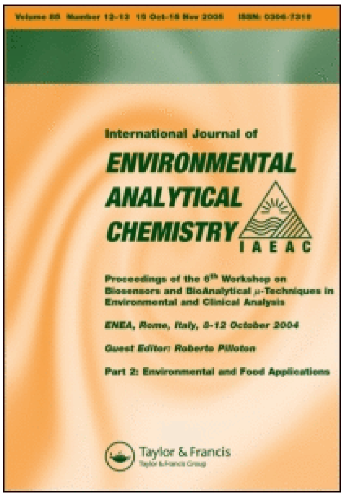

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Leaching of Pesticides from Fields with Recorded Pesticide Applications

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Online publication date: 17 September 2010

To cite this Article Spliid, Niels Henrik(2002) 'Leaching of Pesticides from Fields with Recorded Pesticide Applications', International Journal of Environmental Analytical Chemistry, 82: 8, 571 — 582

To link to this Article: DOI: 10.1080/03067310290009505

URL: http://dx.doi.org/10.1080/03067310290009505

Intern. J. Environ. Anal. Chem., Vol. 82, No. 8–9, pp. 571–582

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LEACHING OF PESTICIDES FROM FIELDS WITH RECORDED PESTICIDE APPLICATIONS

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(Received 24 August 2001; In final form 10 January 2002)

During two winter seasons, 1998/99 and 1999/2000, drainage water was sampled each fortnight from four fields with recorded pesticide application. Water was analysed for a range of pesticides used on the fields. Two of the four fields were equipped with three vertical stainless steel tubes with screens at 1–1.3 m depths. Two other fields were equipped with traditional tile drains, which solely drained the specific fields.

Isoproturon, which was banned from use after 1999, was the most frequently found pesticide in the drainage water. Pendimethalin was another compound frequently found, however in low concentrations.

In drainage water from a field at Silstrup the active ingredients bentazone and propyzamide appeared in the drainage water at the first sampling following treatment and during the following months. The highest concentration levels were 1.3 and 2.8 μg/L, respectively.

Phenoxyacid herbicides, which had been detected at concentration levels up to 0.34 μg/L in an earlier study 10 years ago, no longer appeared in the drainage water.

Keywords: Pesticides; Leaching; Drainage water; Liquid chromatography mass spectrometry

INTRODUCTION

Risk assessment of pesticide leaching is normally based on simple batch experiments where the soil–water distribution ratio Kd, or Koc, is determined [1]. Lysimeters, where pesticides are applied to the top of an undisturbed soil column and the pesticide or carbon-14 content in the drainage water is measured, is another way of evaluating pesticide leaching. However, the most realistic way to get an impression of the mobility of pesticides in soil is to determine the pesticide content in drainage water from fields treated in accordance with good agricultural practices. Lennartz *et al.* [2] have described a setup for full-scale studies of leaching from fields.

In the period 1989–1991, our institute made an investigation of leaching of phenoxy acid herbicides from clayey till fields located at Zealand, Denmark [3,4]. Crops and pesticide treatments were recorded and during the winter period water samples were collected with 14 days intervals. Leaching of phenoxyacids from the fields investigated was demonstrated. Since 1997, the use of phenoxyacid herbicides in Denmark has been

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ISSN 0306-7319 print: ISSN 1029-0397 online
DOI: 10.1080/03067310290009505

reduced from 557 tons in 1996 to 163 tons in 2000 caused by limitations in approved applications.

The present project elucidates whether phenoxyacid leaching still occurs from the soil matrix after use on the actual fields has ceased. Another objective for the project has been to evaluate leaching risks for pesticides used today. Until 1999 isoproturon was used for autumn applications but from year 2000 the compound is no longer allowed in Denmark. Bentazone is another herbicide with a leaching potential with respect to physical chemical properties [5].

Based on information about pesticide treatments of the fields multiple analytical methods were developed which covered relevant pesticides.

