Table A1.1 Chemical Abstracts nomenclature for the pesticides and degradation products encompassed by the PLAP.

Parameter	Chemical Abstracts nomenclature
AMPA	Amino-methylphosphonic acid
Amidosulfuron	N-[[[[(4,6-dimethoxy-2-pyrimidinyl)amino]carbonyl]-amino]sulfonyl]-N-methylmethanesulfonamide
Bentazone	3-(1-methylethyl)-1H-2,1,3-benzothiadiazin-4(3H)-one 2,2 dioxide
Bromoxynil	3,5-dibromo-4-hydroxybenzonitrile
Clomazone	2-[(2-chlorphenyl)methyl]-4,4-dimethyl-3-isoxazolidione
Clopyralid	3,6-dichloro-2-pyridinecarboxylic acid
Desmedipham	Ethyl 3-(phenylcarbamoyloxy)phenylcarbamate
Dimethoate	O,O-dimethyl S-methylcarbamoylmethyl-phosphorodithioate
EHPC*	Ethyl 3-hydroxy-phenylcarbamate
Ethofumesate	(±)-2-ethoxy-2,3-dihydro-3,3-dimethylbenzofuran-5-yl-methanesulfonate
Fenpropimorph	Cis-4-[3-[4-(1,1-dimethylethyl)-phenyl]-2-methylpropyl]-2,6-dimethylmorpholine
Fenpropimorphic acid*	Cis-4-[3-[4-(2-carboxypropyl)-phenyl]-2-methylpropyl]-2,6-dimethylmorpholine
Flamprop (free acid)	N-benzoyl-N-(3-chloro-4-flourophenyl)-D-alanine
Flamprop-M-isopropyl	Isopropyl N-benzoyl-N-(3-chloro-4-flourophenyl)-D-alaninate
Fluazifop-P (free acid)*	(R)-2-[4-(5-trifluoromethyl-2-puyridyloxy)phenoxy]propanoic acid
Fluroxypyr	(4-amino-3,5-dichloro-6-fluro-2-pyridinyl)oxy]acetic acid
Glyphosate	N-(phosphonomethyl)glycine
DPEPU-desamido*	N-((3-(ethylsulfonyl)-2-pyridyl)-4,6 dimethoxy-2 pyrimidinamine
DPEPU*	N-(4,6-dimethoxy-2-pyrimidinyl-N-((3-ethylsulfonyl)-2-pyridinyl)urea
Ioxynil	4-hydroxy-3,5-diiodobenzonitrile
MCPA	(4-cloro-2-methylphenoxy)acetic acid
Metamitron	4-amino-4,5-dihydro-3-methyl-6-phenyl-1,2,4-triazin-5-one
Metamitron-desamino*	4,5-dihydro-3-methyl-6-phenyl-1,2,4-triazin-5-one
Metribuzin-desamino-diketo*	6-tert-butyl-4,5-dihydro-3-methylthio-1,2,4-triazin-3,5-dione
Metribuzin-diketo*	4-amino-6-tert-butyl-4,5-dihydro-1,2,4-triazin-3,5-dione
Metsulfuron-methyl	Methyl 2-[[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]=carbonyl]amino]sulfonyl]benzoic acid
MHPC*	Methyl-N-(3-hydoxyphenyl)-carbamate
Pendimethalin	N-(1-ethyl)-2,6-dinitro-3,4-xynile
Phenmedipham	3-[(methoxycarbonyl)amino]phenyl (3-methylphenyl)carbamate
PHPC*	3-phenyl-4-hydroxy-6-chloropyridazine

**Degradation product*

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

Parameter	Chemical Abstracts nomenclature
Pirimicarb	2-(dimethylamino)-5,6-dimethyl-4-pyrimidinyldimethylcarbamate
Pirimicarb-desmethyl*	2-(dimethylamino)-5,6-dimethyl-4-pyrimidinylmethylcarbamate
Pirimicarb-desmethyl-formamido*	2-methylformamido-5,6-dimethylpyrimidine-4-yl dimethylcarbamate
Propiconazole	1-[[2-(2,4-dichlorophenyl)-4-propyl-1,3-dioxolan-2-yl]methyl]-1H-1,2,4-triazole
Rimsulfuron	N-[[(4,6-dimethoxy-2-pyrimidinyl)amino]carbonyl]-3-(ethylsulfonyl)-2-pyridinesulfonamide
Terbuthylazine	6-chloro-N-(1,1-dimethylethyl)-N-ethyl-1,3,5,triazine-2,4-diamine
Triasulfuron	1-[2-(2-chloroethoxy)phenylsulfonyl]-2-(4-methoxy-6-methyl-1,3,5-triazin-2-yl)-urea
Triazinamin	4-methoxy-6-methyl-1,3,5-triazin-2-amin
Triazinamin-methyl*	1,3,5-triazin-2-2-amine 4-methoxy-N, 6-dimethyl

**) Degradation product*

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

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

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

- The time-proportional sampler is equipped with seven refrigerated bottles such that the water samples can be collected over a 7-day period. Hence during the period of continuous drainage runoff, a 70-ml sample is collected every hour independent of flow rate. 24 samples are collected per bottle giving 1,680 ml per day. Pesticides and inorganic chemicals (Br, Cl, K, Ca, Mg, Mn, Na, NO_3, PO_4, total-N, PO_4, total-P, dissolved total-P and suspended matter) are then analysed on a weekly basis on a pooled sample derived from the seven bottles.
- The flow-proportional sampler is only activated during storm events and sampling is carried out for 1–2 days depending on the intensity of the event. Hence each flow event is activated by a predefined rise in water level/runoff within the preceding 12-hour period. Sampling is controlled by the flow rate, where collection of each sample is initiated when the accumulated flow rate exceeds a predefined level depending on the month of the year. Levels of predefined rise and accumulated flow rate are set/adjusted individually for each site by experience. Each sample volume is 200 ml yielding nine samples per bottle and a maximum of 72 samples per storm event. For each storm event, analysis of pesticides and inorganic chemicals (Br, Cl, K, NO_3, PO_4, total-N, PO_4, total-P, dissolved total-P and suspended matter) is performed on pooled water samples deriving from all seven bottles. In addition, tracer analysis (Br, Cl, Ca and K) is performed on additional water samples deriving from each of the seven individual bottles.

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

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

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

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

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

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

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

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

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

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

Site	Monthly monitoring (Extensive)	Half-yearly monitoring (Intensive)	Not Measured
Tylstrup	M5, M4, S1a, S1b	M1, M3, M4, M5, M6, S1 (1 m b.g.s.)a, S2a*, S1b, S2b*	M7, M2
Jyndevad	M1, M4, S1a, S1b	M1, M2, M4, M5, M7, S1a, S2a,	M6, M3, S2b, S1b
Silstrup	M5, H2.2, H1.2	M4, M5, M6, M12, M13, M9, H1.1, H1.2, H1.3, H2.1, H2.2, H2.3	M10, M11
Estrup	M5, H1.2	M1, M3, M4, M5, M6, H1.1, H1.2, H1.3	M2, M7
Faardrup	M5, H1.3, H2.3	M1, M2, M3, M4, M5, M6, H1.1, H1.2, H1.3, H2.1, H2.2, H2.3	M7
Slaeggerup	M6, H2.2, H1.2	M1, M3, M5, M6, M7, H1.1, H1.2, H1.3, H2.1, H2.2, H2.3	M2, M4

*) *Measured every fourth month*

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

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

Date	Management practice
19.11.98	Ploughing – 20 cm depth
23.04.99	Fertilization – 121 kg N/ha and 8 kg P/ha
27.04.99	Fertilization – 63 kg K/ha
04.05.99	Potatoes planted – cultivar Dianella
25.05.99	Herbicide – 1.0 l/ha Afalon (linuron)
25.05.99	Herbicide – 0.2 kg/ha Sencor WG (metribuzin)
27.05.99	Tracer application – 30 kg/ha potassium bromide
07.06.99	Herbicide – 0.15 kg/ha Sencor WG (metribuzin)
11.06.99	Insecticide – 0.3 l/ha Karate (lambda-cyhalothrin)
22.06.99–14.09.99	Ten fungicide applications – each comprising 2.0 kg/ha Dithane DG (mancozeb)
12.09.99	Irrigation – 33 mm/ha
20.10.99	Potatoes harvested (tuber yield 475 hkg/ha, 24% dry matter)
22.10.99	Disc harrowed – 6 cm depth
01.11.99	Harrowed – 3 cm depth
11.11.99	Harrowed – 5 cm depth
25.11.99	Harrowed – 7 cm depth
17.03.00	Ploughed – 20 cm depth
24.03.00	Rolled with a concrete roller
28.03.00	Fertilization – 124 kg N/ha, 18 kg P/ha and 59 kg K/ha
29.03.00	Spring barley sown – cultivar Bartok
13.05.00	Herbicide – 20 g/ha Logran 20 WG (triasulfuron)
19.06.00	Fungicide – 1.0 l/ha Tilt Top (propiconazole + fenpropimorph)
19.06.00	Insecticide – 0.25 l/ha Pirimor G (pirimicarb)
07.07.00	Irrigation – 31 mm/ha
21.08.00	Spring barley harvested (grain yield 73.3 hkg/ha; 85% dry matter. Straw yield 28.6 hkg/ha; 100% dry matter)
14.09.00	Ploughing – 25 cm depth
01.10.00	Winter rye sown – cultivar Dominator
02.11.00	Herbicide – 20 g/ha Express (tribenuron methyl)
02.11.00	Herbicide – 2.0 l/ha Stomp SC (pendimethalin)
14.05.01	Fungicide – 0.5 l/ha Tilt Top (propiconazole + fenpropimorph)
31.05.01	Irrigation – 23 mm/ha
13.06.01	Fungicide – 0.5 l/ha Tilt Top (propiconazole + fenpropimorph)
21.06.01	Irrigation – 21 mm/ha
28.08.01	Winter rye harvested (grain yield 63.6 hkg/ha; 85% dry matter. Straw yield 36.0 hkg/ha; 100% dry matter)
03.09.01	Winter rape sown – cultivar Artus
05.09.01	Herbicide – 0.25 l/ha Command CS (clomazone)
16.10.01	Herbicide – 1.0 l/ha Matrigon (clopyralid)
22.03.02	Fertilization – 155 kg N/ha, 20 kg P/ha and 72 kg K/ha
24.04.02	Irrigation – 24 mm/ha
16.05.02	Irrigation – 22 mm/ha
31.05.02	Irrigation – 34 mm/ha
27.07.02	Winter rape harvested (seed yield 25.9 hkg/ha; 91% dry matter)

