

Field Persistence Studies on Pendimethalin Residues in Onions and Soil after Herbicide Postemergence Application in Onion Cultivation

Nicholas G. Tsiropoulos*[†] and George E. Miliadis[‡]

Department of Theoretical and Applied Sciences, University of Thessaly, Pedion Areos, Volos 38334, Greece, and Benaki Phytopathological Institute, 7 Ekalis Street, Kifissia 14561, Greece

Field studies were undertaken to evaluate the fate of pendimethalin residues in spring and dry onions, after postemergence application of the herbicide in a clay soil onion planting in central Greece, at rates of 1.32 and 2.0 kg of active ingredient (ai)/ha. Residues were determined with capillary GC-ECD after onion extraction with 2-propanol/toluene and extract cleanup in a AgNO₃-coated alumina column; the recovery of pendimethalin from spiked onions was found to be 82–99% and the limit of determination 0.007 mg/kg. Pendimethalin residues were found to decline rapidly, and it was estimated that 7 days after the treatment only half of the initial concentrations remained for both the low recommended dose (LRD) and the high recommended dose (HRD) experiments. In all cases the residues in dry bulb onion were well below the lowest maximum residue limit (MRL) set by European countries, which is 0.05 mg/kg. Residues in spring onions at harvest time were also below this level when treated at the LRD and were only slightly above in case of the HRD. The pendimethalin concentration in planting soil for the investigated period declined with half-lives of 37 and 39 days for the LRD and the HRD experiments, respectively.

Keywords: *Pendimethalin; residues; dissipation; onion; soil; GC-ECD*

INTRODUCTION

Pendimethalin is the common name of *N*-(1-ethylpropyl)-2,6-dinitro-3,4-xylidine, a dinitroaniline herbicide used for selective control of most annual grasses and many annual broad-leaved weeds in several crops; it is adsorbed by the roots and leaves, and it inhibits cell division and cell elongation (British Crop Protection Council, 1994). Pendimethalin has approved uses in all countries of the European Union. In Greece it is applied in cotton (*Gossypium hirsutum* L.), tobacco (*Nicotiana tabacum*), and winter wheat (*Triticum aestivum* L.) crops and also in vegetable crops, mainly in onions and garlic cultivations. The onion (*Allium cepa*) cultivation, intended for consumption as spring onions or dry bulbs, is a dynamic cultivation (the third in surface cultivation of vegetables in Greece), and it has good prospectives of additional development.

The postemergence application of pendimethalin in onion planting for weed control is recommended to take place only in the onion from seed, and the normal application time is at the growth state of the first leaf. No maximum residue limits (MRLs) have been set by the European Union for this nonsystemic herbicide in onions or generally in vegetables. Different MRLs have been set by some European countries for pendimethalin in vegetables, e.g. 0.1 mg/kg in Germany and 0.15 mg/kg in Switzerland, and in onions, e.g. 0.05 mg/kg in Italy

and Holland. No preharvest application interval (PHI) exists within the European Union for pendimethalin application in onion planting.

Persistence of pendimethalin in soil is influenced by cultivation practices, soil temperature, moisture conditions, and soil type; photodecomposition can occur, especially during the first days of exposure on the soil surface (Zimdahl et al., 1984; Savage and Jordan, 1980; Walker and Bond, 1977). Field studies indicate that the herbicide is persistent and not leaching (Smith et al., 1995). In plants, the 4-methyl group on the benzene ring is oxidized to the carboxylic acid via the alcohol; the amino nitrogen is also oxidized (British Crop Protection Council, 1994). Pendimethalin residues in onions have been studied in transplanting onion cultivation in India (Sharma and Mehta, 1989). Information concerning the persistence of residues of this herbicide in onion plants is lacking, as is information concerning pendimethalin residues in onions cultivated in Europe. The objective of this study was therefore to obtain data on the levels of deposits, on the disappearance rates of pendimethalin residues in onion plants, and on the levels of the residues at harvest time of spring onion and dry onion (the onion bulb) as well. For a better study of the persistence and the behavior of pendimethalin, we examined the partition of pendimethalin in the aboveground part of onion plant (the leaves), which receives the applied active compound, and in the underground part of the plant (the bulb), which communicates with the sink of pendimethalin (i.e. the soil solution). This study includes also additional evaluation of the persistence and the residues levels of pendimethalin in the onion planting soil.

