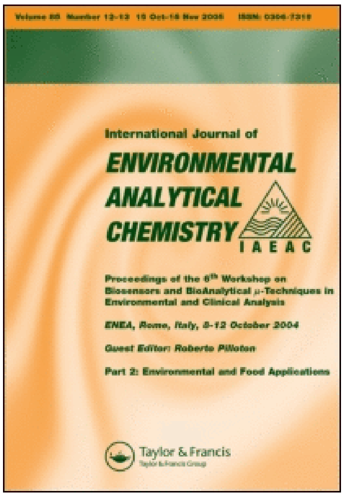

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

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To cite this Article Tsiropoulos, Nicholas G. and Lolas, Peter C.(2004) 'Persistence of pendimethalin in cotton fields under sprinkler or drip irrigation in central Greece', International Journal of Environmental Analytical Chemistry, 84: 1, 199 — 205

To link to this Article: DOI: 10.1080/0306731031000149714

URL: http://dx.doi.org/10.1080/0306731031000149714

Intern. J. Environ. Anal. Chem.
Vol. 84, No. 1–3, pp. 199–205, January–March 2004

PERSISTENCE OF PENDIMETHALIN IN COTTON FIELDS UNDER SPRINKLER OR DRIP IRRIGATION IN CENTRAL GREECE

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(Revised 29 September 2002; In final form 3 April 2003)

The dissipation of pendimethalin was investigated in soils of cotton fields in Thessaly, central Greece, for a period of two years. The fields were irrigated either with sprinkler or with sprinkler for the first two irrigations plus drip for the rest of the experimental period. Pendimethalin was applied at rates of 1.1, 1.32, and 0.96 kg a.i./ha in a clay loam soil at Rizomylos, a clay soil at Kypseli, and a sandy clay loam soil at Karditsa, respectively. Residues were determined with capillary GC-NPD after ethyl acetate extraction. Recovery of pendimethalin from spiked soils was 82–101% with a repeatability of 2–7%, and the limit of quantification was near 0.04 mg/kg. At 150 days after application (DAA) pendimethalin residues found in the soils were 10–18% of the initial measured concentrations. For the drip-irrigated fields, dissipation of pendimethalin varied within the field between the non-irrigated and the irrigated soil regions, indicating a more rapid loss in the irrigated part of the soil. Residues in the wet region (along the drip irrigation line) at 150 DAA were about 75 and 60% of those measured in the dry region (off the irrigation line) of the soil at the Kypseli field for the 1996 and 1997 season, respectively. At the Rizomylos field the corresponding percentage was about 70%, for the 1997 season. The half-life, calculated from the first-order kinetics dissipation equation, was estimated at between 43 and 62 days. No leaching of pendimethalin was observed below 10 cm during the experimental period of 230 days under cotton growing conditions in Thessalian fields.

Keywords: Pendimethalin; Dissipation; Residues; Soil moisture; Cotton

INTRODUCTION

Pendimethalin is the common name of [*N*-(1-ethylpropyl)-2,6-dinitro-3,4-xylidine], a dinitroaniline herbicide used for selective control of many annual grasses and broad-leaved weeds in several crops; it is adsorbed by the roots, and it inhibits cell division and cell elongation [1]. Pendimethalin is registered in all European Union countries and in Greece is approved for use in various vegetable crops, in tobacco (*Nicotiana tabacum L*), winter wheat (*Triticum aestivum L*), and also in cotton (*Gossypium hirsutum L*), which is the major agronomic crop in Thessaly in Central Greece.

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ISSN 0306-7319 print: ISSN 1029-0397 online
DOI: 10.1080/0306731031000149714

Pendimethalin in cotton can be applied preplant incorporated or preemergence with incorporation by irrigation because it has a relatively low vapour pressure. After Walker and Bond [2], pendimethalin is more persistent when incorporated than when applied to the soil surface. Laboratory and field studies indicated that pendimethalin is strongly adsorbed to soil colloids [3], not significantly leached [3,4], and persistent, with residues being carried over to the next crop year [2,4,5]. A certain persistence of herbicides in soil is needed for efficient control of weeds. However, long-term persistence of a herbicide may increase the risk of environmental contamination and toxicity to the following crop. Persistence of herbicides in general is influenced by a number of factors, including molecular properties and environmental conditions such as soil type, temperature, moisture, and cultural practices [6,7].

