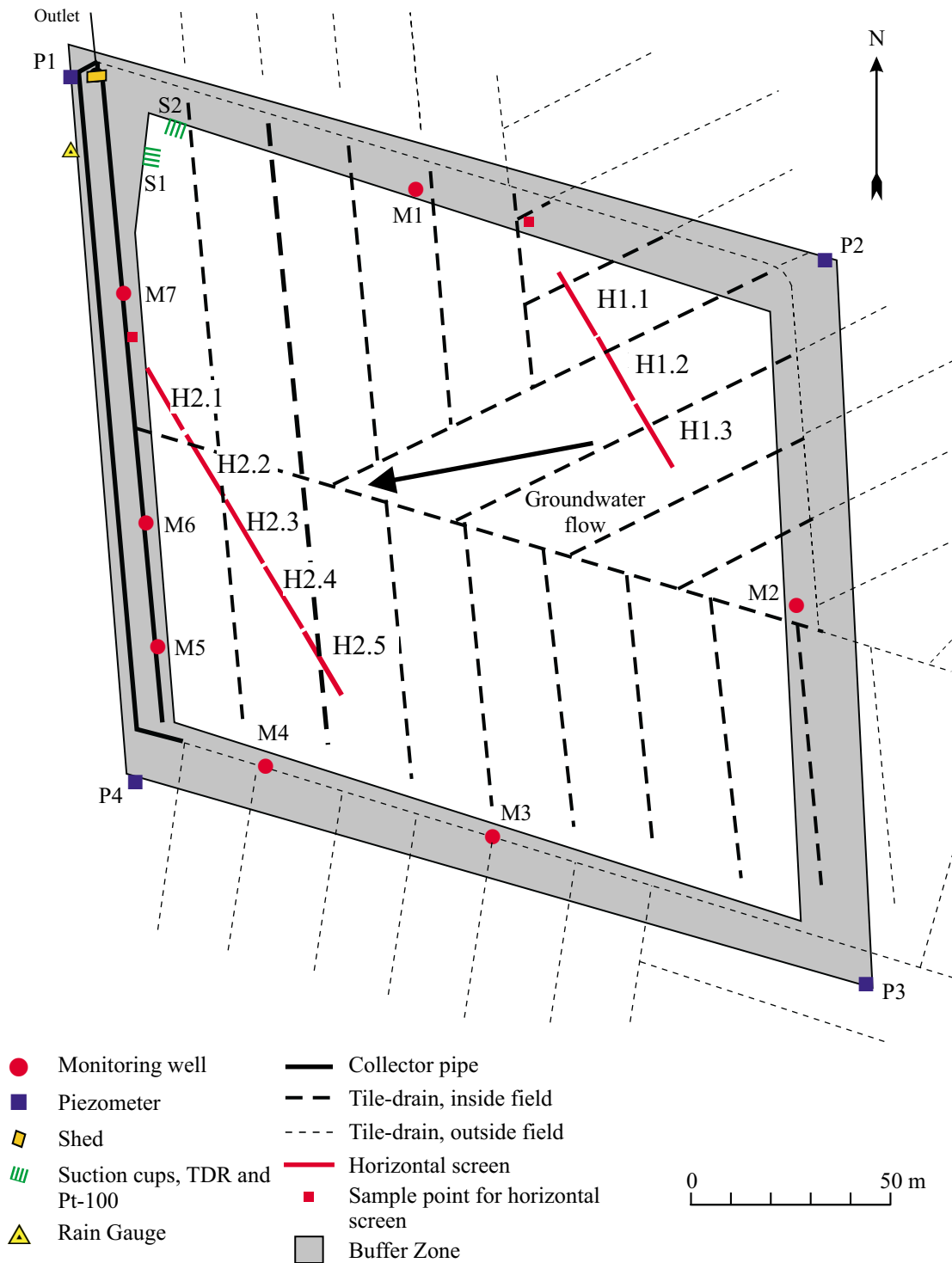


Figure 17. Overview of the Faardrup test site. The innermost white area indicates the cultivated land, while the grey area indicates the surrounding buffer zone. The positions of the various installations are indicated, as is the direction of groundwater flow.

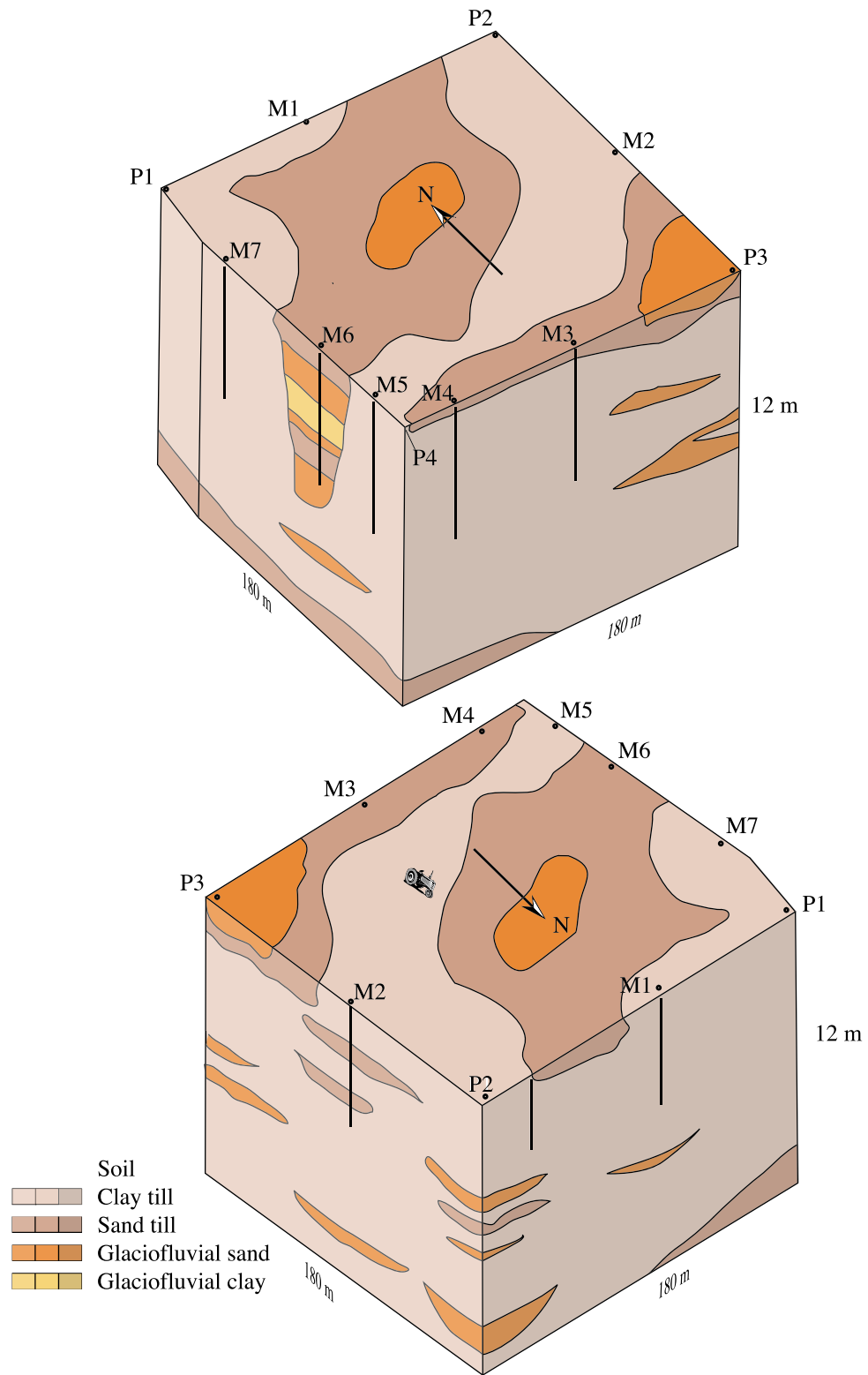


Figure 18. Geological description of the Faardrup site (Lindhardt *et al.* 2001).

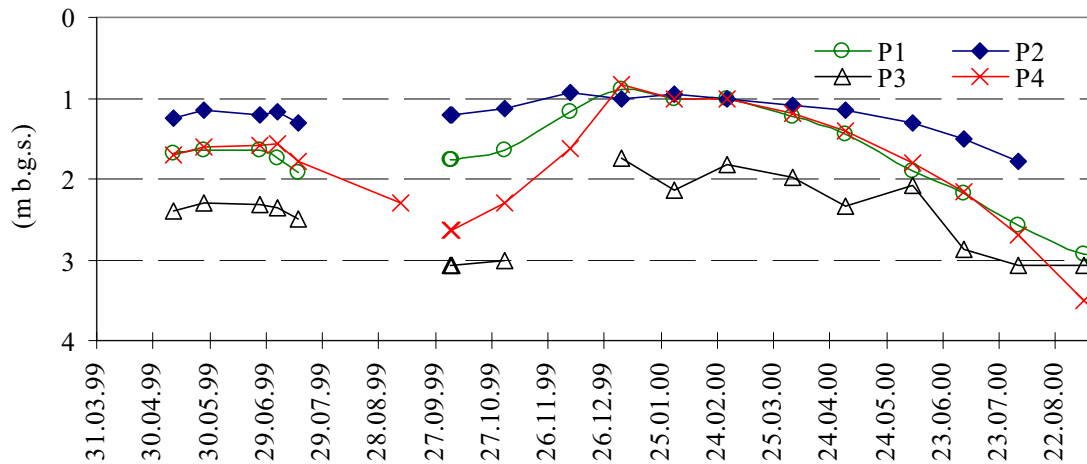


Figure 19. Temporal variation in potential head at Faardrup. The data derive from piezometers P1–P4 with screens located 2.5–3.5 m b.g.s.

Table 13. Management practice at Faardrup. The active ingredients of the various pesticides are indicated in parentheses.

Date	Management practice
11.08.1999	Herbicide application – 2.0 l/ha Roundup 2000 (glyphosate)
10.09.1999	Stubble harrowed – 10 cm depth
19.09.1999	Ploughed – 20 cm depth
19.09.1999	1 st seed bed preparation – with power harrow, 5 cm depth
20.09.1999	2 nd seed bed preparation – with power harrow, 5 cm depth
20.09.1999	Sowing of winter wheat – cultivare Stakado, seeding with 180 kg/ha, sowing depth 4 cm and row distance 12.5 cm
01.10.1999	BBCH stage 09 – emergence, plant density 120 plants/m ²
05.10.1999	Tracer application – 30 kg/ha potassium bromide
14.10.1999	Herbicide application – 1.0 l/ha Briotril (ioxynil and bromoxynil)
15.10.1999	BBCH stage 12 – plant density 270 plants/m ²
28.10.1999	BBCH stage 14 – plant density 310 plants/m ²
21.03.2000	Fertilization – 70 kg N/ha, 10 kg P/ha and 25 kg K/ha
08.04.2000	Herbicide application – 0.8 l/ha Starane 180 (fluroxypyr)
10.04.2000	BBCH stage 24 – biomass measured
19.04.2000	Fertilization – 99 kg N, 14 kg P and 36 kg K /ha
25.04.2000	BBCH stage 31 – first node detectable
05.05.2000	Fungicide application – 0.5 l/ha Tilt Top (propiconazol and fenpropimorph)
05.05.2000	BBCH stage 33 – 3 nodes detectable
12.05.2000	BBCH stage 37 – tip of flag leaf visible
22.05.2000	BBCH stage 50 – biomass measured
31.05.2000	Fungicide application – 0.5 l/ha Tilt Top (propiconazol and fenpropimorph)
19.06.2000	Insecticide application – 0.25 l/ha Pirimor G (pirimicarb)
19.06.2000	BBCH stage 59 – end of heading
30.06.2000	BBCH stage 75 – milky ripe, biomass measured

4.1.3 Monitoring strategy

The bromide and the pesticide concentrations were measured monthly in both the unsaturated and the saturated zone following the procedure already described in Section 2.1.3. The Faardrup site differs from the sandy Tylstrup field, however, in that weekly analysis is carried out on water sampled from the drainage system located approx. 1 m b.g.s. In addition to the vertical monitoring wells, two horizontal monitoring wells were also installed 3.5 m beneath the test site (Figure 17). Each horizontal monitoring well consisted of 18 m screens providing integrated water samples that characterize ground-water quality just beneath the test site. The monthly and quarterly monitoring programme for pesticides was carried out as described in Table 14.