Four fields from clayey areas were included in the study due to the fact that cracks and macropores in clayey soils make the soils vulnerable for pesticide leaching and thereby may provide worst case scenarios [6].

METHODS

Locations, Installations and Cultivation

Four fields were included in the study. The Falkerslev and Gyldenholm locations have been used in an earlier study [3]. Further two fields at Danish Institute for Agricultural Sciences in Silstrup were included in this study, cf. Fig. 1.

At the two locations, Falkerslev and Gyldenholm, three stainless steel tubes were installed in triangles with about 100 m between the tubes. The installation which is

FIGURE 1 Map of Denmark with the three locations for the investigation.

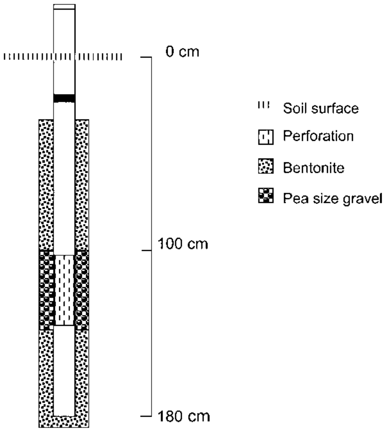

FIGURE 2 Stainless steel tube for water sampling with screen in 1–1.3 m depth.

TABLE I Test field areas, soil types and humus content

Location	*Field area* ha	*Soil type*	*% Humus*
Falkerslev [4]	5	Sandy loam/sandy clay loam	2.2
Gyldenholm [4]	44	Sandy loam	2.2
Silstrup field 22	4.4	Loamy soil	3
Silstrup field 23	6.9	Loamy soil	3

displayed in Fig. 2, consists of a 150 cm tube where it is possible to mount a 50 cm extension tube. The diameter of the tube is 8 cm. In a depth from 1 to 1.3 m below surface, the tube is provided with perforations, which enable soil water to penetrate the sampling tube when water-holding capacity is exceeded. Above and below the perforation the tube is packed with bentonite to avoid leaching along the tube whereas the tube is packed with pea size gravel outside the perforation. The volume below the perforation is about 2 L. The sampling tube design is from Bayer AG, Monheim, Germany [7]. During the summer the extension tube is removed and the tube is capped. A magnet is placed on the cap to make it possible to locate the tube from the surface with a metal detector. When cultivation is finished in the autumn, the tubes are located and the extension tubes are mounted enabling water samples to be collected during the winter. The samples are taken with a sampler made of stainless steel and Teflon.

The fields at Silstrup research station are traditionally drained with tile drains established in 1966. Each field is separately drained and the drain water passes drainage wells where it is possible to collect water samples and where the cumulated drain water flow is currently logged.

Table I gives information about the test field areas, soil types and humus content.

Sampling and Chemical Analysis

During two winter seasons 1998/1999 and 1999/2000 from start of November to end of March, samples were taken once a fortnight. At Silstrup the cumulated amount of

TABLE II Analytical programme and ionisation modes

Compound	*Ionisation*	*Compound*	*Ionisation*
2,4-D	ESI-negative mode	Ioxynil	ESI-negative mode
6-Hydroxybentazone	ESI-negative mode	Isoproturon	ESI-positive mode
8-Hydroxybentazone	ESI-negative mode	Kresoxim-methyl	ESI-positive mode
Azoxystrobin	ESI-positive mode	MCPA	ESI-negative mode
Bromoxynil	ESI-negative mode	Mecoprop	ESI-negative mode
Carbendazim	ESI-positive mode	Napropamide	ESI-positive mode
Dichlorprop	ESI-negative mode	Pendimethalin	APCI-positive mode
Fenpropimorph	APCI-positive mode	Prochloraz	ESI-positive mode
Fenprop.-acid	APCI-positive mode	Propiconazole	ESI-positive mode
Fluroxypyr	ESI-negative mode	Propyzamide	ESI-positive mode

drainage water was logged for each field while the ground water table level was recorded manually at Gyldenholm and Falkerskev. Samples were frozen until analysis.