Several papers report degradation and persistence of pendimethalin in soils [4,5,8–12], its degradation under various soil moisture conditions and microbial activity [12,13] in experiments carried out in the laboratory and in the field. Very few data have been published about pendimethalin behaviour in soils in Greece [14,15] and especially in cotton fields. Degradation of pendimethalin, like other dinitroanilines, [12,13] proceeds more rapidly under anaerobic than aerobic conditions. The present two-year study investigated the dissipation and persistence of pendimethalin in cotton fields under the conditions of three soil types and two irrigation techniques.

EXPERIMENTAL

Field Trials

Three cotton fields were selected in the cotton cropped area in Thessaly. One field was located at Rizomylos (in the south-east part of Thessaly) and was an alkaline clayloam (CL) type soil (pH = 8.1, clay 38.0%, sand 31.3%, silt 30.7%, Organic Matter (O.M) 2.80%, and electrical conductivity 0.377 mS/cm). The second field was located at Kypseli (in the east part of Thessaly) on an alkaline clay (C) type soil (pH = 8.0, clay 52.0%, sand 28.6%, silt 19.4%, O.M. 1.99%, and electrical conductivity 0.281 mS/cm) and the third near Karditsa (in the west central part of Thessaly) on a sandy clay loam (SCL) type soil (pH = 7.7, clay 35.3%, sand 52.6%, silt 12.1%, O.M. 1.84%). The selected fields had two or more years of pendimethalin-free history. The year before the commencement of the experiment cotton was planted at the Rizomylos and Kypseli fields whereas winter wheat was planted at Karditsa.

In each field and for each year an area of about 0.1 ha (12×80 m) was marked out and within this area three randomised plots (200 cm^2 each) were used as replicates and one as a control plot.

Herbicides were applied as a water solution of the commercial EC formulation Stomp® 330E (33% w/v) at a rate of 1.1 kg a.i./ha at Rizomylos (19 April 1996 and 21 April 1997), 1.32 kg a.i./ha at Kypseli (20 April 1996 and 21 April 1997) and 0.96 kg a.i./ha at Karditsa (27 April 1997) with a conventional tractor-mounted boom sprayer. During the application, the weather was calm, sunny in Rizomylos and Kypseli and cloudy in Karditsa. In Rizomylos and Kypseli incorporation of pendimethalin in soil was done by irrigation in the days after application while in Karditsa incorporation was due to rainfall following the days after application.

The fields were ploughed early in the winter to a depth of about 20 cm and were disked and harrowed before herbicide application. In all five fields cotton was sown in rows 90 cm apart and received all the usual cultural practices.

Two irrigation techniques were used in this study. More specifically, the Kypseli (during 1996 and 1997) and Rizomylos (during 1997) fields were sprinkler irrigated for the first two irrigations and by drip for the rest of the experimental period. The Karditsa field in 1997 and Rizomylos in 1996 were sprinkler irrigated for the whole experimental period.

Meteorological data were provided by a Larissa-based station 30 and 40 km from Kypseli and Rizomylos, respectively. The average minimum/maximum daily air temperatures were 12.7/26.3°C, 15.6/30.6°C, 17.6/31.6°C, 17.9/31.3°C, and 13.6/25.6°C during the experimental period in 1996 and 11.1/26.5°C, 16.9/31.7°C, 19.0/33.0°C, 17.3/29.8°C, and 12.7/25.8°C during the experimental period in 1997 for May, June, July, August, and September, respectively. At Karditsa the average minimum/maximum daily air temperatures were 12.4/29.0°C, 17.0/34.3°C, 18.7/35.8°C, 16.6/32.5°C, and 12.6/28.8°C for May, June, July, August, and September 1997, respectively.