Table 14. Pesticide monitoring programme at Faardrup.

	Measured monthly	Measured quarterly	Not measured
Suction cups	S1 – 1 m b.g.s. S2 – 1 m b.g.s.	S1– 2 m b.g.s. S2 – 2 m b.g.s.	-
Monitoring wells	M5, M6	M1, M2, M3, M4	M7
Horizontal wells	H1.3, H2.3	H1.1, H2.1, H2.5	-

4.1.4 Climate

The monitoring period May 1999–June 2000 was rather wet at Faardrup with 773 mm precipitation, which is 19% more than normal. The excess is mainly attributable to unusually high precipitation in August and December 1999 (Table 15). November 1999 was also an unusual month in terms of a precipitation which amounted to 85% less than the monthly normal. The region around Faardrup has one of the lowest precipitation rates in Denmark, with a yearly normal of only 558 mm/y. During the monitoring period the precipitation input in Faardrup was 33% lower than at the Jyndevad site and 26% lower than at the Tylstrup site. The period accounting for the precipitation surplus started as late as December, and covered a much shorter period of only five months (Figure 20).

Table 15. Monthly precipitation (Precip.) and potential evapotranspiration (Pot. evap.) at Faardrup in mm/month. The normal values based on time series for 1961–90 are shown in parentheses. The data derive from the DIAS Flakkebjerg meteorological station located 4 km from the test site.

	1999								2000						Total
	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	
Precip.	54 (45)	117 (47)	58 (59)	111 (55)	25 (59)	68 (53)	8 (55)	104 (51)	27 (41)	46 (26)	60 (33)	41 (34)	25 (45)	29 (47)	773 (650)
Pot. evap. ¹⁾	92 (93)	103 (107)	126 (102)	96 (88)	64 (52)	29 (26)	8 (10)	5 (5)	8 (5)	14 (12)	33 (29)	55 (56)	112 (93)	101 (107)	846 (785)
Precip. surplus ²⁾	-38 (-48)	14 (-60)	-68 (-43)	15 (-33)	-39 (7)	39 (27)	0 (45)	99 (46)	19 (36)	32 (14)	27 (4)	-14 (-22)	-87 (-48)	-72 (-60)	

¹⁾ The potential evapotranspiration (Pot. Evap) is calculated using a modified Makkink equation (Aslyng and Hansen, 1982)

²⁾ Precipitation surplus (Precip. surplus) is defined as the difference between the precipitation and the potential evapotranspiration

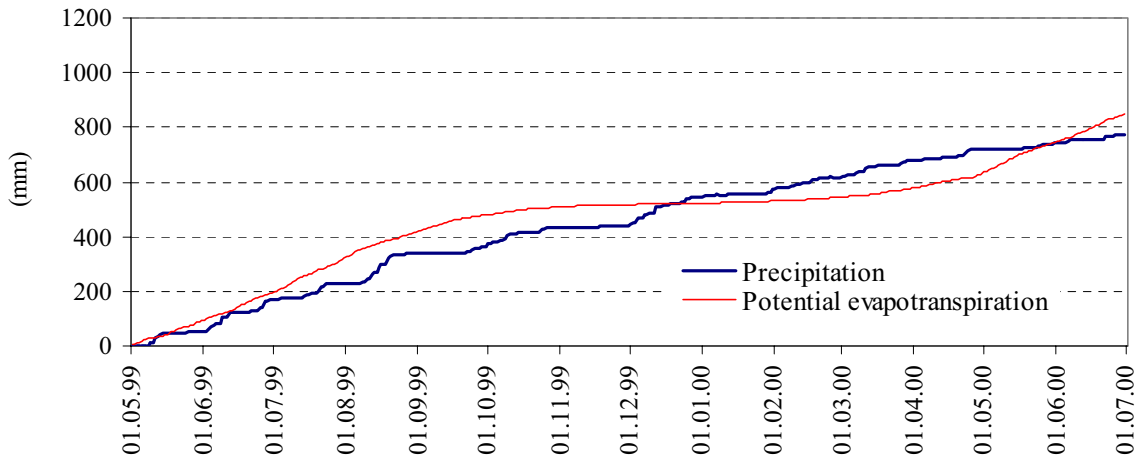


Figure 20. Accumulated precipitation and evapotranspiration at Faardrup. The data derive from the DIAS Flakkebjerg meteorological station located 4 km from the test site.

4.1.5 Drainage runoff

During the monitoring period, continuous drainage runoff occurred from approx. 1 December 1999 until 1 May 2000, but was very low during April 2000 (Figure 21). The late start of continuous drainage runoff reflects the very low precipitation input in November, which corresponded to only 15% of the monthly normal (Table 15). The drainage period was characterized by three storm events. Two of these occurred in December, in part accounting for the high level of precipitation, which was twice the monthly normal. The peak maximum flow rate during these events was 4,800 l/ha/h, corresponding to 0.5 mm per hour. The third storm event occurred in March 2000, when a thunderstorm caused a very sudden, short event in which drainage runoff rose from 65 l/ha/h to 4,920 l/ha/h and returned to 65 l/ha/h all within 4 hours. During the whole of the monitoring period the accumulated drainage runoff amounted to 190 mm, i.e. about 25% of the total precipitation input left the system via drainage runoff.

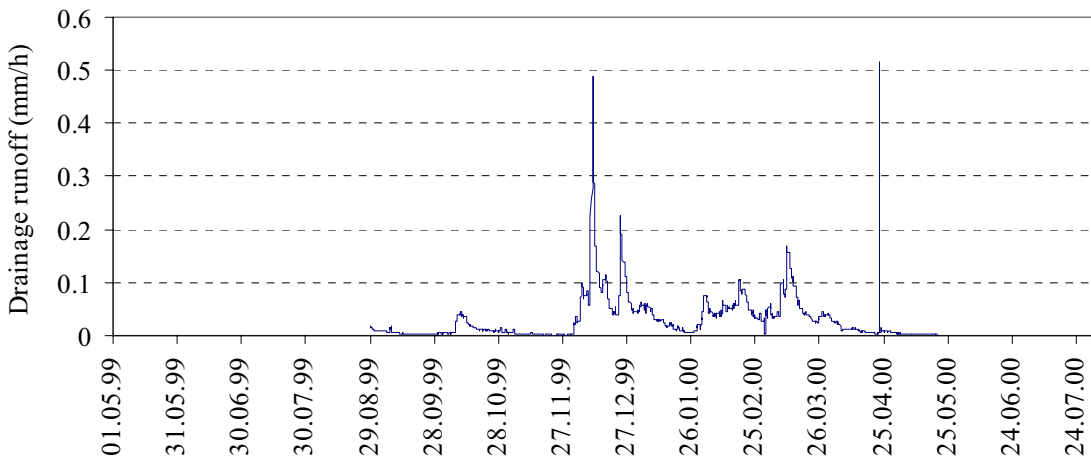


Figure 21. Drainage runoff at Faardrup.

4.2 Results and discussion

4.2.1 Bromide leaching

The bromide tracer was first detected at 1 m b.g.s. in late December, about three months after application (Figure 22A and B). Compared to both Jyndevad and Tylstrup, both the precipitation and the precipitation surplus were much lower at Faardrup (Section 4.1.4). The bromide also leached much later at Faardrup than at Jyndevad, where it was also applied in the autumn.

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 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 during the current monitoring period. Similar evidence of bromide leaching was also found in the analysis of the drainage water derived from the drainage system located 1 m b.g.s. (Figure 22C). The bromide breakthrough was similar to that detected in the suction cups located 1 m b.g.s., although the concentration was much lower. Total recovery of bromide in drainage water during the monitoring period amounted to 1.4 kg/ha, indicating that only 7% of the bromide tracer leached into the drains (Figure 24A).

The results are also indicative of subsequent transport of bromide down to a depth of both 2 and 3.5 m b.g.s. Thus, slightly elevated bromide concentrations of up to 1 mg/l were detected 2 m b.g.s. in the suction cups at S2 (B) and 3.5 m b.g.s. in the horizontal wells (Figure 22D). Bromide was not detected in the suction cups at S1 or the downstream monitoring wells (Figure 23), however, and final assessment of bromide transport in the saturated zone must await the results of the subsequent monitoring period.

Finally, it should be noted that the occurrence of continuous drainage runoff in December 1999 was not reflected by elevated bromide concentrations in either the suction cups or the drainage runoff (Figure 22C & A), possibly because of macropore transport in the topsoil or a dilution effect caused by groundwater mixing.

The presence of macropores causes rapid drainage following precipitation events since large amounts of water may be transported downwards through these pores. When a significant proportion of the precipitation flows into the macropores at the soil surface, it has little contact with the actual soil matrix. If the majority of the bromide is present in the soil matrix, it will thus be “protected” from the bypass flow in macropores as suggested by Larsson *et al.* (1999). In this case large amounts of water with a much lower bromide concentration will enter the drainage system. During the heavy December precipitation the groundwater table on part of the test site rose rapidly above the level of both the drainage system and the uppermost suction cups (Figure 19). During this period, intruding groundwater with a much lower bromide content might have diluted the bromide concentration in the suction cups.

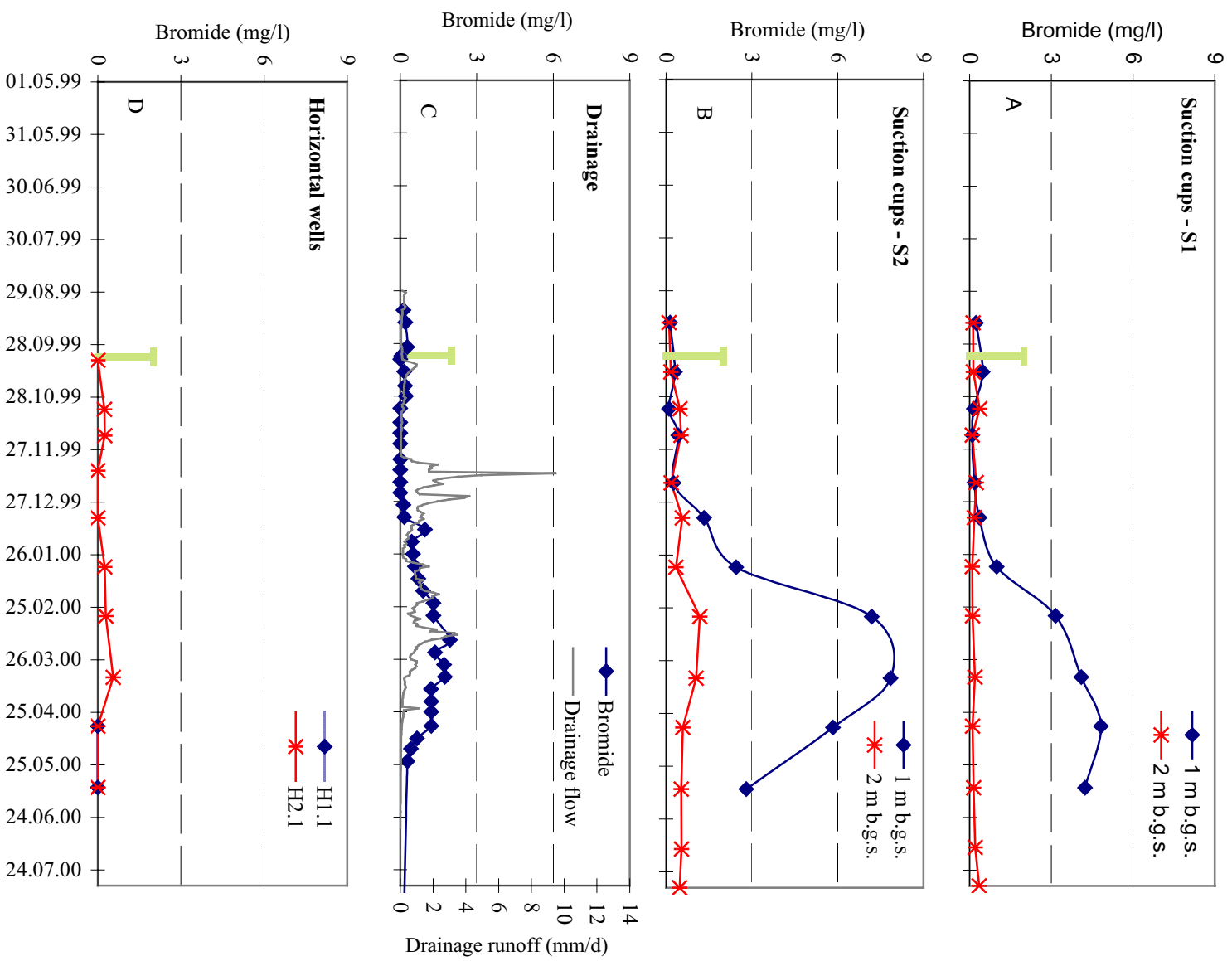


Figure 22. Bromide concentration at Faardrup (suction cups S1 and S2) at 1 and 2 m b.g.s. (A and B). The bromide concentration is also shown for drainage runoff (C) and the horizontal wells H1 and H2 (D). The green vertical line indicates the date of bromide application.