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

Date	Management practice
10.03.99	Rotary cultivated – 5 cm depth
10.03.99	Ploughed – 20 cm depth
15.03.99	Rolled with a concrete roller
25.03.99	Spring barley sown – cultivar Alexis
20.04.99	Fertilization – 49 kg N/ha ammonium nitrate limestone
22.04.99	Fertilization – 17 kg P/ha and 87 kg K/ha
07.05.99	Fertilization – 85 kg N/ha as ammonium nitrate limestone
10.05.99	Herbicide – 15 g/ha Logran 20 WG (triasulfuron)
29.05.99	Irrigation – 31 mm/ha
09.08.99	Spring barley harvested (grain yield 47.7 hkg/ha; 85% dry matter. Straw yield 40.3 hkg/ha; 100% dry matter)
22.09.99	Herbicide – 2.0 l/ha Roundup 2000 (glyphosate)
05.10.99	Rotary cultivated – 5 cm depth
11.10.99	Ploughed – 20 cm depth
11.10.99	Rolled with a concrete roller
13.10.99	Winter rye sown – cultivar Dominator
12.11.99	Tracer application – 30.0 kg/ha potassium bromide
12.11.99	Herbicide – 7.5 g/ha Express (tribenuron methyl)
04.04.00	Fertilization – 115 kg N/ha, 16 kg P/ha and 55 kg K/ha
05.04.00	Fungicide – 0.5 l/ha Tilt Top (propiconazole + fenpropimorph)
05.05.00	Irrigation – 29 mm/ha
07.06.00	Fungicide – 0.5 l/ha Tilt Top (propiconazole + fenpropimorph)
09.08.00	Spring barley harvested (grain yield 56.2 hkg/ha; 85% dry matter. Straw yield 38.1 hkg/ha; 100% dry matter)
24.04.01	Fertilization – cattle slurry 49 tonnes/ha, 68 kg total-N/ha, 34 kg P/ha and 196 kg K/ha
26.04.01	Ploughing – 20 cm depth
30.04.01	Maize sown – cultivar Loft
30.04.01	Fertilization – 59 kg/ha ammonia nitrate
30.04.01	Fertilization – 21 kg N/ha and 40 kg P/ha
14.05.01	Fungicide – 1.5 l/ha Lido (terbuthylazine + pyridate)
30.05.01	Fungicide – 1.5 l/ha Lido (terbuthylazine + pyridate)
04.07.01	Irrigation – 31 mm/ha
23.07.01	Irrigation – 30 mm/ha
01.10.01	Maize harvested (cob yield 84.4 hkg/ha; 100% dry matter. Stalk yield 67.0 hkg/ha; 100% dry matter)
01.04.02	Ploughed – 20 cm depth
20.04.02	Seed bed preparation – 15 cm depth
22.04.02	Potatoes planted – cultivar Oleva
13.05.02	Herbicide – 0.2 kg/ha Sencor WG (metribuzin)
23.05.02	Herbicide – 30 g/ha Titus (rimsulfuron)
01.06.02	Fertilization – 30 kg N/ha
13.06.02	Irrigation – 20 mm/ha
18.06.02– 05.08.02	Eight fungicide applications – each comprising 0.2 l/ha Shirlan (fluazinam)
24.09.02	Potatoes harvested (tuber yield 515.8 hkg/ha; 23.0% dry matter)

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

Date	Management practice
19.04.00	Fertilization – cattle slurry 36.5 tonnes/ha, 150 kg total-N/ha, 36 kg P/ha and 162 kg K/ha
19.04.00	Ploughing – 22 cm depth
04.05.00	Fodder beat sown – cultivar Kyros
15.05.00	Fertilization – 103 kg N/ha, 26 kg P/ha and 78 kg K/ha
22.05.00	Herbicide – 1.0 l/ha Goltix WG and 1 l/ha Betanal Optima (metamitron, phenmedipham, desmedipham and ethofumesate)
22.05.00	Tracer application – 30 kg/ha potassium bromide
15.06.00	Herbicide – 1.0 l/ha Goltix WG and 1 l/ha Betanal Optima (metamitron, phenmedipham, desmedipham and ethofumesate)
28.06.00	Herbicide – 1.5 l/ha Fusilade X-tra (fluazifop-P-butyl)
05.07.00	Insecticide – 0.3 kg/ha Pirimor G (pirimicarb)
12.07.00	Herbicide – 1.0 l/ha Goltix WG and 1 l/ha Betanal Optima (metamitron, phenmedipham, desmedipham and ethofumesate)
15.11.00	Fodder beet harvested (beet yield 134.5 hkg/ha; 100% dry matter)
01.04.01	Ploughing – depth 18 cm
08.05.01	Fertilization – 91 kg N/ha, 13 kg P/ha and 34 K kg/ha
09.05.01	Spring barley sown – cultivar Otira
22.05.01	Fertilization – 27 kg N/ha, 4 kg P/ha and 10 kg K/ha
09.06.01	Herbicide – 20 g/ha Express (tribenuron methyl)
21.06.01	Herbicide – 3.0 l/ha Barnon Plus 3 (flamprop-M-isopropyl)
21.06.01	Fungicide – 0.5 l/ha Tilt Top (propiconazole + fenpropimorph)
04.07.01	Fungicide – 0.5 l/ha Tilt Top (propiconazole + fenpropimorph)
16.07.01	Herbicide – 0.6 l/ha Perfection 500 (dimethoate)
05.09.01	Spring barley harvested (grain yield 74.8 hkg/ha; 85% dry matter. Straw yield 28.6 hkg/ha 100% dry matter)
25.10.01	Herbicide – 4.0 l/ha Roundup Bio (glyphosate)
18.12.01	Ploughed – 22 cm depth
23.04.02	Fertilization – 46.5 kg N/ha
25.04.02	Seedbed preparation – 8 cm depth
25.04.02	Maize sown – cultivar Loft
19.05.02	Herbicide – 1.5 l/ha Lido (terbuthylazine + pyridate)
03.06.02	Herbicide – 1.5 l/ha Lido (terbuthylazine + pyridate)
19.06.02	Herbicide – 1.5 l/ha Matrigon (clopyralid)
23.09.02	Maize harvested (total yield 134.3 hkg/ha; 100% dry matter. Left on field 27.5 hkg/ha in stubble)

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

Date	Management practice
11.04.00	Ploughing – depth 22 cm
12.04.00	Spring barley sown – cultivar Barke
27.04.00	Fertilization – 131 kg N/ha, 19 kg P/ha and 63 kg K/ha
15.05.00	Herbicide – 20 g/ha Ally (metsulfuron-methyl)
15.05.00	Soil treatment – 2.0 l/ha manganese sulphate
15.05.00	Tracer application – 30 kg/ha potassium bromide
31.05.00	Herbicide – 3.0 l/ha Barnon Plus 3 (flamprop-M-isopropyl)
07.06.00	Soil treatment – 2.0 l/ha manganese sulphate
15.06.00	Fungicide – 0.5 l/ha Tilt Top (propiconazole + fenpropimorph)
15.06.00	Insecticide – 0.4 l/ha Perfection 500 S (dimethoate)
05.07.00	Fungicide – 0.5 l/ha Tilt Top (propiconazole + fenpropimorph)
05.07.00	Insecticide – 0.4 l/ha Perfection 500 S (dimethoate)
28.08.00	Spring barley harvested (grain yield 52.6 hkg/ha; 85% dry matter. Straw yield 13.1 hkg/ha; 100% dry matter)
13.10.00	Herbicide – 4.0 l Roundup Bio (glyphosate)
23.10.00	Ploughing – depth 20 cm
01.05.01	Fertilization – 20 kg P/ha and 105 kg K/ha
02.05.01	Peas sown – cultivar Julia
22.05.01	Herbicide – 1.0 l/ha Basagran 480 (bentazone)
22.05.01	Herbicide – 1.5 l/ha Stomp (pendimethalin)
27.06.01	Insecticide – 0.25 kg/ha Pirimor G (pirimicarb)
22.08.01	Peas harvested (seed yield 51.8 hkg/ha; 86% dry matter)
30.08.01	Spreading of pea residues
18.10.01	Ploughed – 20 cm depth
19.10.01	Winter wheat sown – cultivar Ritmo
20.11.01	Herbicide – 1.0 l/ha Oxitril CM (ioxynil + bromoxynil)
22.03.02	Fertilization – 73.5 kg N/ha, 10.5 kg P/ha and 35 kg K/ha
24.04.02	Fertilization – 73.5 kg N/ha, 10.5 kg P/ha and 35 kg K/ha
25.04.02	Herbicide – 20 g/ha Gratil 75 WP (amidosulfuron)
13.05.02	Herbicide – 2.0 l/ha Metaxon (MCPA)
27.05.02	Fungicide – 0.25 l/ha Tilt 250 EC (propiconazole)
17.06.02	Fungicide – 0.25 l/ha Tilt 250 EC (propiconazole)
24.06.02	Insecticide – 0.25 kg/ha Pirimor G (pirimicarb)
09.08.02	Winter wheat harvested (grain yield 69.4 hkg/ha; 85% dry matter)