Soil Sampling

Soil samples were taken at 0 (five hours after application), 10, 20, 40, 60, 90, 120, 150, and about 230 days after application (DAA) by combining six random cores (8 cm diameter) from 0 to 10 cm depth in each plot. Samples were also taken from control plots before application, after application, and at several times during the experimental period. Soil samples from 10 to 20 cm soil depths were also taken at 0, 10, 20 (only at Karditsa), 40, 90, 150, and about 230 DAA to determine if leaching of pendimethalin occurred.

In the drip-irrigated fields, beginning at 60 DAA, the sampling procedure was modified. Specifically, two samples were taken from each plot (combining six random cores each), one from along the drip irrigation line and the second outside the irrigation line (about in the middle of the two cotton lines) to evaluate the persistence of pendimethalin in the irrigated and non-irrigated soil.

Soil samples, from the top 0–10 cm depth soil, were also taken about a year after the 1996 application and before the next pesticide application. The fields were ploughed to a depth of about 20 cm and disked before sample collection.

Soil samples from each plot were put in paper bags, taken to the laboratory, air dried under shade, screened through a 2 mm mesh sieve and sampled in duplicate (20 g) prior to extraction or storage (at −20°C).

Analytical Procedure

Soil Extraction

Herbicide residues were extracted from soil by ethyl acetate according to the Sánchez-Brunete *et al.* [16] and García-Valcárcel *et al.* [17] method, with some modifications. Soil samples (20 g) were extracted twice with 90 mL of ethyl acetate by shaking on a wrist action shaker (for 12 h the first time and 2 h the second). Then, the extracts were filtered through Whatman No 1 filter paper and the filter cake washed with additional ethyl acetate. The filtrate was evaporated to dryness, under vacuum, using a rotary evaporator at 40°C. The residue was transferred with ethyl acetate, concentrated to a suitable volume (1–2 mL), and an aliquot was conducted to GC analysis.

Residues Analysis

Residues were determined in a Hewlett-Packard model 6890 gas chromatograph, fitted with a Nitrogen-Phosphorus detector and with a 30 m × 0.32 mm i.d. fused silica capillary column coated with 0.25 μm of phenyl methyl siloxane (HP-5). The following operating conditions were used: carrier gas (He) flow 2 mL/min; injector and detector temperature 260 and 300°C, respectively, detector fuel gases air and hydrogen flow 60 and 4 mL/min, respectively and makeup gas (helium) flow 10 mL/min. All extracts were injected in the pulsed splitless mode (40 psi for 1.0 min), after which the analysis was taken at constant flow mode. The column temperature was maintained at 60°C for 1 min, then programmed to 150°C at 10°C/min, to 165°C at 3°C/min, to 220°C at 10°C/min, to 280°C at 30°C/min and held there for 3 min. The pendimethalin peak was well separated in all samples and no subtract co-eluates or other compounds interfered with its determination. A gas chromatography column HP-35 (30m × 0.25 μm) was used as a confirmatory column.

RESULTS AND DISCUSSION

Determination of Pendimethalin Residues

Determination of pendimethalin residues in samples was done by comparing the area of the pendimethalin peak in the sample chromatogram with the areas of pendimethalin standard solutions chromatograms and quantified using the external standard method. A good linearity of response was obtained in the range 1 to 40 ng of pendimethalin.

The efficiency of the method was checked by spiking control air-dried soil samples from the three fields with pendimethalin at various levels by the addition of a suitable volume of pendimethalin standard solution. After thorough mixing, the spiked soils were equilibrated in the dark at laboratory temperature for eight hours before extraction. Pendimethalin average recovery (Table I) for all soil types varied from 82 to 101% with a relative standard deviation between 2 and 7 showing that the method had good precision and reproducibility. The recoveries were not influenced by the equilibration

TABLE I Mean recovery (average of three replicates for each level) and relative standard deviation (RSD) of pendimethalin from spiked soils at various fortification levels

Field site (soil type)	*Recovery (%) ± RSD*				
	Fortification level (mg/kg)				*Overall mean*
	1.5	*1.0*	*0.50*	*0.10*	
Rizomylos (CL)	90 ± 4	88 ± 5	82 ± 6	85 ± 7	86
Kypseli (C)	91 ± 5	89 ± 4	94 ± 2	85 ± 5	90
Karditsa (SCL)	96 ± 4	101 ± 3	98 ± 5	95 ± 3	97

time of spiked soil samples since no significant difference was observed for the tested equilibration time of 4,8,12 and 24 h prior to extraction.