At the Silstrup fields, water samples were taken as grab samples directly from the out-flow of the drainage pipes. Samples were taken once a fortnight during the whole study period and with a few exceptions, there was also flow of water during the summer.

In the laboratory, water samples (250 ml) were extracted on Rdx solid phase columns from Waters, Milford, MA, USA.

The compounds were separated on HPLC and detected and quantified with mass spectrometry after atmospheric pressure ionization (API) with electrospray (ESI) or atmospheric pressure chemical ionization interphase (APCI). See Table II. Methods with minor modifications are described by Koppen and Spliid [8] and Spliid [9]. The instrument used in this study was a Hewlett-Packard LC-MSD 1100, Palo Alto, CA, USA.

The pesticides and degradation products, which were included in the analyses, are displayed in Table II. All pesticides were purchased from Dr. Ehrenstorfer, Augsburg, Germany with the exception of fenpropmorphic acid, which was kindly supplied by Novartis. Detection limits were 0.01 μg/L for all substances.

RESULTS AND DISCUSSION

In total 200 water samples were included in the investigation of the four fields. The chemical analyses comprised 20 pesticides and degradation products that had been applied to the fields. Table III displays which compounds were detected, highest detected concentrations, median and mean values, number and percentage of findings, and finally number of findings above 0.1 μg/L.

Some of the pesticides used on the fields were not included in the analyses. The pesticides which have been excluded and the causes for the exclusion are listed in Table IV. In the following sections, results from the individual fields are reported.

Falkerslev

Sampling was performed from the 6th of November 1998 with fortnight intervals until the 26th of March 1999, where the extension tubes were removed and the sampling tubes were hidden 40 cm below surface. During the next winter samples were taken

TABLE III Maximum, median and mean concentrations of different analysed pesticides. Findings in figures, in % and findings above 0.1 μg/L

Pesticide	*Max.* μg/L	*Median* μg/L	*Mean* μg/L	*Findings*	*Findings in % of all samples* (200)	*Findings above* 0.1 μg/L
2,4-D	0	0	0	0	0	0
6-Hydroxybentazone	0	0	0	0	0	0
8-Hydroxybentazone	0	0	0	0	0	0
Azoxystrobin	0.024	0.017	0.017	4	2	0
Bentazone	1.33	0.045	0.260	26	13	11
Bromoxynil	0	0	0	0	0	0
Carbendazim	0	0	0	0	0	0
Dichlorprop	0	0	0	0	0	0
Fenpropimorph	0.021	0.021	0.021	1	0.5	0
Fenpropimorphic-acid	0.331	0.026	0.060	31	15.5	5
Fluroxypyr	1.23	0.98	1.013	3	1.5	3
Ioxynil	0	0	0	0	0	0
Isoproturon	2.56	0.051	0.218	46	23	15
MCPA	0	0	0	0	0	0
Mecoprop	0.023	0.022	0.022	2	1	0
Napropamide	0.018	0.018	0.018	1	0.5	0
Pendimethalin	0.4	0.135	0.164	24	12	13
Prochloraz	0	0	0	0	0	0
Propiconazole	0.045	0.017	0.021	17	8.5	0
Kresoxim-methyl	0	0	0	0	0	0
Tebuconazole	0	0	0	0	0	0
Propyzamide	2.84	0.042	0.243	17	8.5	4