* Author to whom correspondence should be addressed (telephone (+30)42169781-4; fax (+30)42163383, (+30)42163544).

[†] University of Thessaly.

[‡] Benaki Phytopathological Institute.

Table 1. Characteristics of Soil in the Studied Onion Planting

soil type	clay (%)	silt (%)	sand (%)	organic matter (%)	pH	conductivity (mS/cm)
clay	44	28	28	2.3	7.9	0.4

MATERIALS AND METHODS

Chemicals. (a) Analytical standard of pendimethalin was obtained from Chem Service.

(b) The commercial EC formulation Stomp 330E (Lapapharm S.A., Greece), containing 330 g L⁻¹, was used for the field application.

(c) All solvents used were of pesticide residue grade and purchased from Lab-Scan.

(d) The anhydrous granulated sodium sulfate was purchased from Merck (for organic trace analysis). Before use, it was heated at 500 °C for 3 h.

(e) The alumina (type WB-5, basic, activity super I) was purchased from Sigma. The preparation for the cleanup by column chromatography requires a silver nitrate coating of the alumina; a water/acetone solution of AgNO₃ (0.75 g of AgNO₃ in 0.7 mL of H₂O plus 3 mL of acetone) was well mixed with 10 g of alumina, which was deactivated with 5% H₂O (w/w) water, and then the acetone was removed in a rotary evaporator. The silver nitrate coated alumina mixture was kept in darkness for 1 week.

Field Experiment. The field experiment was carried out in an onion planting at Rizomylos near Volos, Thessalia, in central Greece. The physical characteristics of the soil are summarized in Table 1. The field was plowed early in the winter to a depth of 20 cm, and it was disked and harrowed before seeding with onion seed of the Goldmine variety in the first days of March 1996. Seeding was performed in rows, spaced 45 cm from each other, at a seed rate of 1 kg of seed per stremma with simultaneous fertilization with 20 kg per stremma base fertilizer. In the previous season (1995) the field had been seeded with cotton and ethalfuralin and prometryn were applied at the recommended rates for weed control. The experimental area comprised two plots of 20 × 40 m and one other of 20 × 20 m to be used as a control plot. One of the treated plots was sprayed with Stomp at the low recommended dose (LRD), i.e., 1.32 kg of active ingredient (ai)/ha, and the other at the high recommended dose (HRD), i.e., 2.0 kg of ai/ha. Application was performed on June 1 with a conventional motor sprayer with a 12-m boom that had 24 flat-spray nozzles. During application favorable weather conditions prevailed (e.g. temperature ~24 °C, relative humidity 48%, wind velocity <1.0 m s⁻¹), while the field surface was weed-free, and the onion plants were at the growth stage of two to three true leaves.

Immediately following application, the onion planting was irrigated for 2 h by 38 m³ of water per stremma with a sprinkler irrigation system, and thereafter the field was routinely irrigated for 2 or 3 h weekly. The average minimum/maximum daily air temperatures during the experimental period were 16.0/31.8 °C for June, 17.8/32.8 °C for July, 18.1/32.2 °C for August, and 14.4/26.3 °C for September. The mean soil temperature (at 5-cm depth) was 24.9 °C for June, 30.0 °C for July, 28.7 °C for August, and 22.0 °C for September. There was no important rainfall during the experimental period.

Soil Sampling and Processing. Soil was sampled 0, 7, 14, 21, 35, 49, 63, 77, 91, and 119 days after treatment, by collecting three samples from each plot. Each sample consisted of six cores randomly taken from 0–10-cm depths. Samples were similarly taken from the control plot. The soil samples were air-dried, sieved with a 2-mm screen, and sampled in duplicate (20 g) prior to extraction or storage (at -20 °C).