The limit of quantification of the GC-NPD method for pendimethalin was evaluated conservatively near to 0.04 mg/kg, considering a signal-to-noise ratio equal or higher than 10.

The method used for analysis of pendimethalin residues in soil is simple, needs no clean up, and no solvent partition or solvent exchange. It can also be considered friendly, since ethyl acetate is less harmful than other extraction solvents and distilled (by the rotary evaporator) solvent can be recycled. This method is also used for the determination of other dinitroaniline, acetanilide and triazine herbicide residues in soil [18].

Soil Residues and Dissipation

Results for soil residues and the dissipation of pendimethalin with time in the fields are given in Tables II and III for the 1996 and 1997 studies, respectively.

In either study year, ten days following treatment application, 74 to 86% of the initial deposition was recovered from the upper 10 cm of soil at Rizomylos and Kypseli, respectively. The observed loss of almost 20% is mainly attributed to volatilisation, and photodecomposition during the first days after application, as has been previously reported [4,8]. At the Karditsa field the loss observed in the first twenty days was not of the same extent. This was probably due to the cloudy and rainy weather conditions following treatment application, which prevented photodecomposition and volatilisation. However, a considerable loss (52%) was observed in this field one month later.

In the last ten days of September, at the start of the cotton harvest, pendimethalin residues in all fields varied from 0.09 to 0.20 mg/kg, indicating that about 10 to 18% of the initial deposition persisted 150 days after application. A year after pendimethalin application in 1996, residues accounted for 5% of the initial concentration in the upper 0–10 cm of soil.

TABLE II Pendimethalin residues (mean and standard deviation from three replicates) remaining at 0–10 cm depth in experimental fields at various times after application in 1996

Days after application	*Pendimethalin residues (mg/kg)*		
	Rizomylos	*Kypseli*	
0	0.83 ± 0.12	1.11 ± 0.17	
10	0.72 ± 0.19	0.85 ± 0.11	
20	0.51 ± 0.15	0.64 ± 0.16	
40	0.46 ± 0.06	0.63 ± 0.18	
		On the line[a]	Off the line[a]
60	0.23 ± 0.08	0.47 ± 0.03	0.49 ± 0.04
90	0.25 ± 0.04	0.27 ± 0.06	0.32 ± 0.06
120	0.13 ± 0.03	0.17 ± 0.02	0.23 ± 0.04
150	0.11 ± 0.02	0.15 ± 0.02	0.20 ± 0.02
230	0.09 ± 0.03	0.13 ± 0.03	0.16 ± 0.04
350	0.04 ± 0.01[b]		

[a]"On the line" and "Off the line" indicate soil sampling from the irrigated and non-irrigated regions, respectively; [b]Soil sampling after fields ploughed and disked.

TABLE III Pendimethalin residues (mean and standard deviation from three replicates) remaining at 0–10 cm depth in experimental fields at various times after application in 1997

Days after application	*Pendimethalin residues* (mg/kg)				
	Rizomylos		*Kypseli*		*Karditsa*
0	0.89 ± 0.16		1.08 ± 0.18		0.73 ± 0.17
10	0.69 ± 0.09		0.80 ± 0.12		–
20	0.41 ± 0.11		0.67 ± 0.10		0.68 ± 0.12
40	0.52 ± 0.09		0.63 ± 0.12		0.33 ± 0.12
	On the line[a]	Off the line[a]	On the line[a]	Off the line[a]	
60	0.29 ± 0.08	0.32 ± 0.05	0.33 ± 0.03	0.38 ± 0.04	0.36 ± 0.06
90	0.17 ± 0.02	0.25 ± 0.05	0.18 ± 0.02	0.28 ± 0.02	0.17 ± 0.02
120	0.14 ± 0.01	0.20 ± 0.03	0.13 ± 0.03	0.23 ± 0.04	0.14 ± 0.01
150	0.09 ± 0.01	0.13 ± 0.02	0.11 ± 0.01	0.18 ± 0.04	0.12 ± 0.02
230	0.07 ± 0.02	0.08 ± 0.02	0.10 ± 0.02	0.13 ± 0.02	0.09 ± 0.03

[a]"On the line" and "Off the line" indicate soil sampling from the irrigated and non-irrigated regions, respectively.