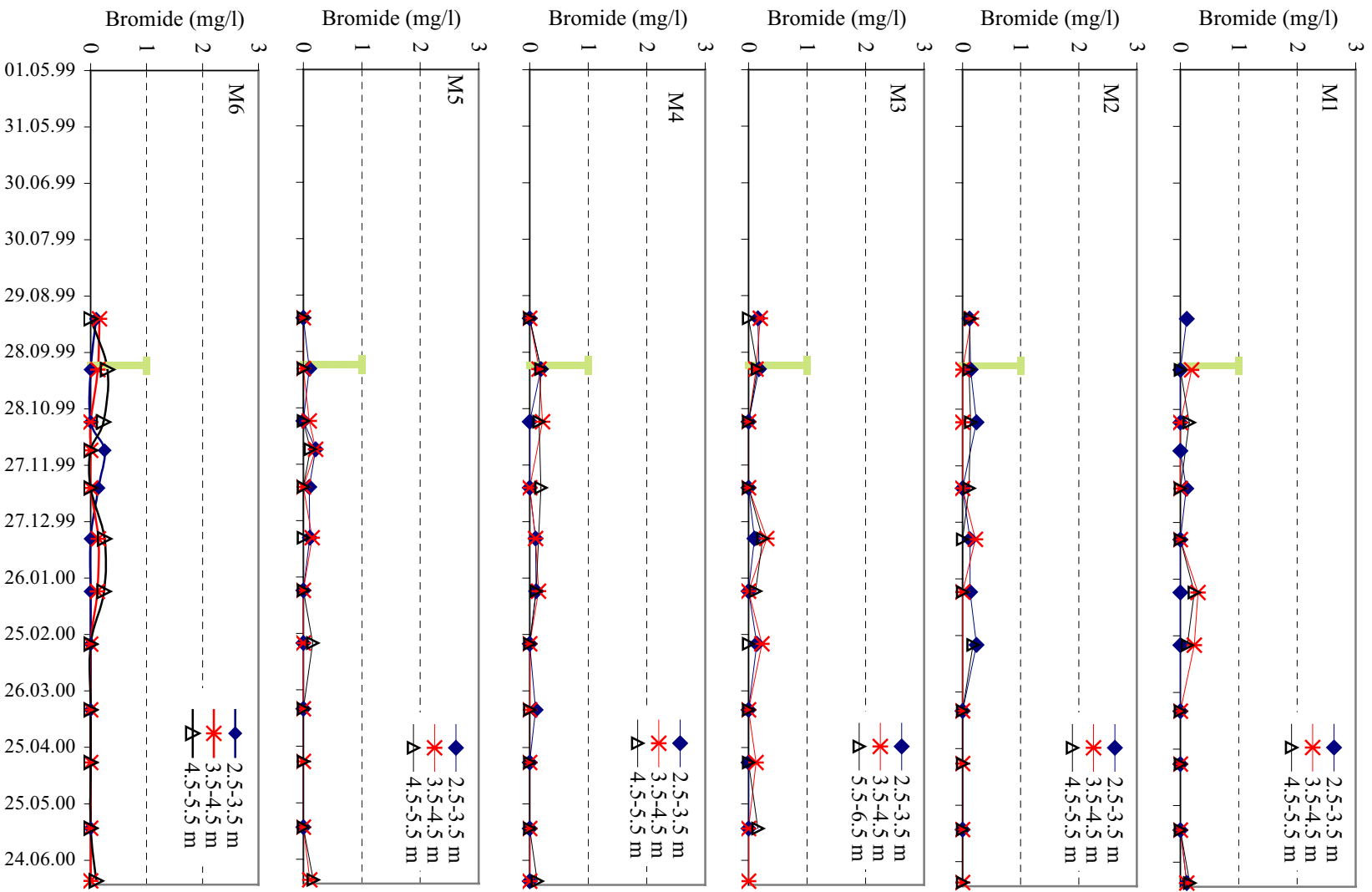


Figure 23. Bromide concentration in the groundwater at Faardrup. The data derive from monitoring wells M1–M6. Screen depth is indicated in m b.g.s. and the green line indicates the date of bromide application.

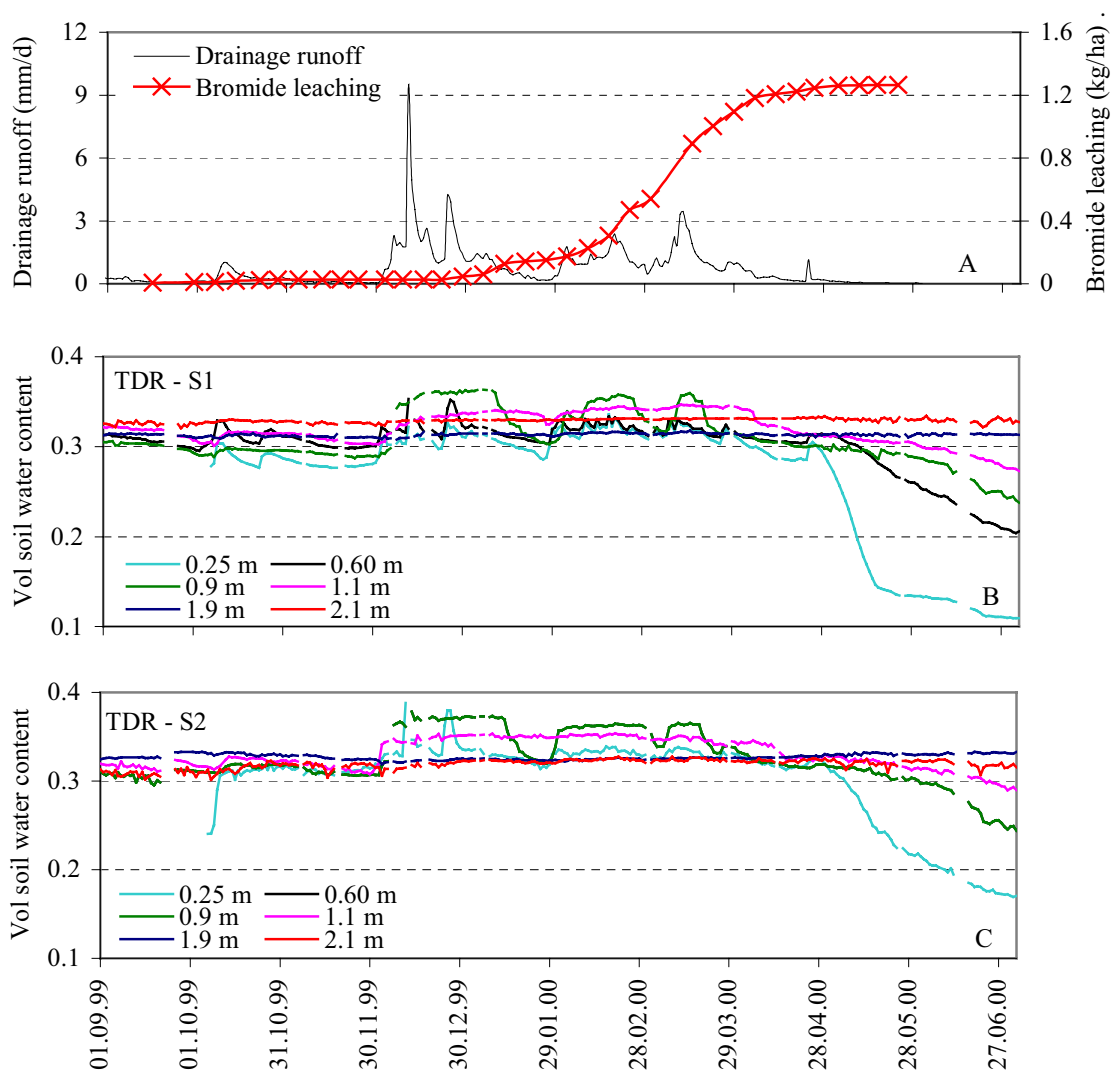


Figure 24. Drainage runoff and accumulated bromide leaching to the drainage water (A) and soil water content (B and C) at Faardrup. The data in B and C derive from TDR probes installed at various depths at S1 and S2, respectively.

4.2.2 Pesticide leaching

The leaching risk of glyphosate, bromoxynil, ioxynil, pirimicarb, propiconazol, fenpropimorph and fluroxypyr was assessed at the Faardrup site during the monitoring period:

Glyphosate – the active ingredient in Roundup – and the degradation product *AMPA* did not leach from the root zone during the monitoring period. However, the mobility of both glyphosate and AMPA is considered to be very low due to their strong sorption capacity. It is therefore still too early to assess the leaching risk.

Ioxynil and bromoxynil – the active ingredients in Briotril – were not detected in any of the water samples analysed. These findings complement those of the degradation studies, indicating that both compounds degrade rapidly in the Faardrup soil. The DT₅₀ thus ranged from <1–5 days for bromoxynil and 1–12 days for ioxynil (Section 5.2.1). During the monitoring period, moreover, the Faardrup soil was characterized by sufficient soil humidity, which also favours the degradation processes (Figure 24B & C). In conclusion, the combination of sufficient soil humidity, low DT₅₀ and relatively long residence time in the root zone indicate good conditions for degradation processes and hence a low risk for leaching of ioxynil and bromoxynil.

Fenpropimorph and propiconazol (the active ingredients in Tilt Top), *fluroxypyr* (the active ingredient in Starane 180) and *pirimicarb* (the active ingredient in Pirimor) were all applied to the field during spring 2000, shortly before the end of the current monitoring period (Table 13). It is consequently too early to assess the leaching risk. Nevertheless, neither of the above substances nor the degradation product *fenpropimorphic acid* have been detected in any of the water samples analysed so far.

Finally, the results provide no evidence of groundwater contamination attributable to earlier application of pesticides. Apart from two samples with a desisopropylatrazine concentration of 0.03 µg/l, no pesticides were detected in the initial screening analysis comprising 42 pesticides (Appendix 7).

4.3 Summary

The results of the monitoring hitherto undertaken at the Faardrup test field can be summarized as follows:

- The tracer studies provide a good indication of the water transport occurring during the monitoring period. Part of the applied bromide leached out of the unsaturated zone during the monitoring period – 7% of the tracer left the site via drainage runoff, and there was evidence of bromide transport down to a depth of 3.5 m. However, the bromide has not yet reached the monitoring wells located downstream of the test site.
- The leaching risk is considered to be small for ioxynil and bromoxynil as they are likely to have degraded. Neither substance was detected in any of the water samples analysed and conditions for degradation processes seem to be good at the Faardrup site: DT₅₀ was very low for ioxynil and bromoxynil, residence time in the root zone was relatively long and soil humidity was sufficient.
- The leaching risk of glyphosate, fenpropimorph, propiconazol, pirimicarb and fluroxypyr could not be assessed within the present monitoring period as it did not fully cover the potential leaching period. It should be noted, however, that there was no evidence of leaching by these pesticides or their degradation products AMPA and fenpropimorphic acid.