TABLE IV Pesticides used but not included in the analysis scheme

Pesticide	*Causes for exclusion*
Tribenuron-methyl	Fast degradation, low dosage and separate analytical method.
Cypermethrin	Used in low dosage on fields fully covered with plants. Strong sorption and separate analytical method.
Chlormequat-chloride	Strong sorption and separate analytical method
Triadimenol	Low mobility
Tridemorph	Low mobility. Separate analytical method.
Chlorothalonil	Separate analytical method. Immobile.
Ethephon	Separate analytical method. Fast degradation.
Mepiquat	Strong sorption. Separate analytical method.
Trifluralin	Low mobility. Separate analytical method.
Esfenvalerate	Used in low dosage on fields fully covered with plants. Strong sorption and separate analytical method.
Tau-fluvalinate	High plant coverage and low dosage.
MCPB	Used once 1 year before first sampling.

from the 12th of October 1999 to the 27th of March 2000. In total 64 samples were collected from the three tubes in the field.

Winter wheat was cropped during the whole study period and the field was treated with 12 different pesticides from 1977 to 1999. Nine of these were included in the

TABLE V Crop and pesticide treatments at the Falkerslev site. Findings indicated together with last application of the compound during the study

Crop/Spraying date	*Product*	*Active ingredient (a.i.)*	*Dose (a.i.)* g/ha	*Pesticide findings n/N*[a] (*Max. conc.*)
Winter wheat (Ritmo). Sowing: 970924. Harvest: 980816				
980428	Express	Tribenuron-methyl	11.2	
980428	Starane 180	Fluroxypyr*	90	
980428	Rival	Fenpropimorph*	187.5	
		Prochloraz*	112.5	
980428	CCC	Chlormequat-chloride	350	
980612	Amistar	Azoxystrobin*	70	
980612	Tilt Mega	Fenpropimorph*	56.3	
		Propiconazole*	19	17/64 (0.045 μg/L)
980612	Cypermetrin	Cypermethrin	12	
980612	Starane	Fluroxypyr*	72	
Winter wheat (Ritmo). Sowing: 980929. Harvest: 1999				
990429	Express	Tribenuron-methyl	11.2	
990429	Starane 180	Fluroxypyr*	72	3/64 (1.2 μg/L)
990429	Corbel	Fenpropimorph*	187.5	
990521	Corbel	Fenpropimorph*	150	29/64[b] (0.33 μg/L)
990615	Amistar	Azoxystrobin*	62.5	4/64 (0.024 μg/L)
Winter wheat (Ritmo). Sowing: 990927. Harvest: 2000				
991011	IPU	Isoproturon*	500	24/64 (2.6 μg/L)
991011	Stomp	Pendimethalin*	400	8/64 (0.36 μg/L)
991011	Express	Tribenuron-methyl	3	

*Included in the analyses.
[a]*n/N*: Finding/samples analysed.
[b]Findings as fenpropimorphic acid.

analyses (Table V) and six of them were detected in the soil water. Isoproturon and fluroxypyr occurred in concentrations above 1 μg/L, while pendimethalin and fenpropimorphic acid occurred in levels above 0.1 μg/L. Two of the pesticides not detected had not been applied in 1998 and 1999, where the water samples were collected. Figure 3 displays date of application and findings of isoproturon in the three tubes. The variation among the tubes is high as a result of the heterogeneity in the field soil.

Gyldenholm

First year sampling was conducted the 23rd of October 1998 and with fortnight intervals until the 26th of March 1999. The extension tubes were removed and the tubes were covered. Second year sampling was started the 11th October 1999 and went on until the 27th of March 2000. In total, 67 soil water samples were analysed from the three tubes in the field.

From 1995 to 1999 the field was treated with 20 different pesticides (cf. Table VI) and the water samples were analysed for nine of these. Four pesticides were detected and isoproturon occurred in concentrations above 1 μg/L, while pendimethalin exceeded 0.1 μg/L.

Napropamide occurred in one sample which was collected 1 year after the last application. Carbendazim, kresoxim-methyl and tebuconazol were not detected as well as ioxynil and mecoprop, which have not been used on the field since 1995.