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

Date	Management practice
11.08.99	Herbicide – 2.0 l/ha Roundup 2000 (glyphosate)
10.09.99	Stubble harrowed – 10 cm depth
19.09.99	Ploughed – 20 cm depth
19.09.99	1st seed bed preparation – with power harrow, 5 cm depth
20.09.99	2nd seed bed preparation – with power harrow, 5 cm depth
20.09.99	Winter wheat sown – cultivar Stakado
05.10.99	Tracer application – 30 kg/ha potassium bromide
14.10.99	Herbicide – 1.0 l/ha Briotril (ioxynil and bromoxynil)
21.03.00	Fertilization – 70 kg N/ha, 10 kg P/ha and 25 kg K/ha
08.04.00	Herbicide – 0.8 l/ha Starane 180 (fluroxypyr)
19.04.00	Fertilization – 99 kg N/ha, 14 kg P/ha and 36 kg K/ha
05.05.00	Fungicide – 0.5 l/ha Tilt Top (propiconazole + fenpropimorph)
31.05.00	Fungicide – 0.5 l/ha Tilt Top (propiconazole + fenpropimorph)
19.06.00	Insecticide – 0.25 l/ha Pirimor G (pirimicarb)
28.08.00	Winter wheat harvested (grain yield 92.7 hkg/ha; 85% dry matter. Straw yield 76.2 hkg/ha; 100% dry matter)
04.10.00	Herbicide – 2.0 l/ha Roundup 2000 (glyphosate)
16.10.00	Ploughing – depth 20 cm
02.05.01	Fertilization – 110 kg N/ha, 21 kg P/ha and 63 kg K/ha
02.05.01	Sugar beet sown – cultivar Havana
21.05.01, 30.05.01 & 15.06.01	Herbicide – 1.0 l/ha Goltix WG and 1.5 l/ha Betanal Optima (metamitron, phenmedipham, desmedipham and ethofumesate)
21.06.01	Herbicide – 1.5 l/ha Fusilade X-tra (fluazifop-P-butyl)
17.07.01	Insecticide – 0.3 l/ha Pirimor G (pirimicarb)
24.10.01	Sugar beet harvested (beet yield 147.9 hkg/ha; 100% dry matter)
30.10.01	Ploughed – 25 cm depth
27.03.02	Fertilization – 95 kg N/ha, 13 kg P/ha and 35 kg K/ha
28.03.02	Spring barley sown – cultivar Barke
07.05.02	Herbicide – 15 g/ha Express (tribenuron methyl)
22.05.02	Herbicide – 2.0 l/ha Metaxon (MCPA)
25.05.02	Herbicide – 3.0 l/ha Barnon Plus (flamprop-M-isopropyl)
04.06.02	Insecticide – 0.4 l/ha Perfection 500 S (dimethoate)
04.06.02	Fungicide – 0.5 l/ha Tilt 250 EC (propiconazole)
09.08.02	Spring barley harvested (grain yield 65.6 hkg; 85% dry matter. Straw yield 60.2 hkg/ha; 100% dry matter)

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

Date	Management Practice
05.04.00	Ploughing – depth 22 cm
07.04.00	Fertilization – 81.8 kg N/ha, 20.5 kg P/ha and 61.4 kg K/ha
08.04.00	Spring barley sown – cultivar Optic
09.05.00	Herbicide – 20 g/ha Ally (metsulfuron-methyl)
05.06.00	Herbicide – 3.0 l/ha Barnon Plus 3 (flamprop-M-isopropyl)
09.06.00	Fungicide – 0.5 l/ha Tilt Top (propiconazole + fenpropimorph)
09.06.00	Insecticide – 0.6 l/ha Perfection 500 S (dimethoate)
14.06.00	Herbicide – 15 g/ha Express (tribenuron methyl)
26.06.00	Fungicide – 0.5 l/ha Tilt Top (propiconazole + fenpropimorph)
22.08.00	Spring barley harvested (grain yield 39.8 hkg/ha; 85% dry matter. Straw yield 10.2 hkg/ha; 100% dry matter)
20.11.00	Ploughing – depth 22 cm
11.04.01	Peas sown – cultivar Pinocchio
01.05.01	Fertilization – 7.5 kg P/ha and 39.3 kg K/ha
01.05.01	Herbicide – 1.0 l/ha Basagran 480 (bentazone)
01.05.01	Herbicide – 1.5 l/ha Stomp SC (pendimethalin)
01.07.01	Insecticide – 0.25 kg/ha Pirimor G (pirimicarb)
19.08.01	Peas harvested (seed yield 26.6 hkg/ha; 86% dry matter)
26.09.01	Herbicide – 4.0 l/ha Roundup Bio (glyphosate)
13.10.01	Ploughed – 22 cm depth
15.10.01	Winter wheat sown – cultivar Bill
08.11.01	Herbicide – 1.0 l/ha Oxitril CM (ioxynil + bromoxynil)
05.04.02	Fertilization – 64 kg N/ha, 19 kg P/ha and 53 kg K/ha
22.04.02	Herbicide – 20 g/ha Gratil 75 WG (amidosulfuron)
02.05.02	Fertilization – 69 kg N/ha, 16 kg P/ha and 58 kg K/ha
15.05.02	Herbicide – 3.0 l/ha Barnon Plus 3 (flamprop-M-isopropyl)
31.05.02	Fungicide – 0.25 l/ha Tilt 250 EC (propiconazole)
14.06.02	Insecticide – 0.25 kg/ha Pirimor G (pirimicarb)
14.06.02	Fungicide – 0.25 l/ha Tilt 250 EC (propiconazole)
20.08.02	Winter wheat harvested (seed yield 72.3 hkg/ha; 85% dry matter)

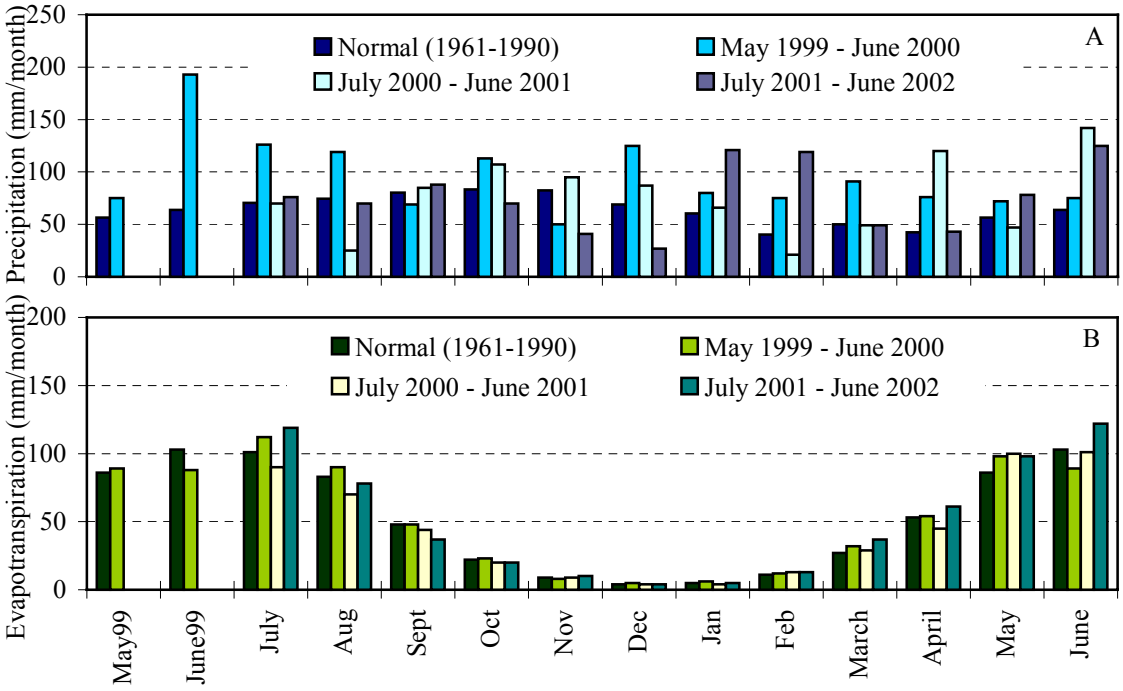

Figure A4.1. Monthly precipitation (A) and potential evapotranspiration (B) at Tylstrup for the monitoring period May 1999–June 2002. Normal values (1961–1990) compared to locally measured (precipitation) or calculated (evapotranspiration).

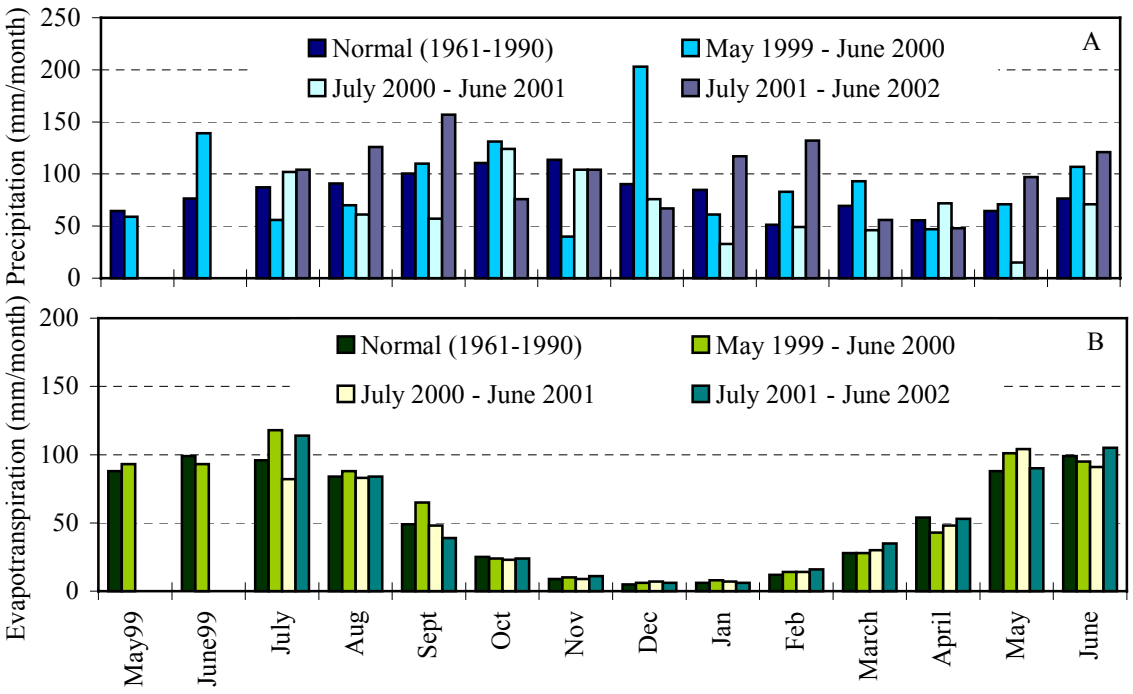

Figure A4.2. Monthly precipitation (A) and potential evapotranspiration (B) at Jyndevad for the monitoring period May 1999–June 2002. Normal values (1961–1990) compared to locally measured (precipitation) or calculated (evapotranspiration).