5 Degradation and sorption parameters

Information on degradation and sorption are of considerable importance when modelling leaching of pesticides in soil. Site-specific information is usually sparse, however, and data from the literature often has 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. It was also decided to determine biomass and microbial activity of the soils at the sites to clarify the level of microbial activity at the time the degradation studies were initiated. The degradation and sorption parameters were determined on a combination of nine pesticides and six soil types encompassing both plough layer and subsoil (Table 16). With a few of the pesticides, important degradation products were also included, e.g. acids of flamprop-M-isopropyl and fenpropimorph. This preliminary report presents degradation and sorption data for bromoxynil and ioxynil in soil from the Faardrup test site along with sorption data for metamiltron in soil profiles from Faardrup and Silstrup. Biomass determined by the SIR method and microbial activity determined by degradation of radiolabelled acetate are also reported.

Table 16. Soil-pesticide combinations investigated in the degradation and sorption studies.

Active ingredient	Trade name	Dose (g a.i./ha)	Investigated sites
Bromoxynil (H)	Briotril	200	Faardrup, Slaeggerup
Dimethoat (I)	Dimethoat 400	320	Silstrup, Estrup, Slaeggerup
Fenpropimorph (F)	Tilt Top	375	Tylstrup, Jyndevad, Faardrup, Slaeggerup
Flamprop-M-isopropyl (H)	Barnon Plus	630	Silstrup, Estrup, Slaeggerup
Ioxynil (H)	Briotril	200	Faardrup, Slaeggerup
Metamiltron (H)	Goltix WG	2100	Silstrup, Faardrup
Propiconazol (F)	Tilt Top	125	Tylstrup, Jyndevad, Faardrup, Slaeggerup
Terbuthylazin (H)	Lido	1150	Jyndevad
Tribenuron-methyl (H)	Express	7.5	Jyndevad, Silstrup

H: Herbicide, I: Insecticide, F: Fungicide

5.1 Materials and methods

5.1.1 Sampling of soil

Degradation and sorption were determined in the laboratory using pooled soil samples. Sampling was done 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 were cleaned with alcohol prior to use.

The plough layer samples were collected using a hand auger (2 cm in diameter and 20 cm long). For the subsoil samples, two 50 x 100 cm pits were excavated in the buffer zone and the samples collected horizontally using a spoon. Each sample consisted of at least 2 kg of soil per substance per field per depth. At Silstrup a sample based on 85 subsamples was collected from the plough layer within the test field while the subsoil samples were pooled from the two excavations in the buffer zone. Pesticides were applied to the Faardrup test field shortly before soil sampling was carried out. In order to avoid interactions with the applied pesticide the plough layer samples were sampled in the buffer zone on three sides of the area and pooled to a composite sample based on 100 samples. The subsoil samples from the excavation pits were also pooled. All samples were stored at 5°C after sampling until needed for the experiments. All results are expressed on oven-dry soil basis. Prior to the experiments the soils were homogenized and any stones and plant parts removed.

5.1.2 Degradation rate

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 5-g 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 depended on the dosage shown in Table 16. The degradation experiments with bromoxynil and ioxynil were performed at a concentration of 0.5 mg a.i./kg. 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 was stored at -18°C until analysis. The time intervals were set for each pesticide according to the half-life reported in the literature such as to ensure that at least three half-lives were covered. Each degradation experiment was performed in duplicate. The extraction procedure was performed in an ASE (Accelerated Solvent Extraction) apparatus: 3 g hydromatrix was added to each duplicate soil sample in ASE tubes and the extraction performed using 0.42% phosphonic acid in methanol at fixed

temperature, pressure and time depending on the pesticide. Bromoxynil and ioxynil were extracted 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.

Stability tests were performed by adding the pesticides to soil samples and storing them at -18°C for a period corresponding to the storage period of the test samples – 73–185 days for subsoil samples containing bromoxynil or ioxynil and 165–212 days for plough layer samples. No significant differences in the content of the stability tests were seen during time. The ioxynil recovery in subsoil exceeded 89% while bromoxynil recovery exceeded 80%. Thus it was not considered necessary to apply a recovery correction to the subsoil samples. With the plough layer samples the recovery of ioxynil ranged from 35–53% while that of bromoxynil ranged from 31–59%. Various attempts to improve the recovery were unsuccessful and the plough layer sample results were therefore corrected on the basis of the recovery rates.

5.1.3 Determination of sorption

The soil samples were sieved (2 mm) and homogenized. To reduce the microbial activity, the soils were sterilized by radiation with 10 Kgray. Sorption experiments were carried out in a manner similar to that described in OECD (1997). The soil:0.01 M CaCl₂ ratio was fixed on the basis of literature values for K_d. All experiments were performed at one concentration (three replicates) with unlabelled pesticides. Sorption was determined in both plough layer and subsoil samples. After shaking the soil with 0.01 M CaCl₂ 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 K_d was calculated as:

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

5.1.4 Microbial activity

Microbial activity was determined both as biomass determined by the SIR method (Anderson and Domsch, 1978) and as the actual microbial activity of the samples measured from the degradation of radiolabelled Na-acetate. ¹⁴C Na-acetate (5 µg/g) was added to the soil in an Erlenmeyer flask and the evolved ¹⁴CO₂ collected and counted using a scintillation counter.

Microbial biomass was measured using the substrate-induced respiration (SIR) method 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 CO₂ was determined. CO₂ evolution was measured by gas chromatography. All studies were performed in quadruplicate.

5.2 Results and discussion

5.2.1 Degradation

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 in the Faardrup soil, and the DT_{50} values of both were much lower than reported in the literature (Table 17).

Degradation of bromoxynil was remarkably fast in both the plough layer and the subsoil, so fast in fact that only a few measurable data points were obtained during the degradation experiment (Figure 25). 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.

With ioxynil there was a sufficient number of data points to enable mathematical modelling using the software TableCurve 2D. The models fitted to the data included $\frac{1}{2}$ order, 2nd order, 3rd order, n^{th} order, 2nd order hyperbolic as well as a 1st order and a two-compartment 1st + 1st order model. The mathematical expressions for the latter two models are:

$$\begin{aligned} 1^{\text{st}} \text{ order model:} & \quad c(t) = a \cdot e^{-k_1 \cdot t} \\ 1^{\text{st}} + 1^{\text{st}} \text{ order model:} & \quad c(t) = a \cdot e^{-k_1 \cdot t} + b \cdot e^{-k_2 \cdot t} \end{aligned}$$

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

1st order kinetics is often assumed when degradation data are presented in the literature, and most of the available leaching models describe the degradation processes through 1st order kinetics. However, the curve fitting analysis showed that the degradation of ioxynil was best described by a 1st + 1st order model, whereas a 1st order model provided a less satisfactory description of the degradation processes (Figure 26). The error introduced by using a 1st order model increases with an increasing number of half-lives. With regard to determination of the first DT_{50} , as is presented in Table 17, the error introduced by applying 1st order kinetics is negligible. As the number of half-lives increases, however, the 1st order model tends to overestimate the degradation rate. This is presumably due to the fact that sorption influences the availability of the compound for

microbial degradation (Scow *et al.* 1992), a factor that is not taken into account by the 1st order model. A number of recent degradation/mineralization studies have also shown that a 1st + 1st order model is often the best expression for degradation of pesticides present in low concentrations (Fomsgaard,1999).

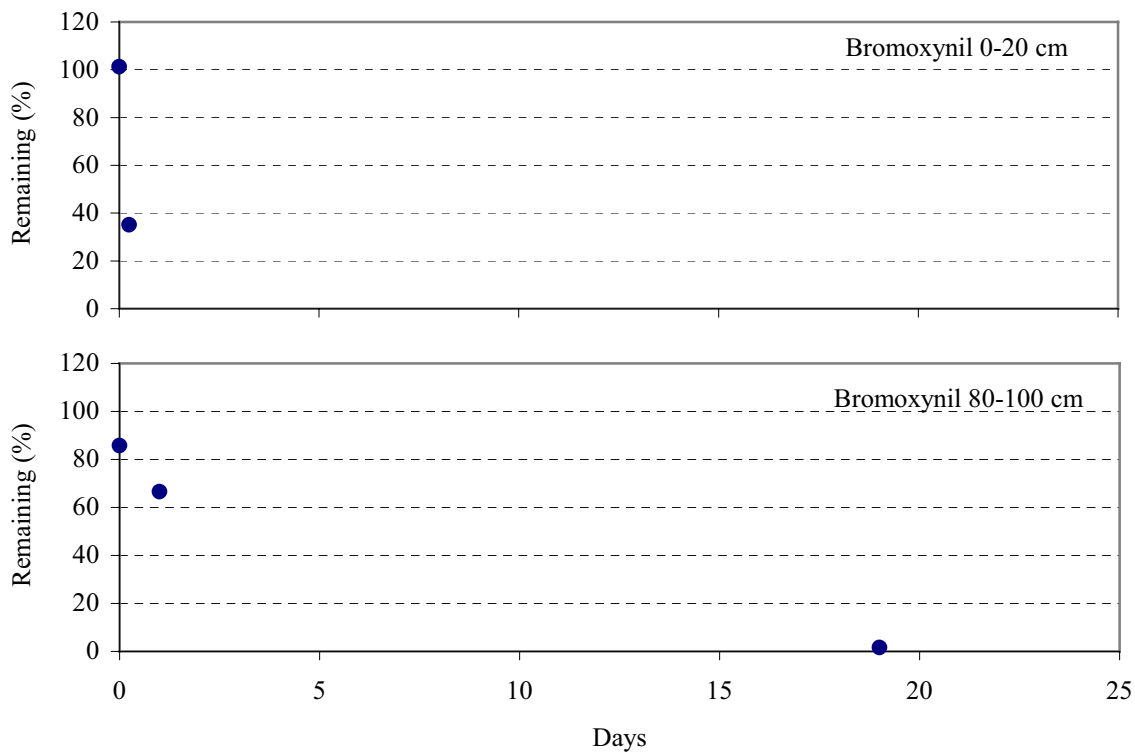


Figure 25. Degradation of bromoxynil in the plough layer (0–20 cm) and subsoil (80–100 cm) from Faardrup. The initial concentration of bromoxynil was 0.5 mg/kg.

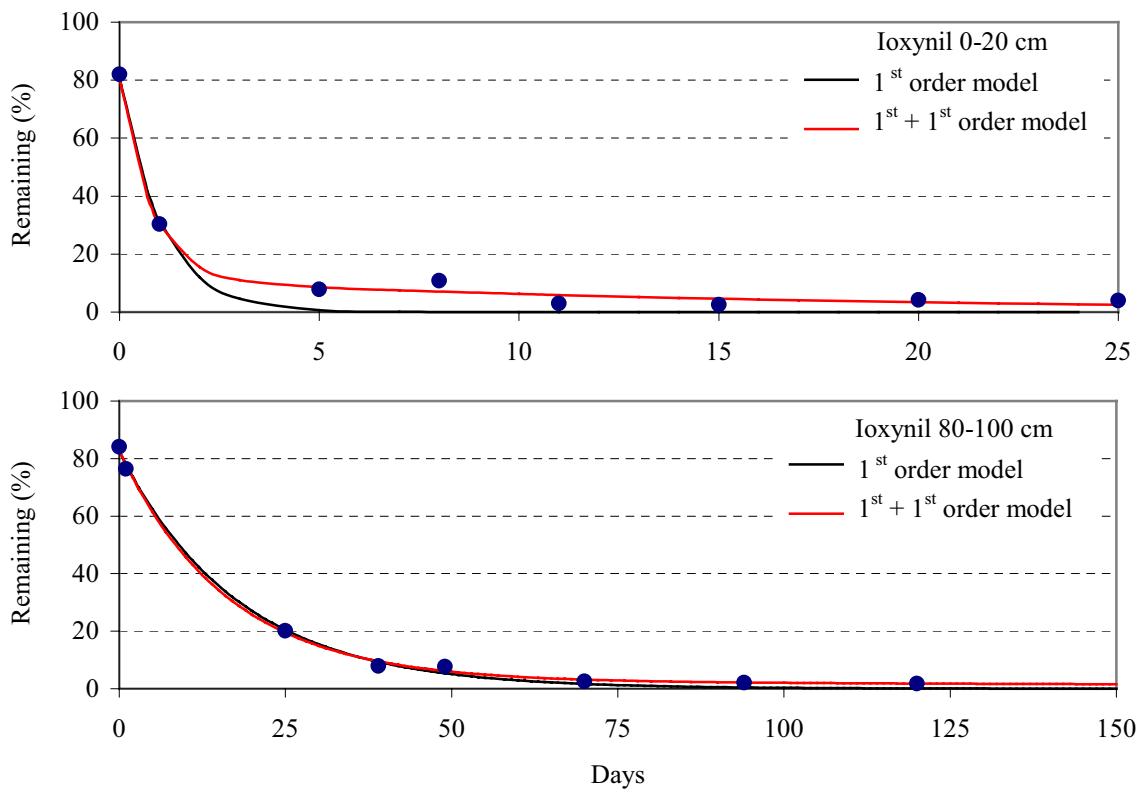


Figure 26. Degradation of ioxynil in the plough layer (0–20 cm) and subsoil (80–100 cm) from Faardrup. Dots indicate the experimental data, while the solid lines indicate the fitted curve for a two-compartment $1^{\text{st}} + 1^{\text{st}}$ order model and a 1^{st} order model. The initial concentration of ioxynil was 0.5 mg/kg.