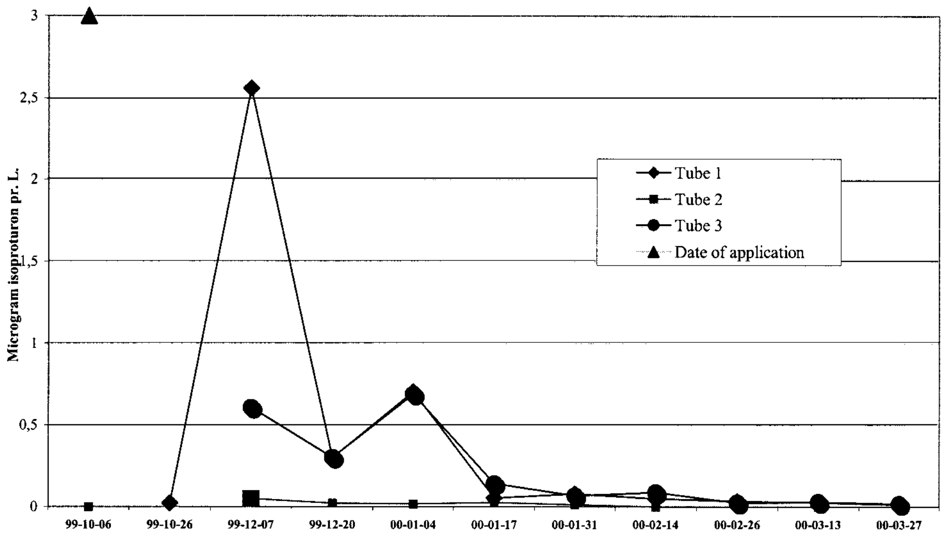

FIGURE 3 Applications and findings of the pesticide isoproturon at the Falkerslev site. Variation among three sampling tubes.

TABLE VI Crop and pesticide treatments at the Gyldenholm site. Findings indicated together with last pesticide application during the study

Crop/Spraying date	*Product*	*Active ingredient (a.i.)*	*Dose (a.i.) g/ha*	*Pesticide findings n/N*[a] *(Max. conc.)*
Winter rape. Sowing: 970814. Harvest: 980803				
970814	Devrinol Combi	Napropamide*	570	1/67 (0.018 μg/L)
		Trifluralin	720	
970915	Sumi-Alfa	Esfenvalerate	10	
980511	Sumi-Alfa	Esfenvalerate	15	
	Derosal	Carbendazim*	361	
Winter wheat. Sowing: 980913. Harvest: 990825				
981004	Stomp	Pendimethalin*	500	
	Tolkan	Isoproturon*	500	
990503	CCC	Chlormequat-chloride	700	
	Mentor	Kresoximmethyl*	30	
		Fenpropimorph*	60	
990615	Amistar	Azoxystrobin*	87.5	
	Folicur	Tebuconazole*	25	
	Mavrik	Tau-fluvalinate	16.8	
Winter wheat				
991006	Arelon	Isoproturon*	625	21/67 (1.3 μg/L)
	Stomp	Pendimethalin*	625	16/67 (0.40 μg/L)

*Included in the analyses.
[a]*n/N*: Finding/samples analysed.

Figure 4 displays treatments and findings of isoproturon in the soil water from Gyldenholm.

Figure 5 displays treatments and findings of pendimethalin in the soil water from Gyldenholm with variations among sampling tubes. The patterns of isoproturon and pendimethalin are the same, but pendimethalin appears at a lower concentration level.