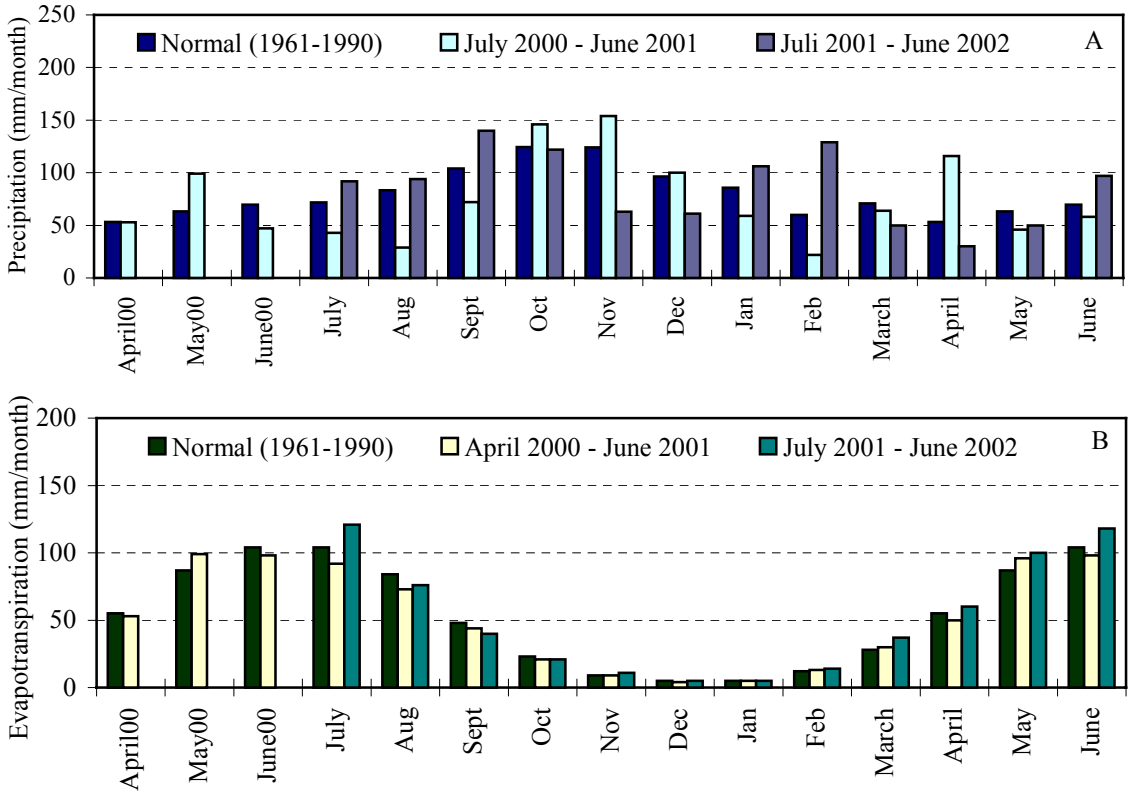

Figure A4.3. Monthly precipitation (A) and potential evapotranspiration (B) at Silstrup for the monitoring period April 2000–June 2002. Normal values (1961–1990) compared to locally measured (precipitation) or calculated (evapotranspiration).

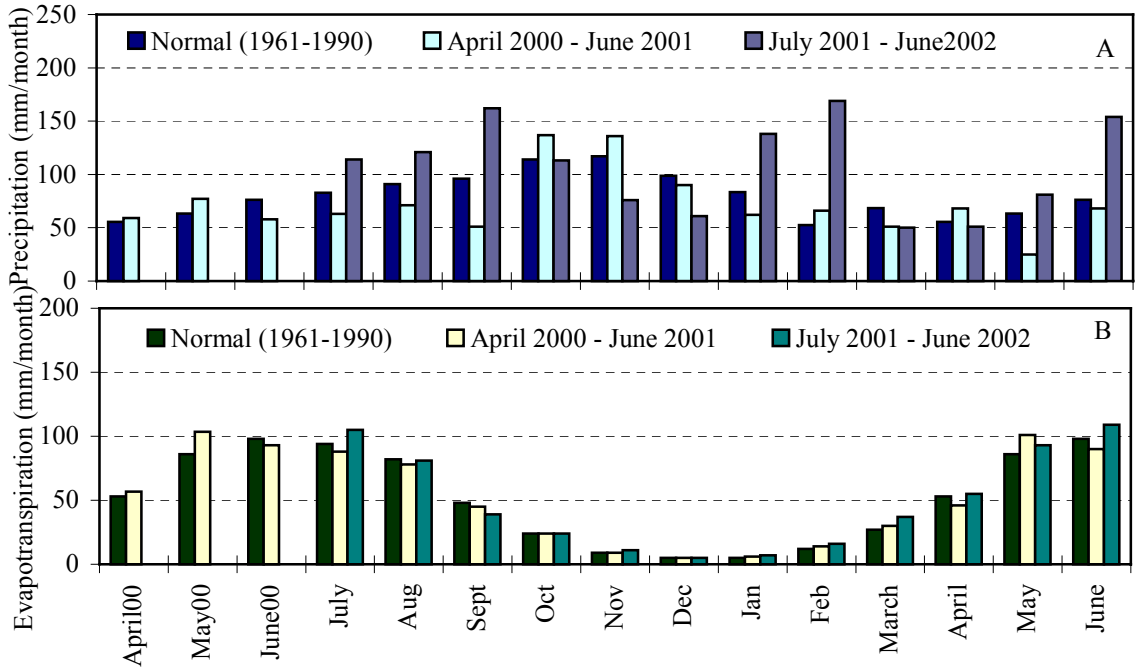

Figure A4.4. Monthly precipitation (A) and potential evapotranspiration (B) at Estrup for the monitoring period June 2000– June 2002. Normal values (1961–1990) compared to locally measured (precipitation) or calculated (evapotranspiration).

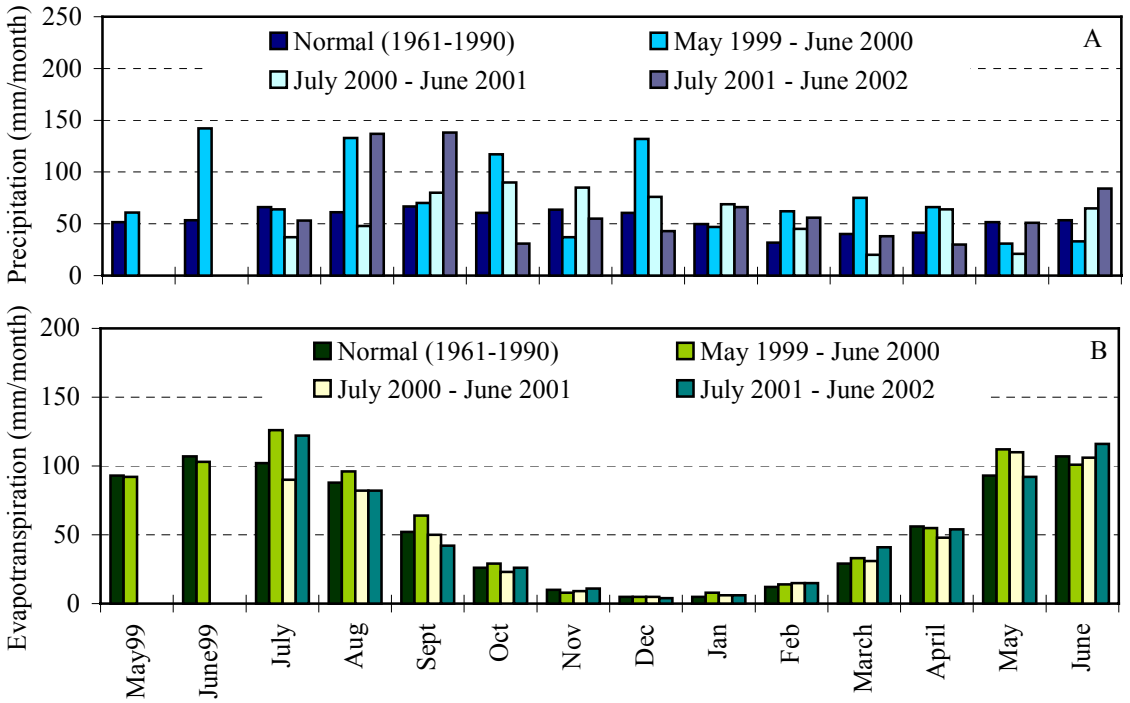

Figure A4.5. Monthly precipitation (A) and potential evapotranspiration (B) at Faardrup for the monitoring period May 1999–June 2002. Normal values (1961–1990) compared to locally measured (precipitation) or calculated (evapotranspiration).

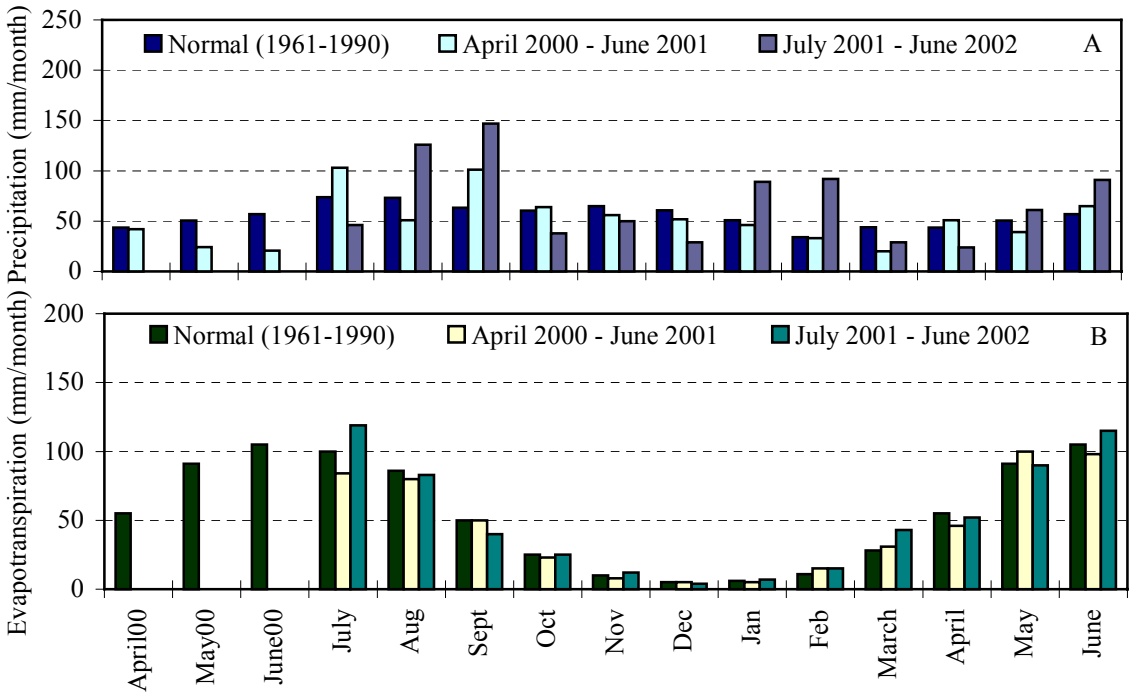

Figure A4.6. Monthly precipitation measured (A) and potential evapotranspiration (B) at Slaeggerup for the monitoring period April 2000–June 2002. Normal values (1961–1990) compared to locally measured (precipitation) or calculated (evapotranspiration).