Table 17. DT_{50} for bromoxynil and ioxynil. Literature values are the median with the range in parentheses.

Pesticide	Depth (cm)	DT_{50} (days)
Bromoxynil	Faardrup 0–20	<1
	Faardrup 80–100	<5
	Literature Plough layer	10 (1.5–52)
Ioxynil	Faardrup 0–20	<1
	Faardrup 80–100	12
	Literature Plough layer	38 (1.5–75)

5.2.2 Sorption

The sorption parameters were all in the lower end of the literature values (Table 18). K_{oc} was particularly low in the case of bromoxynil (85 ml/g in the plough layer) and ioxynil (52 ml/g in the subsoil). The data also confirmed the very low sorption generally found in the subsoil. Hence, the K_d and K_{oc} were considerably lower in the subsoil than in the plough layer. This was not the case with the Silstrup soil, however, where K_d was the same in both the plough layer and the subsoil. Moreover, the sorption capacity of Silstrup soil towards metamitron was stronger than that of Faardrup soil (Table 18).

It should be noted that organic carbon content data are not yet available, and data in Table 18 derive from Lindhardt *et al.* (2001). These findings will be corrected with the actual values as soon as the analyses are completed.

Table 18. Experimental and literature values of K_d and K_{oc} . The experimental data are means of triplicate measurements with the standard deviation in parentheses. The literature values are median values with the range indicated in parentheses.

Pesticide	Field and soil depth	Pest. conc. mg/l	Water:soil ratio	K_d (ml/g)	Org. C (%)	K_{oc} (ml/g)
Bromoxynil	Faardrup (0–20 cm)	5	5	1.16 (0.02)	1.36	85 (1.5)
	Faardrup (80–100 cm)	5	1	N.D.*)	0.174	N.D.*)
	Literature			(2–13)	–	371 (108–634)
Ioxynil	Faardrup (0–20 cm)	5	5	2.90 (0.03)	1.36	213 (2)
	Faardrup (80–100 cm)	5	1	0.09 (0.02)	0.174	52 (11)
	Literature			(2–20)	–	278 (235–321)
Metamitron	Faardrup (0–20 cm)	5	5	1.69 (0.22)	1.36	124
	Faardrup (80–100 cm)	5	1	0.13 (0.01)	0.174	75
	Silstrup (0–20 cm)	5	5	3.47 (0.1)	2.17	160 (5)
	Silstrup (80–100 cm)	5	1	0.41 (0.05)	0.232	177 (25)
	Literature			(1–7)	–	207 (17–700)

*) N.D. Not detectable

5.2.3 Microbial activity

As could be expected, the microbial activity at all test sites was significantly greater in the plough layer than in the subsoil. This difference is clearly illustrated in Table 19, which shows both microbial activity and microbial biomass as determined by the Na-acetate and SIR methods, respectively (see Section 5.1.5).

The biomass and microbial activity data will be correlated to pesticide degradation data when more studies have been performed. The findings from Faardrup already appear to be in good agreement with the degradation studies, thus suggesting the occurrence of much faster degradation in the plough layer than in the subsoil (see Section 5.1.5).

It should be noted that all experiments were performed on homogenous soil samples. $^{14}\text{CO}_2$ evolution from the eight individual determinations of acetate degradation (two replicates) was almost identical during the whole experimental period (Figure 27). Even though the ^{14}C -Na-acetate method is not very sensitive towards minor differences in soil microbial activity, the identical evolution of $^{14}\text{CO}_2$ from the individual soil samples seems to indicate that homogenization of the soil samples was satisfactory.

Table 19. Microbial activity and biomass determined in the plough layer (0–20 cm) and the subsoil (80–100 cm) at Tylstrup, Jyndevad, Silstrup and Faardrup.

Site	Soil depth (cm)	Microbial activity (% ^{14}C evolved ¹⁾)	Microbial biomass (mg C/kg)
Tylstrup	0–20	16.0	142
	80–100	1.8	17
Jyndevad	0–20	17.5	194
	80–100	1.3	42
Silstrup	0–20	14.3	641
	80–100	0.9	48
Faardrup	0–20	9.0	372
	80–100	0.8	35

¹⁾ in 2 hours from ^{14}C -Na-acetate

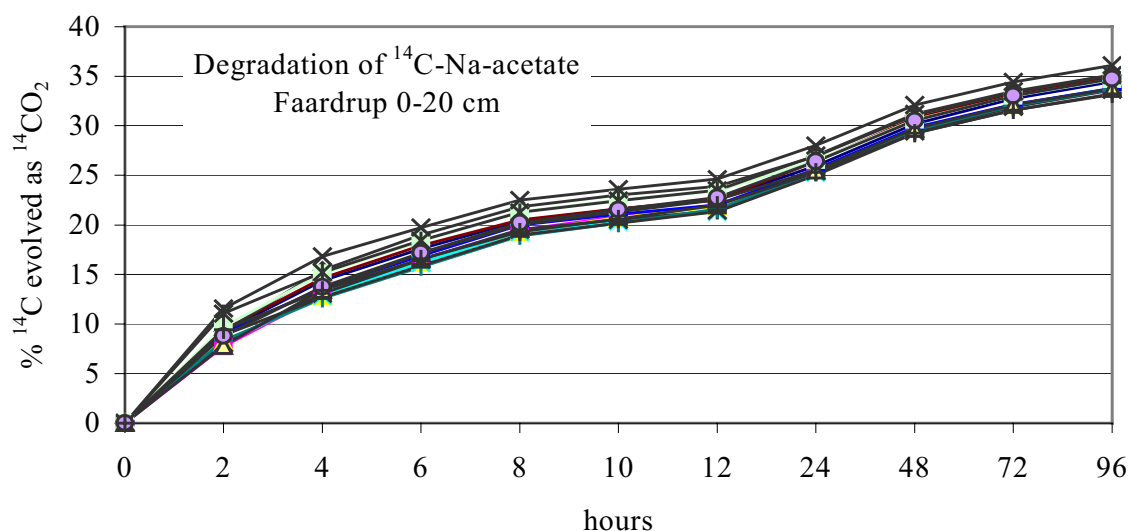


Figure 27. $^{14}\text{CO}_2$ evolution from eight duplicate soil samples from Faardrup (0–20 cm) supplemented with ^{14}C -Na-acetate.

5.3 Summary

The pesticide leaching studies within the PLAP programme were supported by site-specific determination of sorption and degradation parameters. These determinations were performed 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 the importance of the availability of site-specific parameters when carrying out root zone modelling. Thus, the determined sorption and degradation parameters (DT_{50} values) were all in the lower end of the literature values, particularly in the case of bromoxynil, the DT_{50} of which was remarkably low, ranging from <1 day in the plough layer to <5 days in the subsoil. Ioxynil also degraded very fast, DT_{50} ranging from <1 day in the plough layer to 12 days in the subsoil. Finally, the K_{oc} of bromoxynil and ioxynil only reached 85 ml/g in the plough layer and 52 ml/g in the subsoil, respectively.

6 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.

6.1 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 control procedure and an external control procedure.

6.1.1 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.

6.1.2 External QA

Every third month, two control samples were analysed at the laboratories along with the various water samples from the six test sites. The control samples were prepared in the field by the staff collecting the samples. An ampoule containing pesticide spike solution in acetonitrile as the solvent was opened and 150 µl (high-level) or 50 µl (low-level) of the spike solution was pipetted into 3 l of groundwater collected from the upstream monitoring well. The pesticide concentration in the solution is indicated in Table 20. 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. Ampoules of the pesticide spike solution were from Labor Dr. Ehrenstorfer, Germany. During the current monitoring period, the spike samples were analysed with the samples from Tylstrup and contained ETU, linuron and metribuzin.

Table 20. 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)
ETU	2.5	125	42
Linuron	2.5	125	42
Metribuzin	2.5	125	42

6.2 Results and discussion

6.2.1 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 21.

Table 21. 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}
AMPA	0.005	0.012	0.013	7.38	1.89
Glyphosate	0.005	0.011	0.012	4.80	2.23
Bromoxynil	0.005	<0	0.005	0.35	3.23
ETU	0.007	0.010	0.012	2.88	3.02
Fenpropimorph	0.005	0.005	0.007	1.98	2.18
Fluroxypyr	0.002	0.006	0.007	9.39	2.85
Ioxynil	0.007	<0	0.007	0.80	3.02
Linuron	0.007	0.000	0.007	1.00	3.23
Metribuzin	0.003	0.007	0.007	7.39	2.72
Pirimicarb	0.005	0.007	0.008	3.15	2.60
Propiconazol	0.006	0.010	0.012	3.49	2.85

1) s_w and s_b are the standard deviations within one day and between days, respectively

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

With about half of the pesticides the day-to-day variation accounted for most of the uncertainty. $F > F_{critical}$ 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.

The standard deviation (s_t) of the pesticides analysis lay within the range 0.005–0.013 µg/l Table 21.

Finally, the analysis of the control samples revealed that the observed concentrations were close to the nominal concentrations for most pesticides (Appendix 8–10). Some of the glyphosate and AMPA sample analyses differed from the nominal concentrations by about 50%, however. These compounds are difficult to analyse, though, and given the low concentration, the results are acceptable.

6.2.2 External QA

No pesticides were detected in any of the blank samples, indicating that contamination of the samples did not take place at the laboratories.

All pesticides in the spiked samples were detected in all samples. However, the observed concentrations were considerably lower than the nominal concentrations (Table 22 and Figure 28).

Table 22. Recovery (%) of the control samples and spike solution. Recovery refers to the ratio of the observed and nominal concentrations.

	ETU		Linuron		Metribuzin	
	Low	High	Low	High	Low	High
18.08.99	86	65	72	52	26	28
04.11.99	60	74	55	58	60	66
03.02.00	48	70	70	66	55	70
Average	65	69	66	59	47	55
Spike solution	96	96	84	84	103	103

Particularly notable is the remarkable low recovery of metribuzin on 18.08.99 (only 26–28%). In the remaining analyses, recovery ranged from 48 to 72%. It is difficult to find an unambiguous explanation for the low recovery rate, which is probably attributable to uncertainty in the spiking procedure in the field.

The discrepancies found should be seen in relation to the fact that the QA procedure comprises three different methods of analysis performed by two different laboratories with three different persons preparing the spiked samples in the field. Taking these factors into account, the recovery (apart from that of metribuzin on 18.08.99) can be considered to be at a similar low level. The similarity of the recovery level is thus indicative of a systematic error introduced somewhere in the QA procedure. Possibilities are:

1. Low accuracy of the pesticide analyses at the laboratories
2. Errors in the spike solution
3. Uncertainties introduced in the spiking procedure in the field.