In drip-irrigated fields, pendimethalin residues 150 DAA were different between irrigated and non-irrigated (dry) regions of the fields; at Kypseli, residues in the irrigated regions were about 61% and 75% of those in the dry regions in 1996 and 1997, respectively, while at Rizomylos the corresponding percentage was about 69% in 1997.

For the drip-irrigated fields, pendimethalin residues on and off the irrigation lines, from 60 to 150 DAA, were compared by Two-Way ANOVA (sampling region and time). Pendimethalin dissipated significantly faster ($P < 0.05$ with F values 7.315 and 42.050 for Kypseli in 1996 and 1997, respectively, and 12.202 for Rizomylos in 1997) in the irrigated regions (sampling on the irrigation line) compared with the non-irrigated or dry regions (sampling off the irrigation line). This effect may be attributed to the faster microbial breakdown of pendimethalin in the wet regions of soil along the drip line, since soil moisture is one of the environmental factors affecting herbicide degradation [12,13] through its effect on microbial populations and by decreasing herbicide sorption on soil colloids.

The half-life ($t_{1/2}$) of pendimethalin in the experimental soils was calculated (from the relationship $t_{1/2} = \ln 2/k$) assuming that dissipation follows first-order kinetics for the investigation period of 150 days. The first-order constant k was derived from the slopes of the linear regression of the logarithm of concentration against the time, assuming the linear relationship $\ln C = \ln C_0 - kt$, where C_0 is the initial concentration and k is the rate constant. In all cases degradation followed first-order kinetics (with correlation coefficients $r > 0.964$).

For the 1997 season, the half-life was estimated to approximately 43 and 48 days for the region along the drip line (wet region) and 58 and 60 days for the region outside the drip line (dry region) in the plots at Kypseli and Rizomylos fields, respectively. In the sprinkler-irrigated field of Karditsa the half-life was approximately 52 days. For the 1996 season, pendimethalin half-life was estimated at 51 days at Rizomylos field while at Kypseli field it was 52 and 62 days for the irrigated and non-irrigated regions, respectively. The estimated half-life values of pendimethalin degradation are in agreement with those reported for field soils by other investigators [5,7,15].

Considering the half-lives of pendimethalin in the three fields of this study for both years, it appears that there is no relationship between half-life and soil type (clay content, percentage O.M.). The half-life of pendimethalin at Rizomylos and Kypseli fields varied mainly between the dry and the wet soil regions indicating a more rapid loss in the wet part of the soil. It seems that, in this study, the soil moisture rather than the soil type was the more important factor influencing the degradation of pendimethalin. The same conclusion is also reported by Zimdahl *et al.* [5], who observed that pendimethalin degradation was affected more by temperature and moisture than by soil type.

Pendimethalin residues in soils from 10 to 20 cm depths were found below the quantification limit of 0.04 mg/kg for all seven samplings at all the studied sites, indicating that there was no leaching of the herbicide below 10 cm during the experimental period of 230 days. These results are in accordance with previous observations [3,4,6,7] suggesting that pendimethalin is a non-leachable compound.

CONCLUSIONS

The results obtained in this study show that residues of pendimethalin, following application in cotton drip-irrigated fields, were more persistent in the non-irrigated than in the irrigated regions of the soil. This indicates that at nearly the same temperatures the effect of soil moisture content is more important than the soil type in pendimethalin degradation. Between 10 and 18% of the measured initial concentration of pendimethalin was found to persist in the soil of the Thessalian cotton fields at harvest time, about five months after the pendimethalin application, while 5% was recovered in the ploughed soil one year after application. Pendimethalin was not leached below 10 cm under cotton growing conditions in Thessalian fields.

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