Pesticide concentrations measured in suction cups S1 and S2 were assumed to be representative for each sample period. Moreover, accumulated percolation rates deriving from the MACRO model were assumed to be representative for both suction cup S1 and suction cup S2. For each of the measured concentrations, the corresponding percolation (Perc.) was estimated according to the equation:

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

Where
t = sampling date
$t_1 = 0.5(t_{i-1}+t_i)$; $t_2=0.5(t_i+t_{i+1})$
P_t = Daily percolation at 1 m b.g.s. as estimated by the MACRO model (mm)

The average concentration was estimated according to the equation:

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

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

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

Suction cup S1 – 1 m b.g.s.				Suction cup S2 – 1 m b.g.s.			
Date	Perc. (mm)	MDD (µg/l)	MD (µg/l)	Date	Perc. (mm)	MDD (µg/l)	MD (µg/l)
t_i	P_i	C_i	C_i	t_i	P_i	C_i	C_i
23.08.99	93	n.a.	n.a.	23.08.99	93	n.a.	n.a.
09.09.99	47	*	*	09.09.99	47	*	<0.2
04.11.99	98	*	<0.2	04.11.99	127	*	<0.2
08.12.99	87	0.25	0.22	10.01.00	154	0.25	0.08
10.01.00	98	0.72	0.62	03.02.00	57	0.23	0.11
03.02.00	54	2.05	0.39	02.03.00	67	0.23	0.07
02.03.00	67	2.10	0.17	06.04.00	56	0.20	0.14
06.04.00	56	1.96	0.50	10.05.00	26	0.21	0.09
10.05.00	26	1.39	n.a.	07.06.00	38	0.21	<0.02
07.06.00	38	1.06	0.48	03.10.00	39	0.11	0.09
03.10.00	10	0.28	0.15	05.12.00	165	0.30	0.12
31.10.00	91	0.10	0.17	04.01.01	71	0.24	0.08
05.12.00	212	0.11	0.01	07.02.01	42	0.37	0.10
30.04.01	93	0.74	0.20	06.03.01	19	0.30	0.11
30.05.01	20	0.56	0.18	03.04.01	19	0.42	0.12
04.07.01	12	0.21	0.09	30.04.01	56	0.66	0.23
08.08.01	1	0.07	0.21	04.07.01	26	0.52	0.13
13.09.01	5	0.03	0.09	08.08.01	1	0.37	0.18
10.10.01	40	0.03	0.15	13.09.01	5	0.18	0.08
06.11.01	27	<0.02	0.15	10.10.01	40	0.14	0.05
04.12.01	31	0.04	0.09	06.11.01	27	0.14	<0.02
07.01.02	26	0.06	0.10	04.12.01	31	0.12	0.06
06.02.02	138	0.05	0.16	07.01.02	26	0.12	0.11
05.03.02	75	0.07	<0.02	06.02.02	138	0.19	0.13
03.04.02	24	0.20	0.08	05.03.02	75	0.23	0.08
30.04.02	17	0.06	0.14	03.04.02	24	0.16	0.04
28.05.02	30	<0.02	0.11	30.04.02	17	0.12	0.11
02.07.02	13	0.05	0.12	28.05.02	30	0.12	0.12
				02.07.02	13	0.06	0.07
1.7.99–30.6.00		**0.87–0.97**	**0.26–0.36**	**1.7.99–30.6.00**		**0.14–0.27**	**0.05–0.10**
1.7.00–30.6.01		**0.33**	**0.13**	**1.7.00–30.6.01**		**0.33**	**0.12**
1.7.01–30.6.02		**0.06**	**0.11**	**1.7.01–30.6.02**		**0.19**	**0.09**

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

As the analysis methods for these degradation products were developed during the present project, results are only available from September 1999 onwards. The bromide transport studies indicate that the degradation products are unlikely to have reached the suction cups before late August 1999. The percolate concentration was therefore assumed to be zero during the period 1.6.99–23.8.99. The first analyses (October and November) were also subject to some uncertainty due to the high detection limit of 0.2 µg/l. The average concentration for 1999/2000 is therefore given as a range representing the maximum and minimum concentrations estimated by applying a concentration equal to either zero or the detection limit.

Table A6.1 Measured concentration of AMPA and glyphosate in drainage water at Silstrup. Drainage runoff refers to the accumulated runoff for each of the analysed samples. Glyphosate was applied to the field on 25.10.01.

Time-proportional samples				Flow-proportional samples			
Date	AMPA (µg/l)	Glyphosate (µg/l)	Drainage runoff (mm)	Date	AMPA (µg/l)	Glyphosate (µg/l)	Drainage runoff (mm)
18.09.01			5				
25.09.01			12				
02.10.01			5				
09.10.01	<0.01	<0.01	14	08.10.01	<0.01	<0.01	10
16.10.01	<0.01	<0.01	22				
23.10.01	<0.01	<0.01	0				
30.10.01	0.14	1.90	2				
06.11.01	0.19	1.10	2	31.10.01	0.06	4.70	2
13.11.01	0.16	0.65	3	12.11.01	0.35	1.20	3
27.11.01	0.18	0.41	3	27.11.01	0.14	0.18	2
04.12.01	0.07	0.17	9	30.11.01	0.07	0.42	2
				04.12.01	0.11	0.24	5
11.12.01	0.17	0.13	5	06.12.01	0.05	0.23	2
27.12.01	0.08	0.06	5	27.12.01	0.10	0.07	4
02.01.02	0.21	0.06	5	03.01.02	0.10	0.05	4
08.01.02	0.06	0.05	1	17.01.02	0.06	0.05	1
22.01.02	0.03	0.03	10	22.01.02	0.04	0.03	8
29.01.02	0.04	0.04	38	28.01.02	0.05	0.05	34
05.02.02	0.03	0.03	11				
13.02.02	<0.01	<0.01	24	13.02.02	n.a.	n.a.	11
19.02.02	0.05	0.03	1				
26.02.02	0.05	0.03	14	26.02.02	0.10	0.07	14
05.03.02	0.06	0.05	25	01.03.02	0.11	0.08	16
12.03.02	0.05	0.02	10	08.03.02	0.05	0.03	6
				12.03.02	0.04	0.03	2
19.03.02	0.05	0.02	<1				
25.06.02	0.22	0.05	<1				

n.a:. Not analysed

Table A6.2. Measured concentration (µg/l) of glyphosate and AMPA in vertical monitoring well M5 and horizontal monitoring well H1 at Silstrup. The location of the monitoring installations is indicated in Figure 20.

Monitoring well	H1.2	H1.3	M5			
Screen depth (m b.g.s..)	3.5	3.5	1.5–2.5	2.5–3.5	3.5–4.5	4.5–5.5
AMPA						
09.10.01	<0.01	<0.01	<0.01	<0.01	<0.01	
06.11.01	<0.01		0.01	0.08	<0.01	
04.12.01	<0.01		<0.01	0.01	<0.01	
08.01.02	0.014		0.01	<0.01	<0.01	
05.02.02	<0.01		<0.01	<0.01	<0.01	
05.03.02	0.01		0.01	<0.01	<0.01	
02.04.02	<0.01		<0.01	<0.01	<0.01	
30.04.02	<0.01			<0.01	<0.01	<0.01
28.05.02	<0.01		<0.01	<0.01	<0.01	
Glyphosate						
09.10.01	<0.01	<0.01	<0.01	<0.01	<0.01	
06.11.01	<0.01		0.01	0.03	<0.01	
04.12.01	<0.01	<0.01	<0.01	0.01	<0.01	
08.01.02	<0.01		<0.01	<0.01	<0.01	
05.02.02	<0.01		<0.01	<0.01	<0.01	
05.03.02	<0.01		<0.01	<0.01	<0.01	
02.04.02	<0.01		<0.01	<0.01	<0.01	
30.04.02	<0.01			<0.01	<0.01	<0.01
28.05.02	<0.01		<0.01	<0.01	<0.01	

Table A7.1 Concentration (µg/l) of ethofumesate, metamitron and metamitron-desamino in the vertical monitoring wells at Faardrup. The location of the monitoring installations is indicated in Figure 38.

Monitoring well	M2				M4				M5			M6			
Screen number	1	2	3	4	1	2	3	4	1	2	3	1	2	3	4
Ethofumesate															
03.05.01	<	<	<		<	<	<		<	<	<	<	<	<	
30.05.01									<	<	<	<	<	<	
04.07.01									<	<	<	<	<	<	
08.08.01		<	<	<	<	<		<	1.40	0.29	0.44	<	<		<
12.09.01									0.03	0.07	0.10			<	<
10.10.01									0.33	0.15	0.14	<	<	<	
05.12.01									0.07	0.04	0.06	<	<	<	
07.02.02			<	<	<	<	<		0.01	0.02	0.02				
06.03.02									0.01	0.01	0.02				
04.04.02									0.01	0.01	0.01				
28.05.02									0.00	0.01	0.02	<	<	<	
03.07.02									0.01	0.01	0.01	<	<	<	
Metamitron															
03.05.01	<	<	<		<	<	<		<	<	<	<	<	<	
30.05.01									<	<	<	<	<	<	
04.07.01									<	<	<	<	<	<	
08.08.01		<	<	<	<	<		<	0.63	0.15	0.21	<	<		<
12.09.01									0.27	0.08	0.10			<	<
10.10.01									0.08	0.05	0.05	<	<	<	
05.12.01									0.03	0.04	0.03	<	<	<	
07.02.02			<	<	<	<	<		0.02	0.01	0.01				
06.03.02									<	<	0.01				
04.04.02									0.01	0.01	0.01				
28.05.02									<	0.01	0.01	<	<	<	
03.07.02									0.01	<	<	<	<	<	
Metamitron-desamino															
03.05.01	<	<	<		<	<	<		<	<	<	<	<	<	
30.05.01									<	<	<	<	<	<	
04.07.01									<	<	<	<	<	<	
08.08.01		<	<	<	<	<		<	1.30	0.33	0.62	<	<		<
12.09.01									0.50	0.18	0.21			<	<
10.10.01									0.23	0.16	0.15	<	<	<	
05.12.01				<					0.16	0.27	0.15	<	<	<	
07.02.02			<		<	<	<		0.04	0.05	0.05				
06.03.02									0.03	0.04	0.04				
04.04.02									0.02	0.02	0.02				
28.05.02									0.00	0.02	0.02	<	<	<	
03.07.02									0.01	0.02	0.02	<	<	<	
04.04.01									<	<	<	<	<	<	
03.05.01	<	<	<		<	<	<		<	<	<	<	<	<	

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

None of the compounds listed in Table A7.1 were found in any of the water samples from the horizontal monitoring wells.