The deviation relative to the nominal concentration is generally much lower for the internal laboratory QA than for the external QA control samples (Figure 28), thus precluding that the low recovery could be due to low accuracy of the laboratory analyses.

Analysis of the concentration of pesticides in the spike solution at the laboratories revealed good recovery, thus precluding that errors in the spike solution could be responsible for the low recovery in the samples spiked in the field (Table 22).

It thus seems that the spiking procedure in the field may have introduced a systematic error. The procedure has thus been amended for the second monitoring period. There are already indications that the amended procedure has resulted in higher recovery rates in the external QA samples. However, a final conclusion cannot be drawn until additional results become available using the amended procedure. .

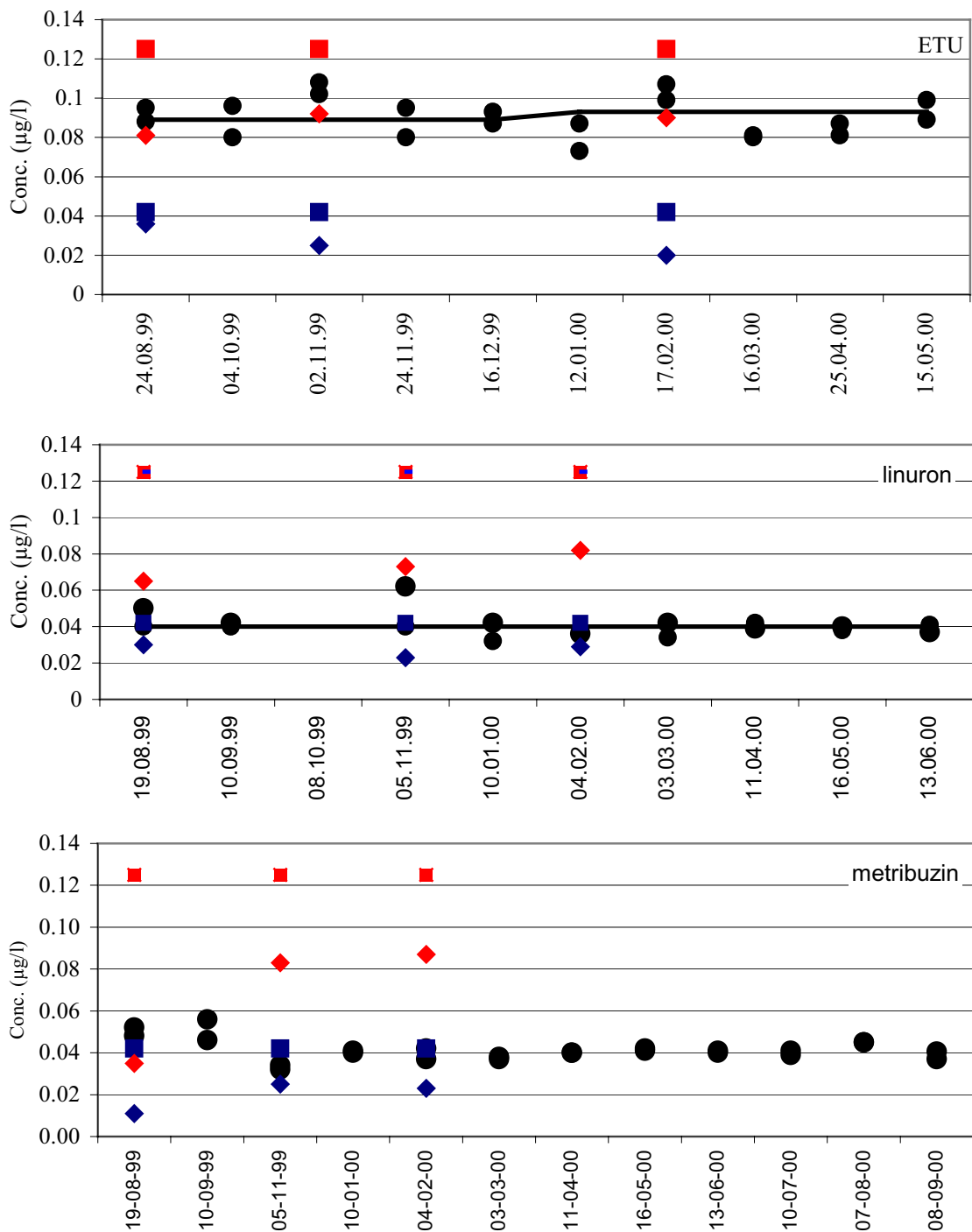


Figure 28. Concentration of ETU, linuron and metribuzin in QA samples. The solid line and the closed circles indicate the nominal and observed concentrations, respectively, in internal laboratory controls. The red/blue squares indicate the nominal concentrations of the high-level/low-level external control samples. The red and blue diamonds indicate the observed concentrations of the high-level/low-level external control samples.

6.3 Summary

The overall quality of the pesticide analysis was considered satisfactory, the QA system showing that:

- Reproducibility of all the analyses was good, standard deviation ranging from 0.005–0.013 µg/l. Moreover, the internal control samples were acceptably close to the nominal concentrations.
- No contamination of the samples took place at the laboratories.
- All the pesticides in the spiked samples were detected, although the observed concentrations were low compared to the nominal concentrations, with recovery ranging from 25–85%. It is difficult to find an unambiguous explanation for the low recovery rate. However, it is most likely caused by uncertainty in the spiking procedure in the field. A new spiking procedure, which is expected to improve the results, has already been introduced.

7 Conclusion

The findings indicate that bromide transport will continue throughout the subsequent monitoring period. Thus no final conclusion can be drawn concerning bromide transport and pesticide leaching risk until the results of the subsequent monitoring period are available. The findings hitherto suggest that the monitoring system in terms of instrumentation, sampling procedure etc. is suitable for describing the transport of pesticides through the root zone down to the upper aquifer. The tracer application studies thus provide a good indication of the water transport occurring during the monitoring period and reveal a marked breakthrough of bromide in various parts of the hydrological cycle. In addition, they provide a good indication of the heterogeneity occurring at field level. The preliminary findings concerning pesticide leaching are briefly summarized in Table 23.

Table 23. Overview of the applied pesticides and pesticide occurrence at the Tylstrup, Jynde vad and Faardrup test sites.

	Tylstrup	Jynde vad	Faardrup
Soil type	Fine sand	Coarse sand	Clayey till
Pesticides applied	ETU Linuron Metribuzin	Fenpropimorph Fenpropimorphic acid Glyphosate Propiconazol Tribenuron-methyl	Bromoxynil Ioxynil Fenpropimorph Fluroxypyr Glyphosate Pirimicarb Propiconazol
Root zone leaching	Desamino-diketo-metribuzin Diketo-Metribuzin	None	None
Detected in groundwater	Desamino-diketo-metribuzin ¹⁾ Diketo-metribuzin ¹⁾	Desamino-diketo-metribuzin ¹⁾ Diketo-metribuzin ¹⁾	None
Detected in drainage water			None

1) Derived from previous application of metribuzin

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Sampling procedures

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 as described in Section 2.1.3. The chemical analysis for each group was performed on single pooled water samples.

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 so as to ensure sampling of flowing drainwater 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 1680 ml per day. Chemical analysis is then performed 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 parameters is performed on pooled water samples deriving from all seven bottles. In addition, tracer analysis (Br, Cl, Ca and K) is performed on additional water samples deriving from each of the seven individual bottles.

Inorganic analysis methods

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 reacted with salicylate-dichloroisocyanurate to form an emerald green complex, the absorbance of which was measured on a spectrophotometer. The method used is that 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 that described in DS 259 (1982) and DS 238 (1985).

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

NO₃-N, NO₂-N, PO₄-P, SO₄-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).

Pesticide analysis methods

The pesticide analyses were carried out by two commercial laboratories. The pesticides analysis was all performed on a decanted water sample, and the main principle of the applied methods 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).

Site	Pesticide	Extraction	Detection	Detection limit (µg/l)	Accredited by DANAK	Approved by Danish EPA	Laboratory
Tylstrup	ETU	LLE	GC/MS	0.01	No	Yes	Miljø-Kemi
	Linuron	LLE	LC/MS	0.01	No	Yes	Rovesta
	Metribuzin	LLE	LC/MS	0.01	No	Yes	Rovesta
	Desamino-metribuzin	LLE	LC/MS	0.02	No	No	Rovesta
	Desamino-diketo-metribuzin-	LLE	GC/MS	0.02	No	No	Rovesta
	Diketo-metribuzin	LLE	GC/MS	0.02	No	No	Rovesta
	Jydevad	Triazinamin-methyl	SFE	LC-MS	0.02	No	No
Fenpropimorph		SFE	LC-MS	0.01	No	Yes	Miljø-Kemi
Fenpropimorphic acid		SFE	LC-MS	0.01	No	No	Miljø-Kemi
Propiconazol		SFE	LC-MS	0.01	No	Yes	Miljø-Kemi
AMPA		¹⁾	GC/MS	0.01		Yes	Miljø-Kemi
Glyphosate		¹⁾	GC/MS	0.01		Yes	Miljø-Kemi
Faardrup	Pirimicarb	SFE ²⁾	GC/MS	0.01	No	Yes	Miljø-Kemi
	Bromoxynil	SFE ²⁾	GC/MS	0.01	Yes	Yes	Miljø-Kemi
	Ioxynil	SFE ²⁾	GC/MS	0.01	Yes	Yes	Miljø-Kemi
	Fenpropimorph	SFE ²⁾	GC/MS	0.01	No	Yes	Miljø-Kemi
	Fenpropimorphic acid	SFE ²⁾	GC/MS	0.01	No	No	Miljø-Kemi
	Fluroxypyr-acid	SFE ²⁾	GC/MS	0.01	No	No	Miljø-Kemi
	AMPA	¹⁾	GC/MS	0.01		Yes	Miljø-Kemi
	Glyphosate	¹⁾	GC/MS	0.01		Yes	Miljø-Kemi

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 methylized with diazomethane

Measured concentrations of ETU, metribuzin, desamino-diketo-metribuzin and diketo-metribuzin in the unsaturated zone at Tylstrup. The data derive from suction cups S1 and S2, respectively.

		Suction cup S1		Suction cup S2	
		1 m b.g.s.	2 m b.g.s.	1 m b.g.s.	2 m b.g.s.
ETU	03.06.99	<			<
	30.06.99	<			
	18.08.99	<	<	<	<
	09.09.99	<		<	
	07.10.99	<		<	
	04.11.99	0.014	<	0.038	<
	08.12.99	<			
	10.01.00	0.013		0.032	
	03.02.00	<	<	0.025	<
	02.03.00				
	06.04.00				
	10.05.00	<		<	0.018
Metribuzin	17.05.99	<	<	<	<
	03.06.99	<			<
	30.06.99	<			
	18.08.99	<	<	<	<
	09.09.99	<		<	
	07.10.99	<		<	
	04.11.99	<	<	<	0.024
	08.12.99	<			
	10.01.00	<		<	
	03.02.00	<	<	<	0.01
	02.03.00	<		<	
	06.04.00	<		<	
	10.05.00	<	<	<	<
07.06.00	<		<		
Desamino-diketo-metribuzin	09.09.99	*	<	*	
	04.11.99	*		*	*
	08.12.99	0.25	<0.2		
	10.01.00	0.72		0.25	
	03.02.00	2.0	0.23	0.23	0.16
	02.03.00	2.1		0.23	
	06.04.00	2.0		0.20	
	10.05.00	1.4	1.4	0.21	0.13
	07.06.00	1.1		0.21	
Diketo-metribuzin	09.09.99	*		<0.2	
	04.11.99	<0.2	<0.2	<0.2	*
	08.12.99	0.22			
	10.01.00	0.62		0.08	
	03.02.00	0.39	0.20	0.11	0.20
	02.03.00	0.17		0.071	
	06.04.00	0.50		0.14	
	10.05.00		0.1	0.09	0.13
	07.06.00	0.48		<	

>) Below the detection limit of 0.02 µg/l

*) Degradation product detected in the range of 0.05–0.5 µg/l

Results of the initial screening analysis of groundwater from the Tylstrup test field carried out in April 1999.