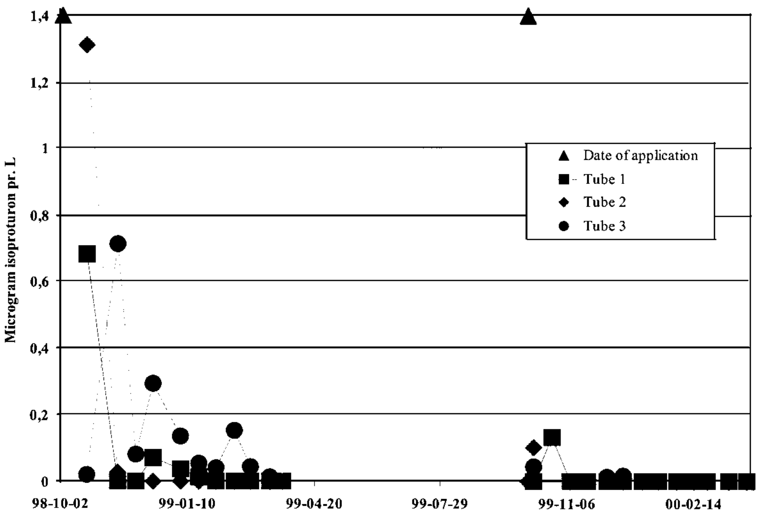

FIGURE 4 Applications and findings of the pesticide isoproturon at the Gyldenholm site. Variation among three sampling tubes.

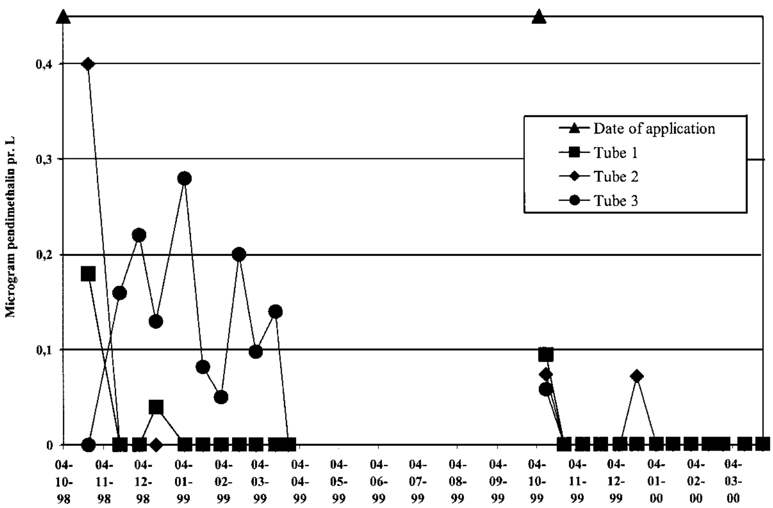

FIGURE 5 Applications and findings of the pesticide pendimethalin at the Gyldenholm site. Variation among three sampling tubes.

Silstrup, Field 22

Sampling of drainage water was started the 9th of November 1998 and went on with fortnight intervals until the 27th of March 2000. On a couple of occasions in August and September 1999 no drainage water was produced. In total 37 samples were analysed from this field.

Eight different pesticides were used in the period from 1997 to 1999. Four were included in the analyses (Table VII). Pendimethalin, which was applied to the field in spring, was not detected here, in contrast to the Falkerslev and Gyldenholm sites,

TABLE VII Crop and pesticide treatments at the Silstrup field 22. Findings indicated together with last pesticide application during the study

Crop/Spraying date	*Product*	*Active ingredient (a.i.)*	*Dose (a.i.)* g/ha	*Pesticide findings n/N*[a] (*Max. conc.*)
Spring barley (Bartok). Sowing: 980401.				
980518	Express	Tribenuron-methyl	3.75	
Pea (Agadir). Sowing: 990421				
990526	Stomp SC	Pendimethalin*	300	
990526	Basagran MCPA	Bentazone*	125	18/37 (1.3 µg/L)
		MCPA*	37.5	
990806	Round-up	Glyphosate	720	
Lucerne (Daisy). Sowing: 990818				
991111	Kerb	Propyzamide*	400	9/37 (2.8 µg/L)

*Included in the analyses.
[a]*n/N*: Finding/samples analysed.