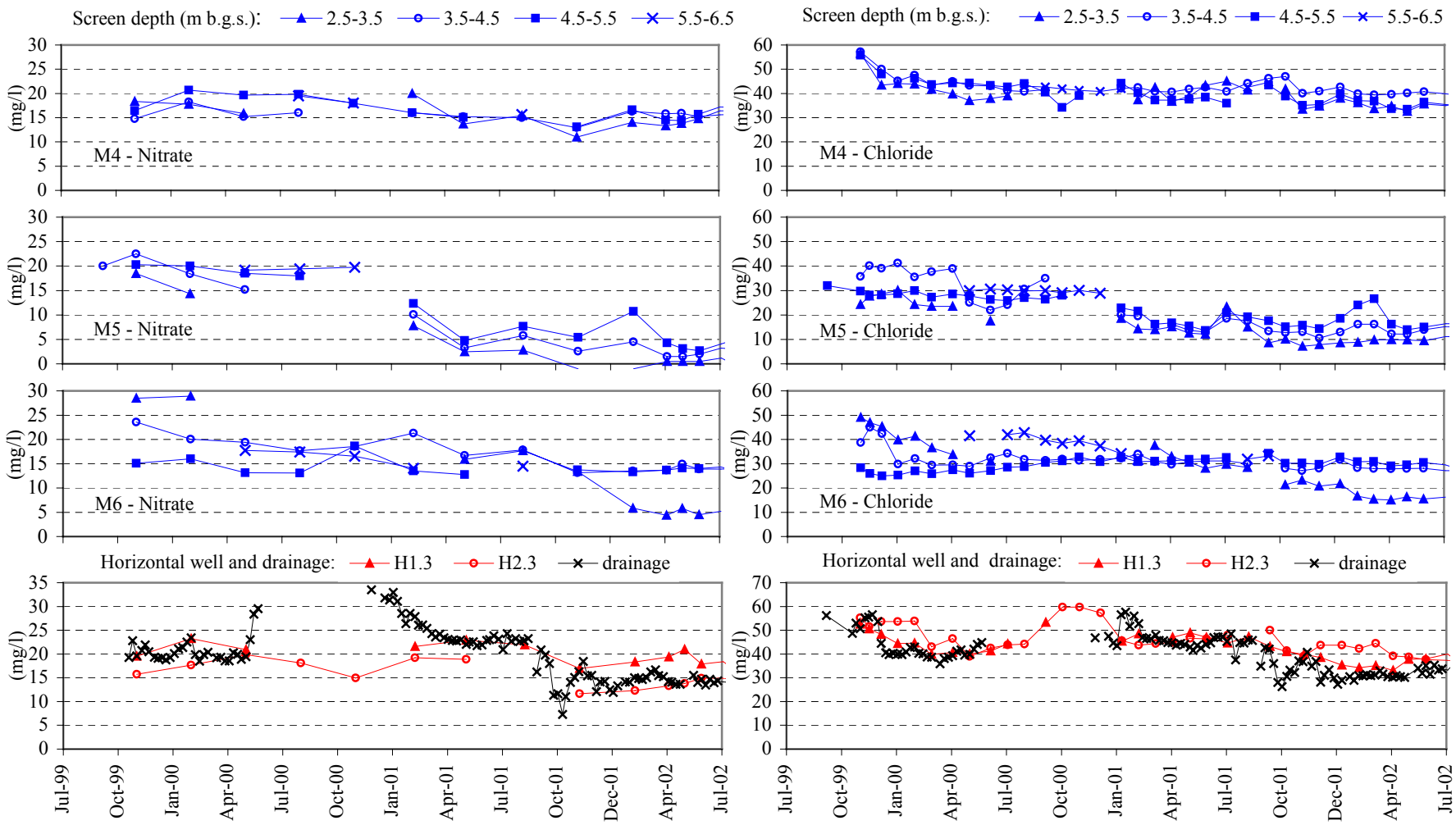

Figure A8.1 Chloride and nitrogen concentrations at Faardrup. Data derive from the vertical monitoring wells M4, M5 and M6. The concentrations in water sampled from the drainage water and horizontal monitoring well are included for comparison. The location of the monitoring installations is indicated in Figure 38.

Table A9.1. Measured concentrations of AMPA and glyphosate in drainage water at Slaeggerup. Drainage runoff refers to the accumulated runoff for each of the analysed samples. Glyphosate was applied to the field on 26.09.01.

Time-proportional samples				Flow-proportional samples			
Date	AMPA (µg/l)	Glyphosate (µg/l)	Drainage runoff (mm)	Date	AMPA (µg/l)	Glyphosate (µg/l)	Drainage runoff (mm)
25.09.01	<0.01	<0.01	1				
02.10.01	0.01	0.16	1				
09.10.01	0.01	0.09	1				
15.10.01	0.01	0.34	<1				
23.10.01	n.a.	n.a.	<1				
13.11.01	5.4	5.1	<1				
27.11.01	3.5	1.8	<1				
04.12.01	1.1	0.46	1				
11.12.01	0.1	0.05	1				
27.12.01	0.17	0.14	<1				
02.01.02	0.04	0.05	<1				
08.01.02	0.02	0.04	<1				
15.01.02	0.03	0.03	<1				
22.01.02	0.01	0.01	<1				
29.01.02	0.03	0.02	15	29.01.02	0.05	0.03	14
06.02.02	0.02	0.01	17	06.02.02	0.03	0.02	13
13.02.02	0.02	0.01	7				
20.02.02	0.01	0.01	4				
26.02.02	0.02	0.02	19				
05.03.02	0.03	0.02	35	01.03.02	0.12	0.05	22
12.03.02	0.01	<0.01	5				
19.03.02	<0.01	<0.01	<1				
26.03.02	0.01	<0.01	<1				
03.04.02	<0.01	<0.01	<1				

n.a.: Not analysed

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

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

Table A10.1 Parameters obtained in the curve fitting analyses of degradation data with the 1st order and 1st + 1st order model.

Pesticide	Field	Depth (cm b.g.s.)	a	k_1	b	k_2	r^2
Bromoxynil	1st order Slaeggerup	0–20	99.56	2.328			0.98
	1st +1st order Slaeggerup	0–20	42.28	8.03	63.85	1.37	1.00
	1st order Slaeggerup	80–100	105.26	0.056			0.93
	1st +1st order Slaeggerup	80–100	52.59	0.056	52.67	5.58E-02	0.93
Dimethoate	1st order Estrup	80–100	121.57	0.0093			0.95
	1st +1st order Estrup	80–100	20.78	0.025	103.48	8.12E-03	0.95
	1st order Slaeggerup	0–20	117.73	0.375			0.99
	1st +1st order Slaeggerup	0–20					
	1st order Slaeggerup	80–100	117.26	0.040			0.97
	1st +1st order Slaeggerup	80–100	113.43	0.043	4.37	0.0020	0.97
Fenpropimorph	1st order Tylstrup	0–20	90.45	0.0018			0.86
	1st +1st order Tylstrup	0–20	13.83	0.032	81.19	0.0011	0.94
	1st order Jyndevad	0–20	92.46	0.0056			0.72
	1st +1st order Jyndevad	0–20	62.88	0.029	44.09	1.0E-12	0.97
	1st order Faardrup	0–20	84.14	0.046			0.96
	1st +1st order Faardrup	0–20	54.51	0.38	38.48	1.9E-02	1.00
Flamprop-M-isopropyl	1st order Estrup	0–20	91.43	0.0055			0.88
	1st +1st order Estrup	0–20	69.02	0.0109	25.85	1E-12	0.90
	1st order Slaeggerup	0–20	91.33	0.0444			0.96
	1st +1st order Slaeggerup	0–20	61.78	0.1084	35.58	0.0134	1.00
Ioxynil	1st order Faardrup	0–20	81.74	0.96			0.96
	1st +1st order Faardrup	0–20	70.50	1.29	11.52	6.1E-02	0.99
	1st order Faardrup	80–100	82.51	0.056			1.00
	1st +1st order Faardrup	80–100	79.96	0.062	2.80	3.9E-03	1.00
	1st order Slaeggerup	0–20	92.89	0.61			0.94
	1st +1st order Slaeggerup	0–20	77.41	1.37	23.14	0.05758	1.00
Propiconazole	1st order Tylstrup	0–20	94.80	0.0022			0.97
	1st +1st order Tylstrup	0–20	11.80	0.013	84.60	1.7E-03	0.98
	1st order Jyndevad	0–20	95.75	0.0036			0.95
	1st +1st order Jyndevad	0–20	67.31	0.0088	33.83	1.2E-05	1.00
	1st order Faardrup	0–20	96.52	0.0063			0.99
	1st +1st order Faardrup	0–20	22.99	0.031	82.36	4.9E-03	1.00
	1st order Slaeggerup	0–20	86.14	0.0016			0.61
	1st +1st order Slaeggerup	0–20	18.75	0.26	79.85	0.00092	0.91