Monitoring well	M1	M1	M1	M3	M5	M5	M5	M6
Screen depth (m b.g.s.)	3-4	4-5	5-6	3-4	3-4	4-5	5-6	3-4
2,4-D	<	<	<	<	<	<	<	<
2,4-dichlorphenol	<	<	<	<	<	<	<	<
2,6-dichlorbenzamid	<	<	<	<	<	<	<	<
3-hydroxycarbofuran	<	<	<	<	<	<	<	<
4-chlor-2-methylphenol	<	<	<	<	<	<	<	<
Atrazine	<	<	<	<	<	<	<	<
BAM (2,6-dichlorbenzamid)	<	<	<	<	<	<	<	<
Bentazone	<	<	<	<	<	<	<	<
Bromoxnyl	<	<	<	<	<	<	<	<
Carbofuran	<	<	<	<	<	<	<	<
Chloridazon	<	<	<	<	<	<	<	<
Chlorsulfuron	<	<	<	<	<	<	<	<
Desethylatrazine	<	<	<	<	<	<	<	<
Desethylterbuthylazin	<	<	<	<	<	<	<	<
Desisopropylatrazine	<	<	<	<	<	<	<	<
Dichlobenil	<	<	<	<	<	<	<	<
Dichlorprop	<	<	<	<	<	<	<	<
Dimethoate	<	<	<	<	<	<	<	<
Dinoseb	<	<	<	<	<	<	<	<
Diuron	<	<	<	<	<	<	<	<
DNOC	<	<	<	<	<	<	<	<
Ethofumesat	<	<	<	<	<	<	<	<
Fenpropimorph	<	<	<	<	<	<	<	<
Fluazifop-P-buthyl	<	<	<	<	<	<	<	<
Hexazinon	<	<	<	<	<	<	<	<
Hydroxycarbofuran	<	<	<	<	<	<	<	<
Ioxnyl	<	<	<	<	<	<	<	<
Isoproturon	<	<	<	<	<	<	<	<
Lenacil	<	<	<	<	<	<	<	<
Linuron	<	<	<	<	<	<	<	<
MCPA	<	<	<	<	<	<	<	<
MCPP	<	<	<	<	<	<	<	<
Mechlorprop	<	<	<	<	<	<	<	<
Metamitron	<	<	<	<	<	<	<	<
Metribuzin	<	<	<	<	<	<	<	<
Metsulfuron methyl	<	<	<	<	<	<	<	<
Pendimethalin	<	<	<	<	<	<	<	<
Phenmedipham	<	<	<	<	<	<	<	<
Pirimicarb	<	<	<	<	<	<	<	<
Propiconazol	<	<	<	<	<	<	<	<
Simazine	<	<	<	<	<	<	<	<
Terbuthylazin	<	<	<	<	<	<	<	<

>) Below the detection limit

Results of the initial screening analysis of groundwater from the Jydevad test field carried out in October 1999.

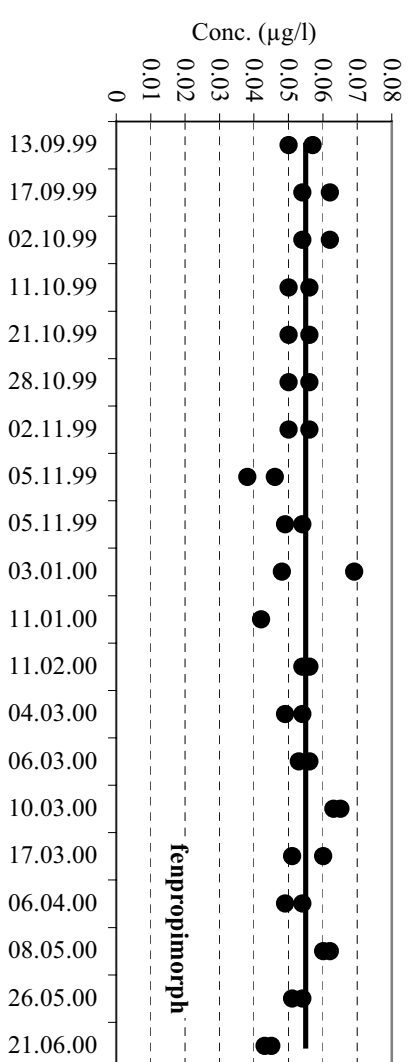
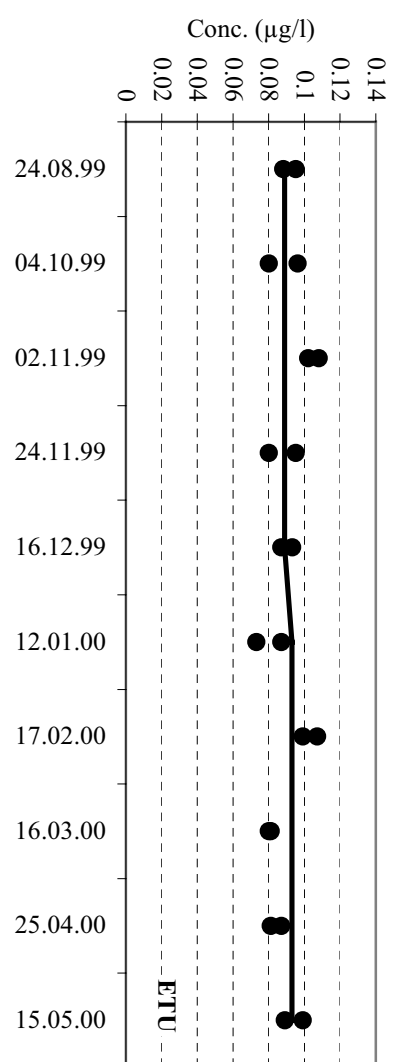
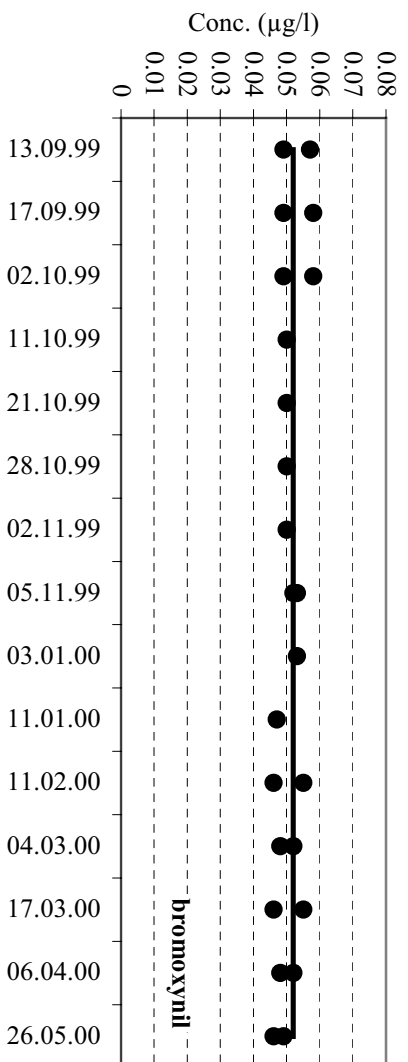
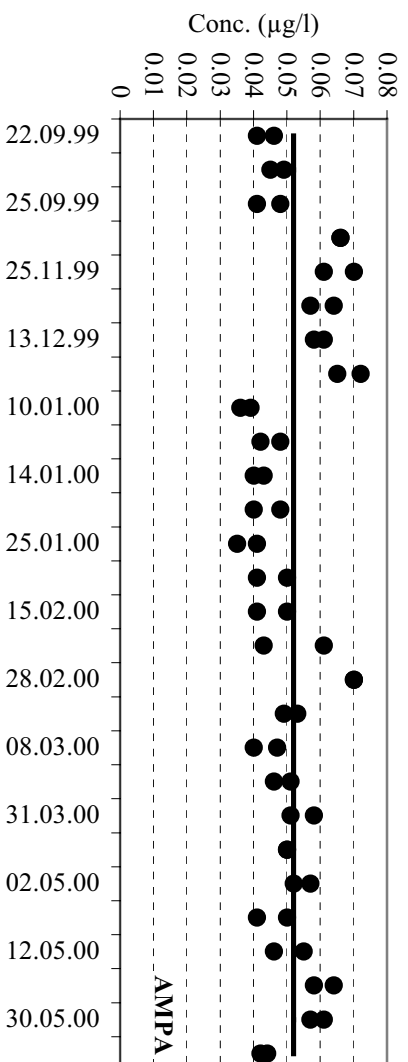
Monitoring wells	M1	M2	M2	M2	M5	M7	M7	M7
Screen depth (m b.g.s.)	2-3	2-3	3-4	4-5	2-3	2-3	3-4	4-5
2,4-D	<	<	<	<	<	<	<	<
2,4-dichlorphenol	<	<	<	<	<	<	<	<
2,6-dichlorbenzamid	<	<	<	<	<	<	<	<
3-hydroxycarbofuran	<	<	<	<	<	<	<	<
4-chlor-2-methylphenol	<	<	<	<	<	<	<	<
Atrazine	<	<	<	<	<	<	<	<
BAM (2.6-dichlorbenzamid)	<	<	<	<	<	<	<	<
Bentazone	<	<	<	<	<	<	<	<
Bromoxnyl	<	<	<	<	<	<	<	<
Carbofuran	<	<	<	<	<	<	<	<
Chloridazon	<	<	<	<	<	<	<	<
Chlorsulfuron	<	<	<	<	<	<	<	<
Desethylatrazine	<	<	<	<	<	<	<	0.03
Desethylterbuthylazin	<	<	<	<	<	0.01	<	<
Desisopropylatrazine	<	<	<	<	<	0.021	0.01	<
Dichlobenil	<	<	<	<	<	<	<	<
Dichlorprop	<	<	<	<	<	<	<	<
Dimethoate	<	<	<	<	<	<	<	<
Dinoseb	<	<	<	<	<	<	<	<
Diuron	<	<	<	<	<	<	<	<
DNOC	<	<	<	<	<	<	<	<
Ethofumesat	<	<	<	<	<	<	<	<
Fenpropimorph	<	<	<	<	<	<	<	<
Fluazifop-P-buthyl	<	<	<	<	<	<	<	<
Hexazinon	<	<	<	<	<	<	<	<
Hydroxycarbofuran	<	<	<	<	<	<	<	<
Ioxnyl	<	<	<	<	<	<	<	<
Isoproturon	<	<	<	<	<	<	<	<
Lenacil	<	<	<	<	<	<	<	<
Linuron	<	<	<	<	<	<	<	<
MCPA	<	<	<	<	<	<	<	<
MCPP	<	<	<	<	<	<	<	<
Mechlorprop	<	<	<	<	<	<	<	<
Metamitron	<	<	<	<	<	<	<	<
Metribuzin	<	<	<	<	<	<	<	<
Metsulfuron methyl	<	<	<	<	<	<	<	<
Pendimethalin	<	<	<	<	<	<	<	<
Phenmedipham	<	<	<	<	<	<	<	<
Pirimicarb	<	<	<	<	<	<	<	<
Propiconazol	<	<	<	<	<	<	<	<
Simazine	<	<	<	<	<	<	<	<
Terbuthylazin	<	<	<	<	<	<	<	<