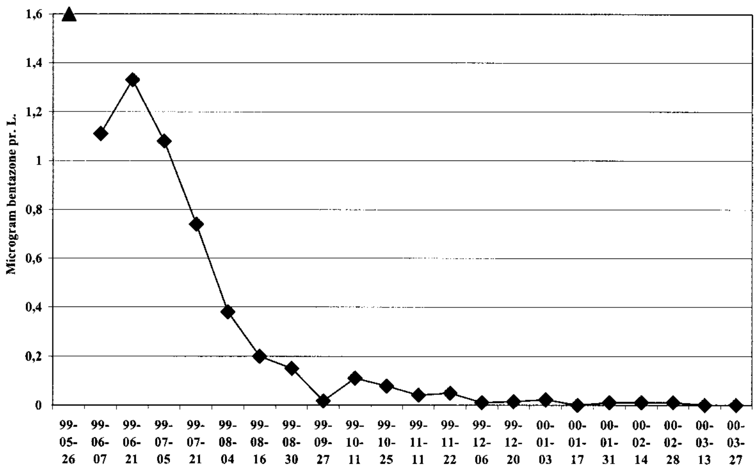

FIGURE 6 Occurrence of bentazone in the drainage water from Silstrup field 22 after spraying with Basagran May 26, 1999.

where it was applied in the autumn and detected on both locations. Bentazone, in contrast to pendimethalin, which was applied on the same date, appeared in the drainage water 12 days after spraying in 1.1 µg/L concentration. Bentazone remained in the drainage water until February in the next year, see Fig. 6.

The phenoxyacid MCPA, which was applied together with bentazone was not detected in the drainage water.

The Field was sprayed with 400 g propyzamide per hectare the 11th of November 1999. Propyzamide was detected the 22nd of November (0.09 µg/L) and the maximum level was detected the 6th of December (2.8 µg/L). The compound was detected in the drainage water in the rest of the study period (Fig. 7).

In two samples traces of mecoprop were detected despite no use of the herbicide during the period of investigation.

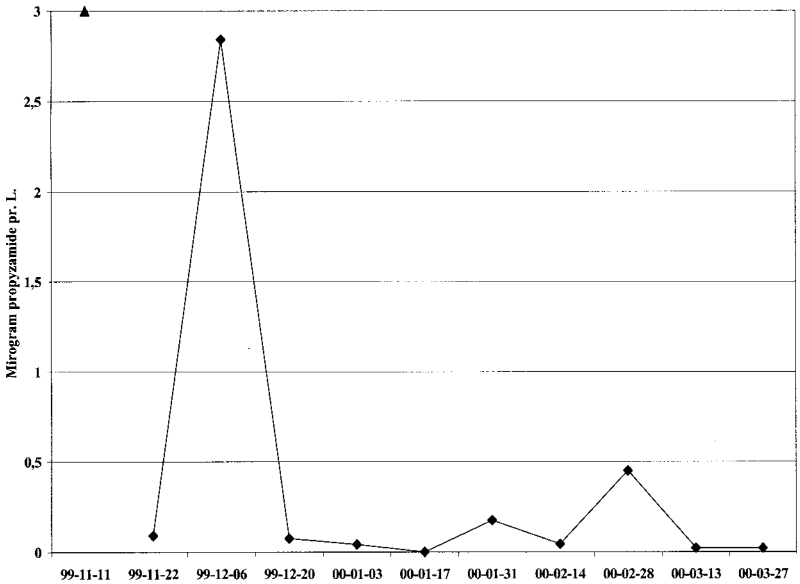

FIGURE 7 Occurrence of propyzamide in the drainage water from Silstrup field 22 after spraying with Kerb November 11, 1999.