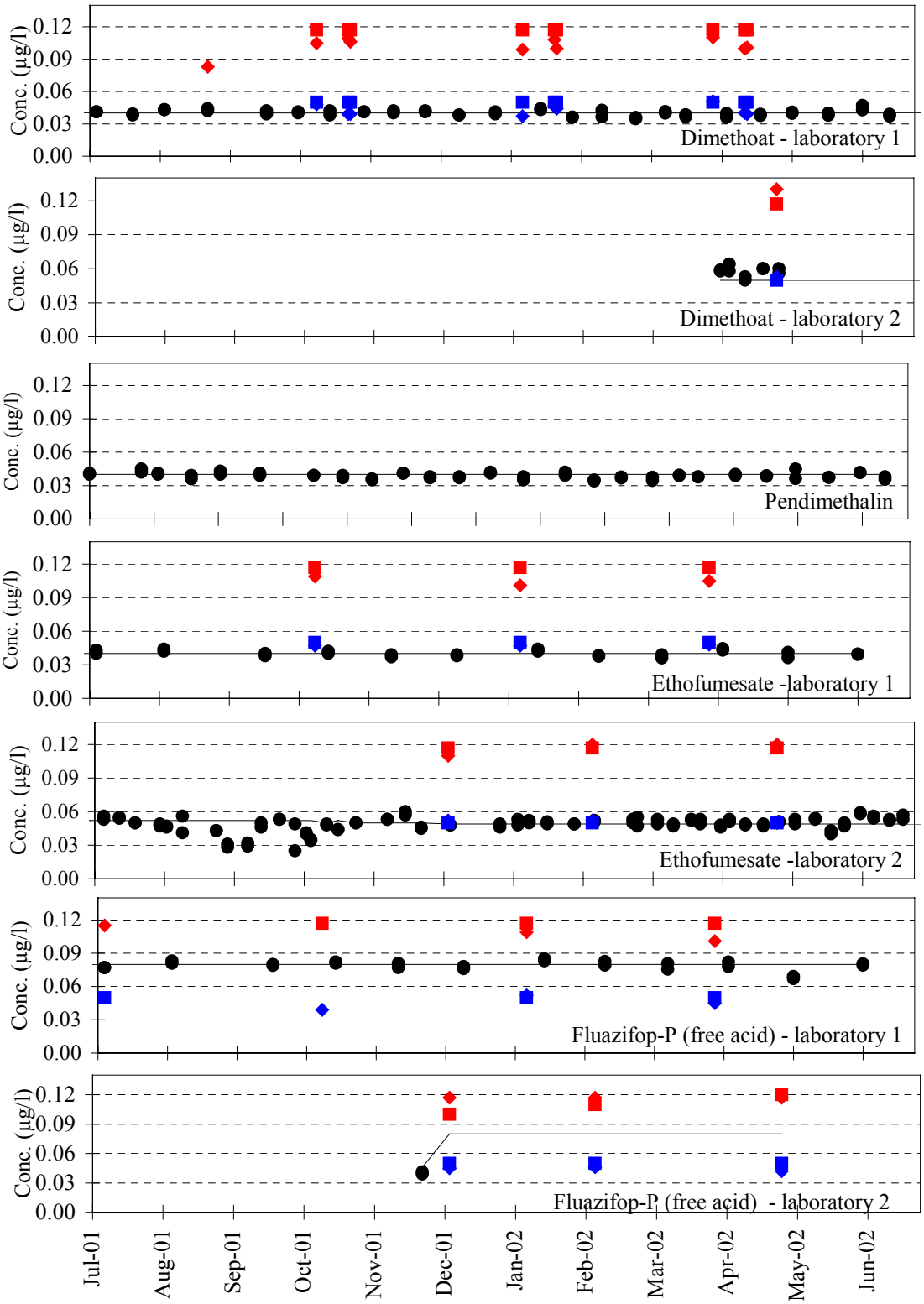

Figure A11.1 Pesticide concentrations in QA samples. The solid line and the closed circles indicate the nominal and observed concentrations, respectively, in internal laboratory controls. The closed red/blue squares indicate the nominal concentrations of the high-level/low-level external control samples. The red/blue diamonds indicate the observed concentrations of the high-level/low-level external control samples.

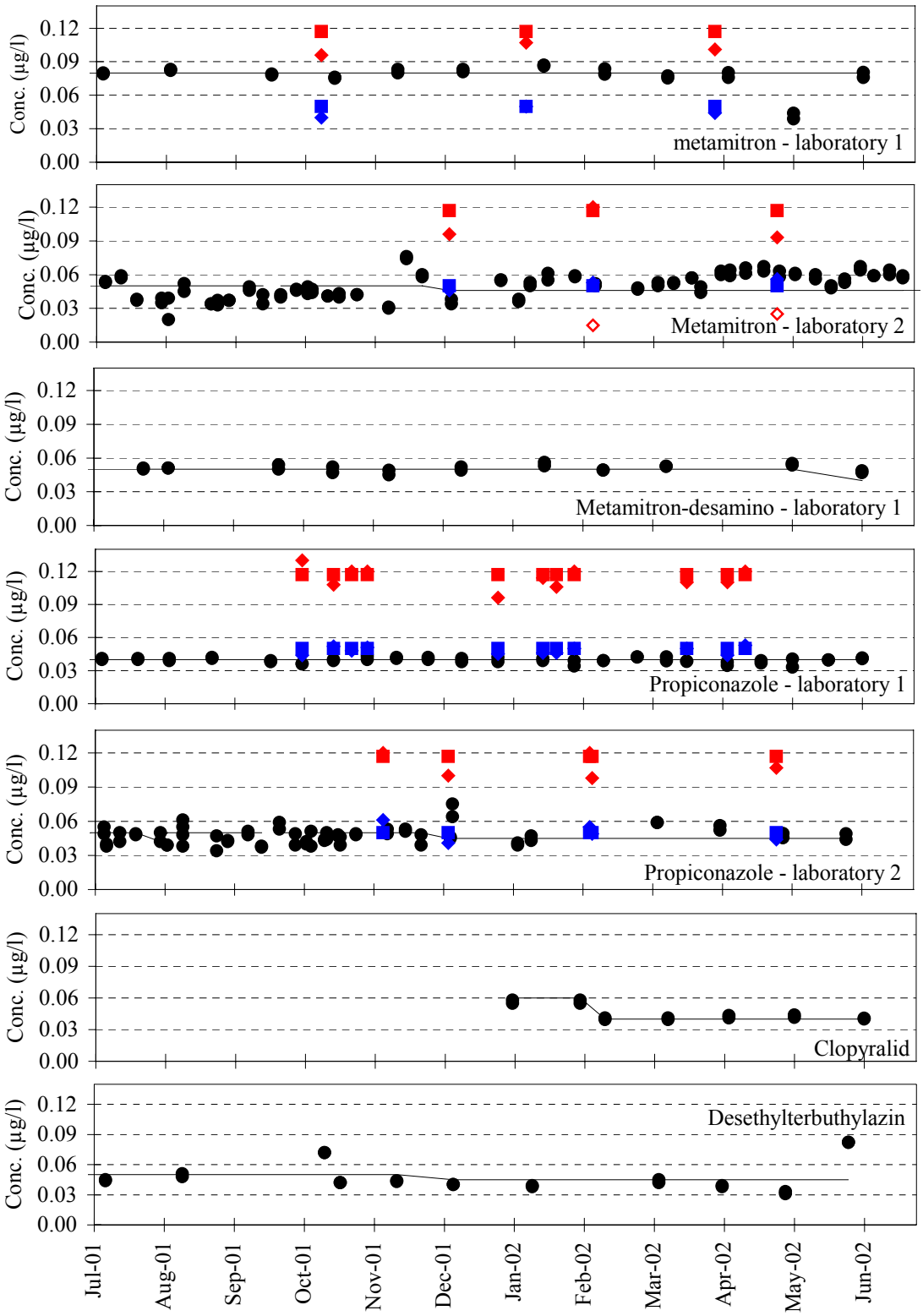

Figure A11.2 Pesticide concentrations in QA samples. The solid line and the closed circles indicate the nominal and observed concentrations, respectively, in internal laboratory controls. The closed red/blue squares indicate the nominal concentrations of the high-level/low-level external control samples. The red/blue diamonds indicate the observed concentrations of the high-level/low-level external control samples. Open diamonds indicate degradation products that are not present in the spike mixture.