>) Below the detection limit

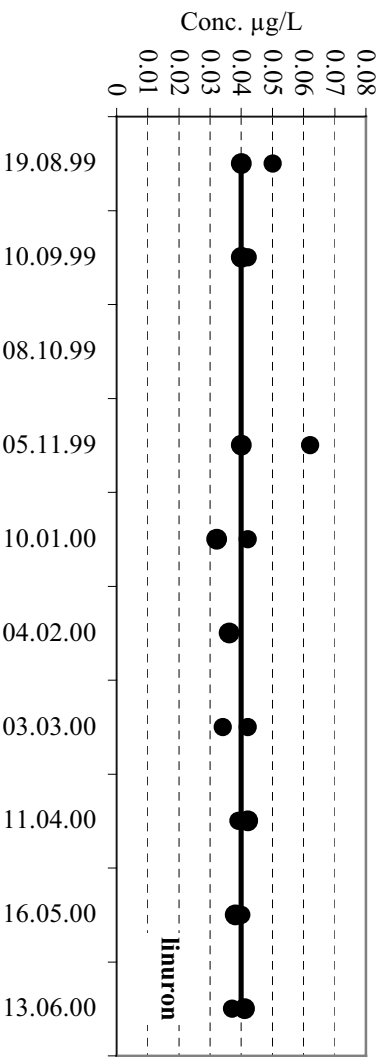
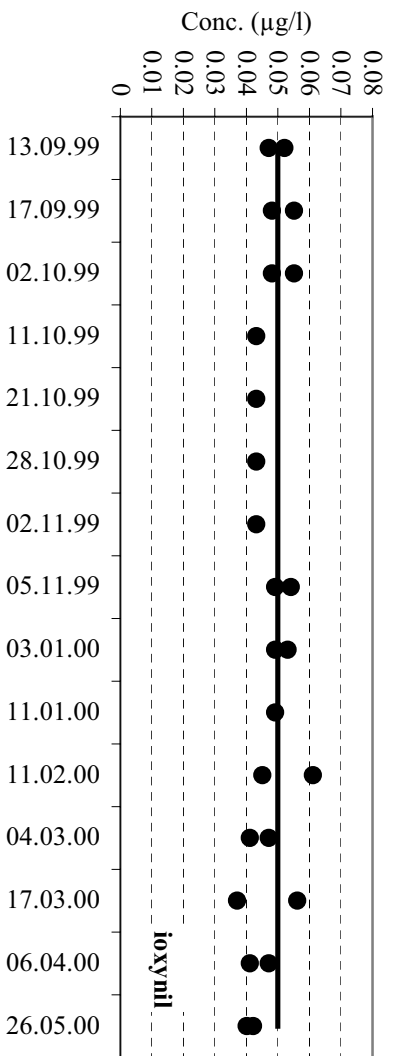
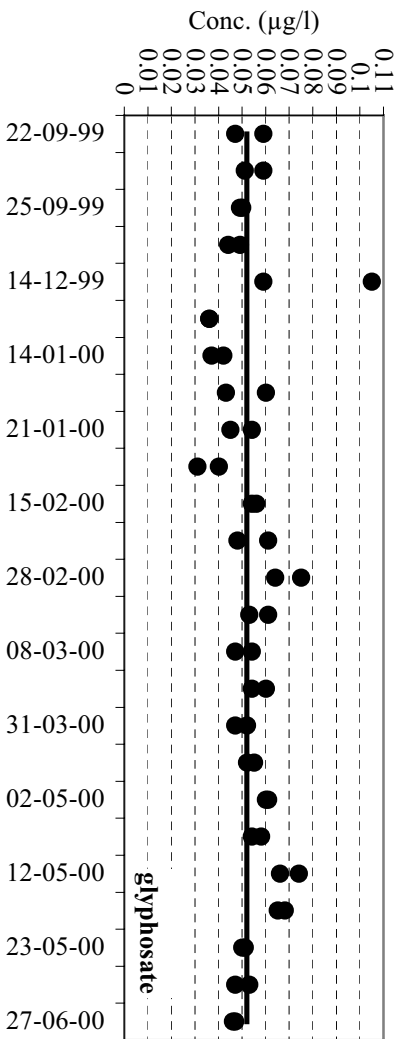
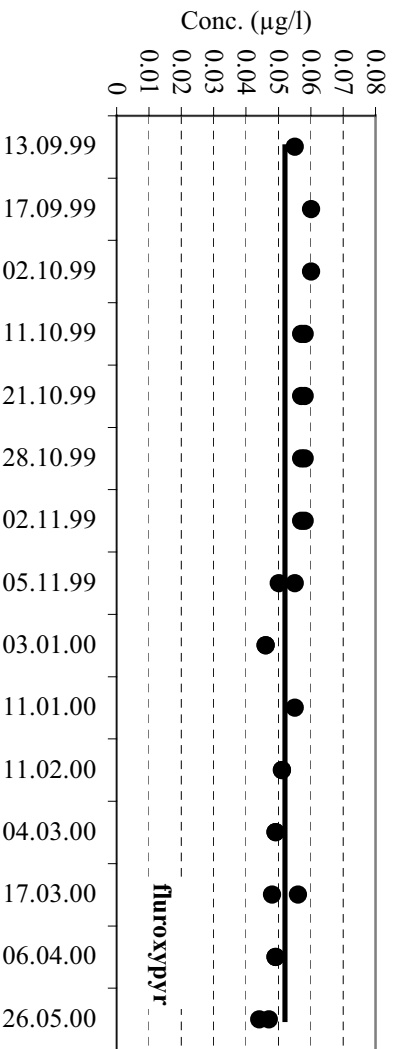
Results of the initial screening analysis of groundwater from the Faardrup test field carried out in October 1999.

Monitoring well	H1	H2	M2	M2	M2	M6	M6	M6
Screen depth (m b.g.s.)	3.5	3.5	1.5–2.5	2.5–3.5	3.5–4.5	1.5–2.5	2.5–3.5	3.5–4.5
2,4-D	<	<	<	<	<	<	<	<
2,4-dichlorphenol	<	<	<	<	<	<	<	<
2,6-dichlorbenzamid	<	<	<	<	<	<	<	<
3-hydroxycarbofuran	<	<	<	<	<	<	<	<
4-chlor-2-methylphenol	<	<	<	<	<	<	<	<
Atrazine	<	<	<	<	<	<	<	<
BAM (2.6-dichlorbenzamid)	<	<	<	<	<	<	<	<
Bentazone	<	<	<	<	<	<	<	<
Bromoxynil	<	<	<	<	<	<	<	<
Carbofuran	<	<	<	<	<	<	<	<
Chloridazon	<	<	<	<	<	<	<	<
Chlorsulfuron	<	<	<	<	<	<	<	<
Desethylatrazine	<	<	<	<	<	<	<	<
Desethylterbuthylazin	<	<	<	<	<	<	<	<
Desisopropylatrazine	0.031	0.031	<	<	<	<	<	<
Dichlobenil	<	<	<	<	<	<	<	<
Dichlorprop	<	<	<	<	<	<	<	<
Dimethoate	<	<	<	<	<	<	<	<
Dinoseb	<	<	<	<	<	<	<	<
Diuron	<	<	<	<	<	<	<	<
DNOC	<	<	<	<	<	<	<	<
Ethofumesat	<	<	<	<	<	<	<	<
Fenpropimorph	<	<	<	<	<	<	<	<
Fluazifop-P-buthyl	<	<	<	<	<	<	<	<
Hexazinon	<	<	<	<	<	<	<	<
Hydroxycarbofuran	<	<	<	<	<	<	<	<
Ioxynil	<	<	<	<	<	<	<	<
Isoproturon	<	<	<	<	<	<	<	<
Lenacil	<	<	<	<	<	<	<	<
Linuron	<	<	<	<	<	<	<	<
MCPA	<	<	<	<	<	<	<	<
MCPP	<	<	<	<	<	<	<	<
Mechlorprop	<	<	<	<	<	<	<	<
Metamitron	<	<	<	<	<	<	<	<
Metribuzin	<	<	<	<	<	<	<	<
Metsulfuron methyl	<	<	<	<	<	<	<	<
Pendimethalin	<	<	<	<	<	<	<	<
Phenmedipham	<	<	<	<	<	<	<	<
Pirimicarb	<	<	<	<	<	<	<	<
Propiconazol	<	<	<	<	<	<	<	<
Simazine	<	<	<	<	<	<	<	<
Terbuthylazin	<	<	<	<	<	<	<	<

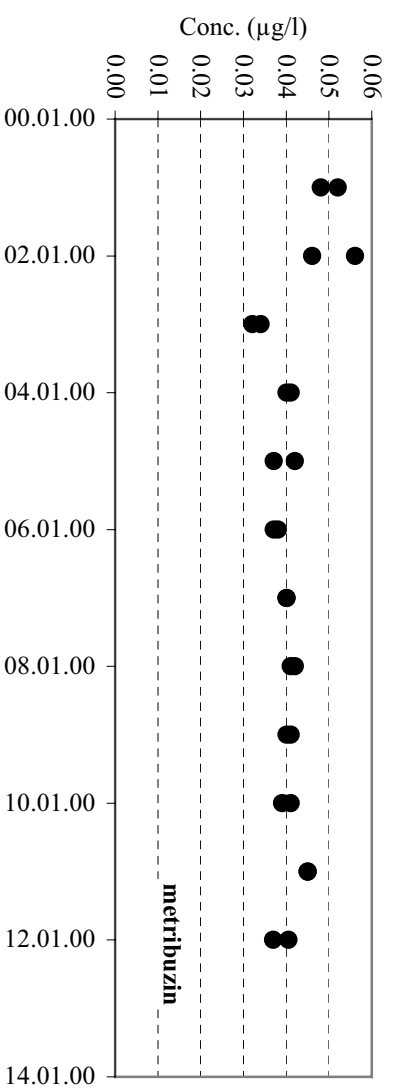
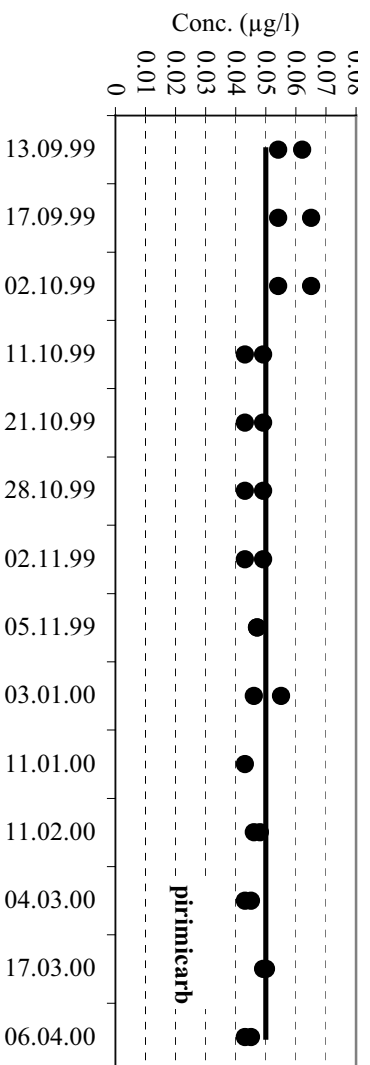
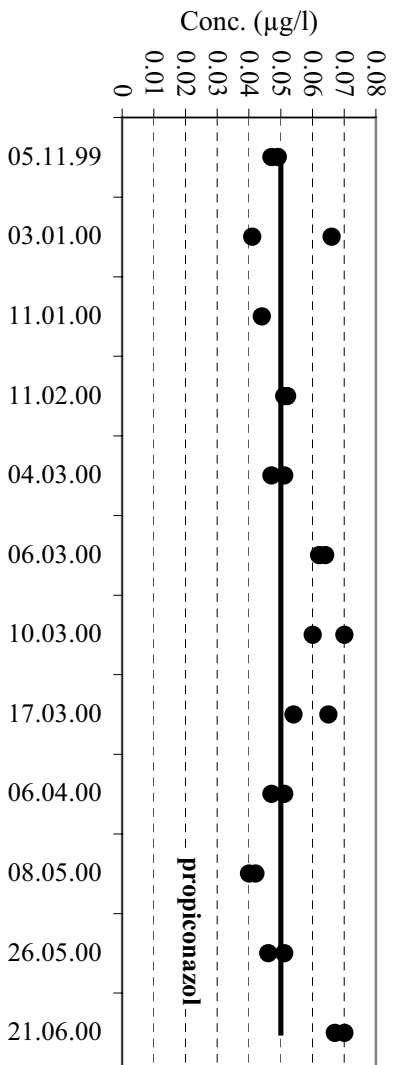
>) Below the detection limit



Internal laboratory control data illustrated by the control cards for AMPA, bromoxynil, ETU and fenpropimorph. Please note that the scale of both axes varies.



Internal laboratory control data illustrated by the control cards for fluroxypyr, glyphosate, ioxynil and linuron. Please note that the scale of both axes varies.



Internal laboratory control data illustrated by the control cards for propiconazol, pirimicarb and metribuzin. Please note that the scale of both axes varies.