TABLE VIII Crop and pesticide treatments at the Silstrup field 23. Findings indicated together with last pesticide application during the study

Crop/Spraying date	*Product*	*Active ingredient (a.i.)*	*Dose (a.i.)* g/ha	*Pesticide findings* n/N^a *(Max. conc.)*
Winter wheat (Ritmo). Sowing: 970923. Harvest: 980902				
971021	IPU	Isoproturon*	500	
971021	Stomp	Pendimethalin*	600	
980529	Bravo	Chlorothalonil	?	
980529	Tilt EC	Propiconazole*	25	
980619	Tilt Top	Propiconazole*	62.5	
		Fenpropimorph*	187.5	$3/32^b$ (0.026 μg/L)
Winter wheat (Ritmo). Sowing: 981005. Harvest: 990825. Stubble harrowing 990831 and 991022				
990420	Express	Tribenuron-methyl	4.7	
990420	Oxitril	Ioxynil*	80	
		Bromoxynil*	80	
990625	Express	Tribenuron-methyl	3.8	
990805	Round-up	Glyphosate	720	

*Included in the analyses.
[a]*n/N*: Finding/samples analysed.
[b]Findings as fenpropimorph or fenpropimorphic acid.

Silstrup, Field 23

Sampling of drainage water was started the 9th of November 1998 and went on with fortnight intervals until the 27th of March 2000. On a couple of occasions in August and September 1999, no drainage water was produced. In total 32 samples were analysed from this field.

The field was treated with nine different pesticides during the years 1997, 1998 and 1999. Six of these have been analysed in this study (see Table VIII).

Isoproturon was detected in only one sample 1 year after application. The fungicide fenpropimorph and the degradation product fenpropimorphic acid were each detected once. Propiconazole, ioxynil and bromoxynil were not detected in any of the samples. Surprisingly, bentazone and propyzamide, which were used solely on field 22, appeared in the drainage water from field 23 – in lower concentrations. However, a thorough study of the drainage map showed that one drainage string from field 22 ran to the drainage well from field 23 and that was the explanation for the occurrence of the pesticides in both drainage wells.

CONCLUSIONS

During two winter seasons, 1998/99 and 1999/2000, drainage water was sampled each fortnight from four fields with recorded pesticide application. The soil water was analysed for a range of pesticides which have been used on the fields. Two of the fields, Gyldenholm and Falkerslev in Zealand and Falster were each equipped with three vertical stainless steel tubes with screens in 1–1.3 m depths. Two fields at the research station Silstrup in Northern Jutland were equipped with traditional tile drains installed in 1966, which solely drained the specific fields. In total 200 water samples were analysed in the study.

Isoproturon, not allowed for use in Denmark after 1999, was the most frequently found pesticide in the drainage water. Pendimethalin was another compound frequently found, however in lower concentration. Both pesticides were primarily used for autumn application.

In drainage water from a field at Silstrup, the active ingredient bentazone, applied in May and propyzamide applied in November appeared in the drainage water at the next sampling following treatment and during the following months. The highest concentration levels were 1.3 and 2.8 μg/L, respectively.

Phenoxyacid herbicides, which were detected at concentration levels up to 0.34 μg/L in an earlier study 10 years ago, no longer appeared in the drainage water after use has been restricted since 1997. Ioxynil, bromoxynil, carbendazim, kresoxim-methyl, MCPA, tebuconazole and prochloraz, which were applied to the fields and the degradation product hydroxy-bentazone, were not detected in any of the samples.

It is concluded from the study that autumn application of pesticides might possess a risk for leaching to drain water. Furthermore, mobile degradation products have to be taken into consideration when the mobility and risk for ground water contamination of pesticides is assessed. The present study indicates that isoproturon might cause leaching problems and this study has further demonstrated leaching of bentazone and propyzamide with considerable concentrations in the drainage water. Future studies might further elucidate the risk for ground water contamination with these substances.

Acknowledgements

The project was supported by the Danish Ministry of Food, Agriculture and Fisheries. The author wishes to thank Hanne Baek for skilful sampling and chemical analysis and Lars Stenvang Hansen is thanked for valuable comments during planning and performance of the study.

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