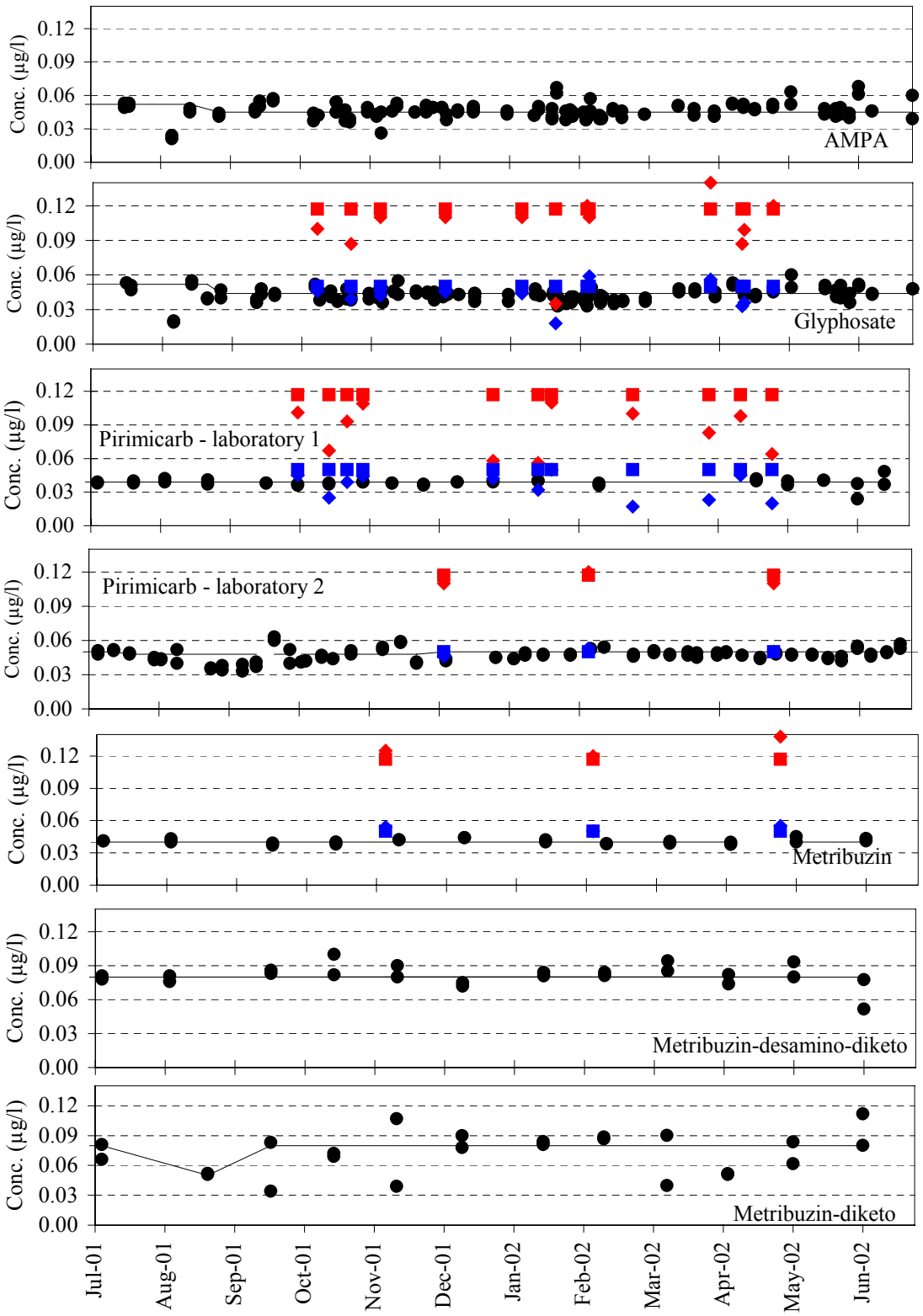

Figure A11.3 Pesticide concentrations in QA samples. The solid line and the closed circles indicate the nominal and observed concentrations, respectively, in internal laboratory controls. The closed red/blue squares indicate the nominal concentrations of the high-level/low-level external control samples. The red/blue diamonds indicate the observed concentrations of the high-level/low-level external control samples.

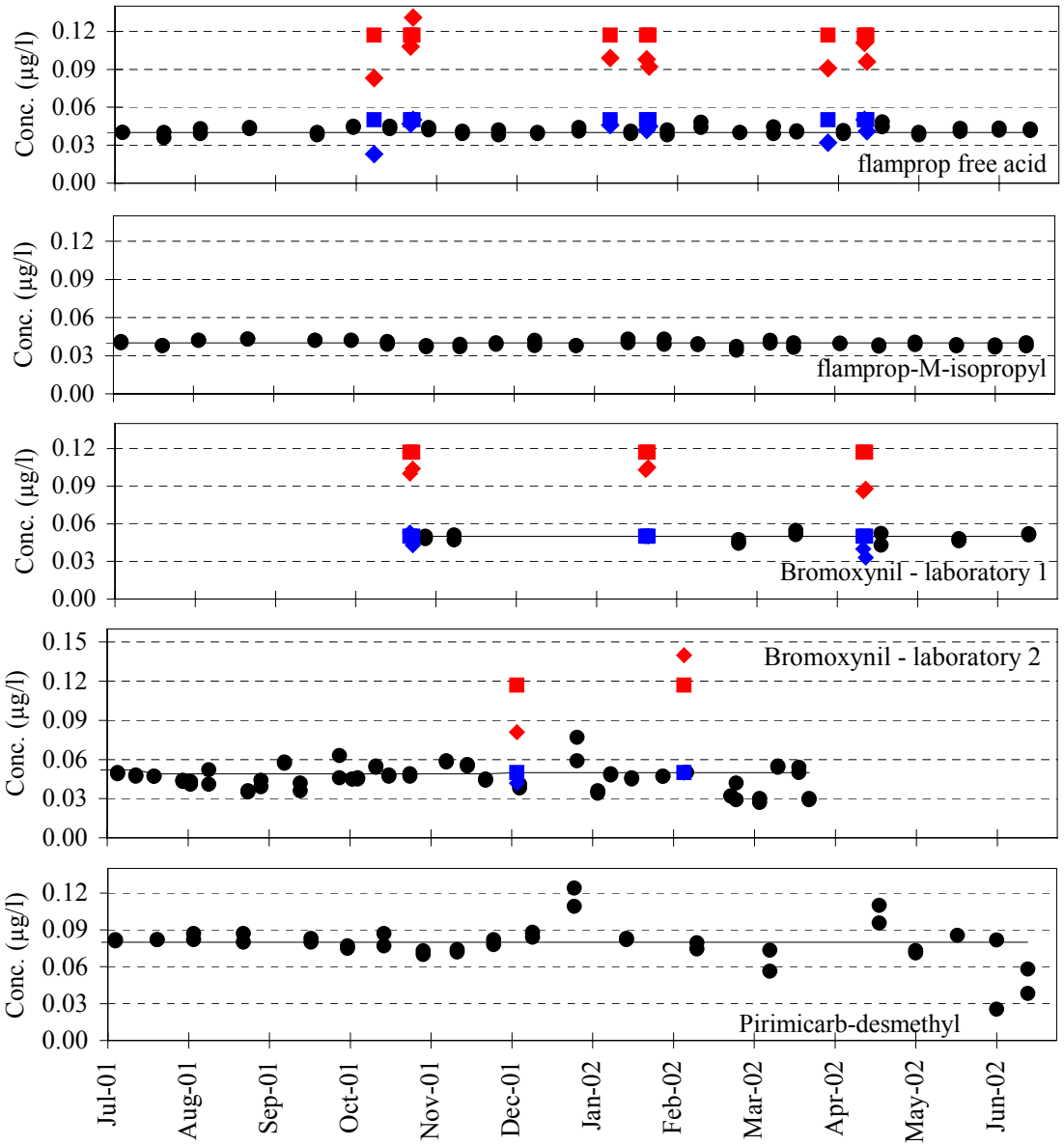

Figure A11.4 Pesticide concentrations in QA samples. The solid line and the closed circles indicate the nominal and observed concentrations, respectively, in internal laboratory controls. The closed red/blue squares indicate the nominal concentrations of the high-level/low-level external control samples. The red/blue diamonds indicate the observed concentrations of the high-level/low-level external control samples.

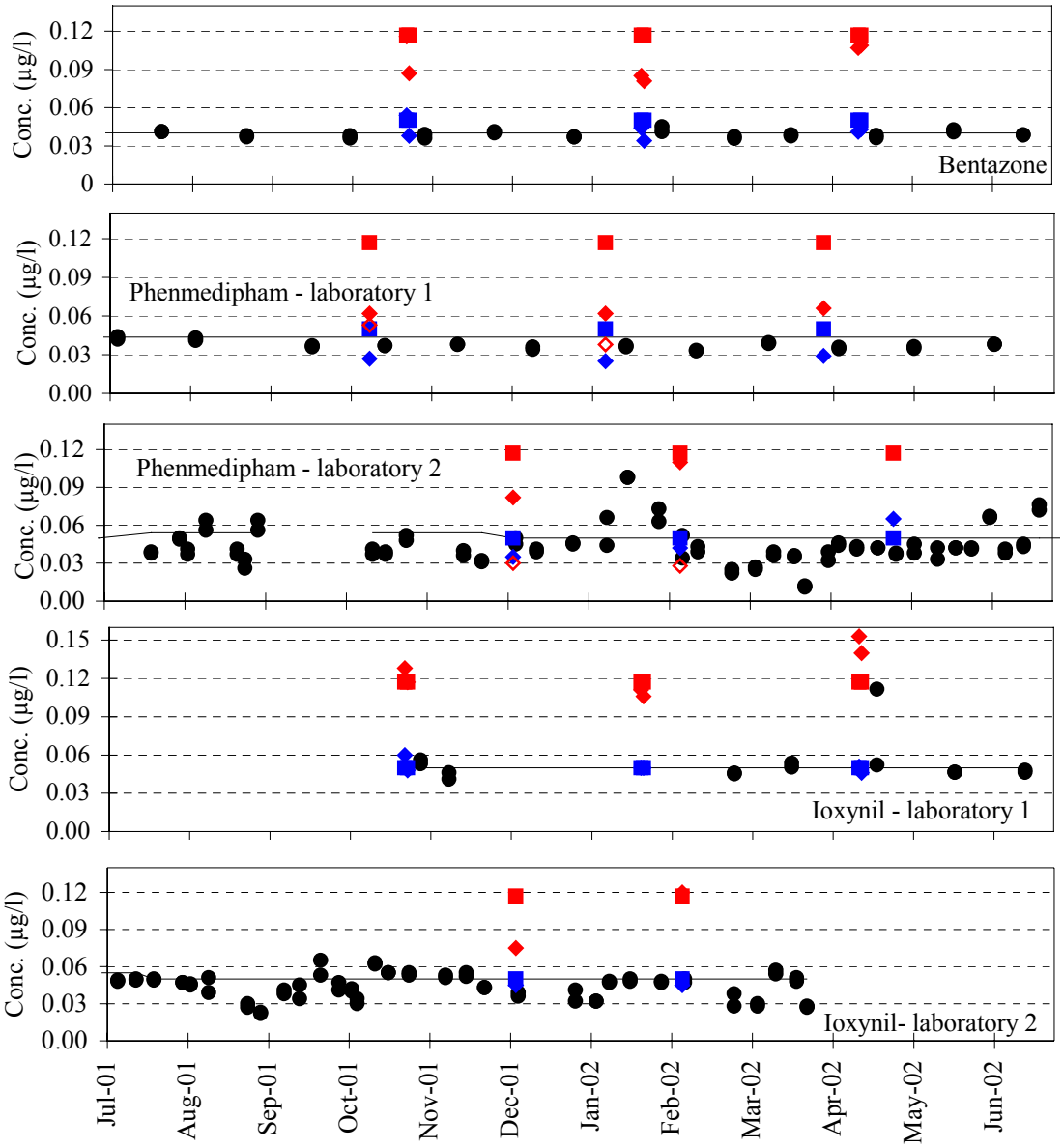

Figure A11.5 Pesticide concentrations in QA samples. The solid line and the closed circles indicate the nominal and observed concentrations, respectively, in internal laboratory controls. The closed red/blue squares indicate the nominal concentrations of the high-level/low-level external control samples. The red/blue diamonds indicate the observed concentrations of the high-level/low-level external control samples. Open diamonds indicate degradation products that are not present in the spike mixture.