Onion Sampling and Processing. Sampling was performed by taking two 2-kg samples, by randomly collecting plants from various places of each plot, according to the FAO/WHO (1986) recommendations. For the first two samplings only one sample was taken, by collecting from various places of each plot. The first sampling took place after the irrigation

following the herbicide application, considering that as the initial deposit (0 days) of the herbicide. Onion samples were also taken 7, 14, 21, 28, 35, 42, 49, 63, 77, and 91 days following application, to study the dissipation of the herbicide. The commercial harvest for the spring onions took place on June 29th, that is ~28 days after application, and for the dry bulbs from the 17th until the 31st of August, that is 77–91 days after application.

To study the partition of the herbicide in the different parts of the plant and the evolution of the residues in those, we separated the plant into the underground part, i.e., the bulb, and the aboveground part (named in this work the leaves) for the samples taken 21, 28, 35, 42, and 49 days after application. For the samples taken before the 21st day the bulbs were of small size and we therefore studied the whole onion plant; for the samples taken after the 49th day, we studied only the bulb, because the foliage was almost dry. The bulbs were separated by cutting the leaves 1 cm above the bulb. The roots were removed and discarded. The plant, and particularly the bulb, was rubbed gently by hand with a paper, to remove any adhering soil. The total onion sample was then chopped and blended and sampled in duplicate (50 g), prior to storage at -20 °C.

Analytical Procedure. (a) *Plant Sample Extraction and Cleanup.* All plant samples were analyzed according to a general method suitable for electron captive compounds (Ministry of Welfare, Health and Cultural Affairs, 1988), properly modified. According to the method, 50 g of the homogenized sample was mixed with 100 mL of toluene and 50 mL of 2-propanol and blended for 3 min. After the solids settled, the supernatant liquid was transferred into a separatory funnel and washed gently with 2 × 250 mL of 2% Na₂SO₄ solution. The organic extract was filtered through anhydrous Na₂SO₄, and a 10-mL portion of the filtrate was evaporated to dryness in a rotary evaporator under vacuum at 40 °C. The residue was dissolved in 5 mL of *n*-hexane and cleaned up in a silver nitrate coated alumina column. The 1-cm i.d. column contained 2 g of the coated alumina and 1 cm of anhydrous sodium sulfate on the top. After the *n*-hexane solution was added onto the column, pendimethalin was eluted with 15 mL of *n*-hexane. The eluate was evaporated to dryness under vacuum, and the residue was taken up in a 1-mL volumetric flask with *n*-hexane, ready for gas chromatographic analysis.

(b) *Soil Sample Extraction.* Soil extraction of pendimethalin residues was performed by ethyl acetate, as described by Sánchez-Brunete et al. (1994). The 20-g soil samples were extracted with 100 mL of ethyl acetate by shaking on a wrist action shaker for 1 h, and then the extract was centrifuged. The soil was reextracted and centrifuged as above. The supernatants were filtered through Whatman no. 1 filter paper, and the filter was washed with additional ethyl acetate. The filtrate was evaporated to dryness, under vacuum, using a rotary evaporator (40 °C). The residue was dissolved with a suitable volume of ethyl acetate, and an aliquot was analyzed by gas chromatography.

(c) *Gas Chromatographic Analysis.* A Hewlett-Packard model 6890 gas chromatograph, equipped with a Ni-63 electron capture detector and with a 30 m × 0.32 mm i.d. fused silica capillary column coated with 0.25 μm of 5% phenyl methyl siloxane (HP-5), was used for the determination of the herbicide. The following operating conditions were used: carrier gas (helium) flow at 2.8 mL min⁻¹; makeup gas (nitrogen) flow at 30 mL min⁻¹; injector temperature at 270 °C; detector temperature at 300 °C.

All samples (2 μL) were injected with the injector in the pulsed splitless mode (40 psi for 1.0 min) and after the analysis was taken at constant flow. The oven temperature program used was as follows: 60 °C (1 min) to 150 °C at 10 °C min⁻¹, to 180 °C (0 min) at 3 °C min⁻¹, to 205 °C (2 min) at 10 °C min⁻¹, to 260 °C (8 min) at 30 °C min⁻¹. Under these conditions, the retention time for pendimethalin was ~22.2 min. The temperature program, used for separation and determination of pendimethalin, was found efficient for separating and determining other herbicides as well.

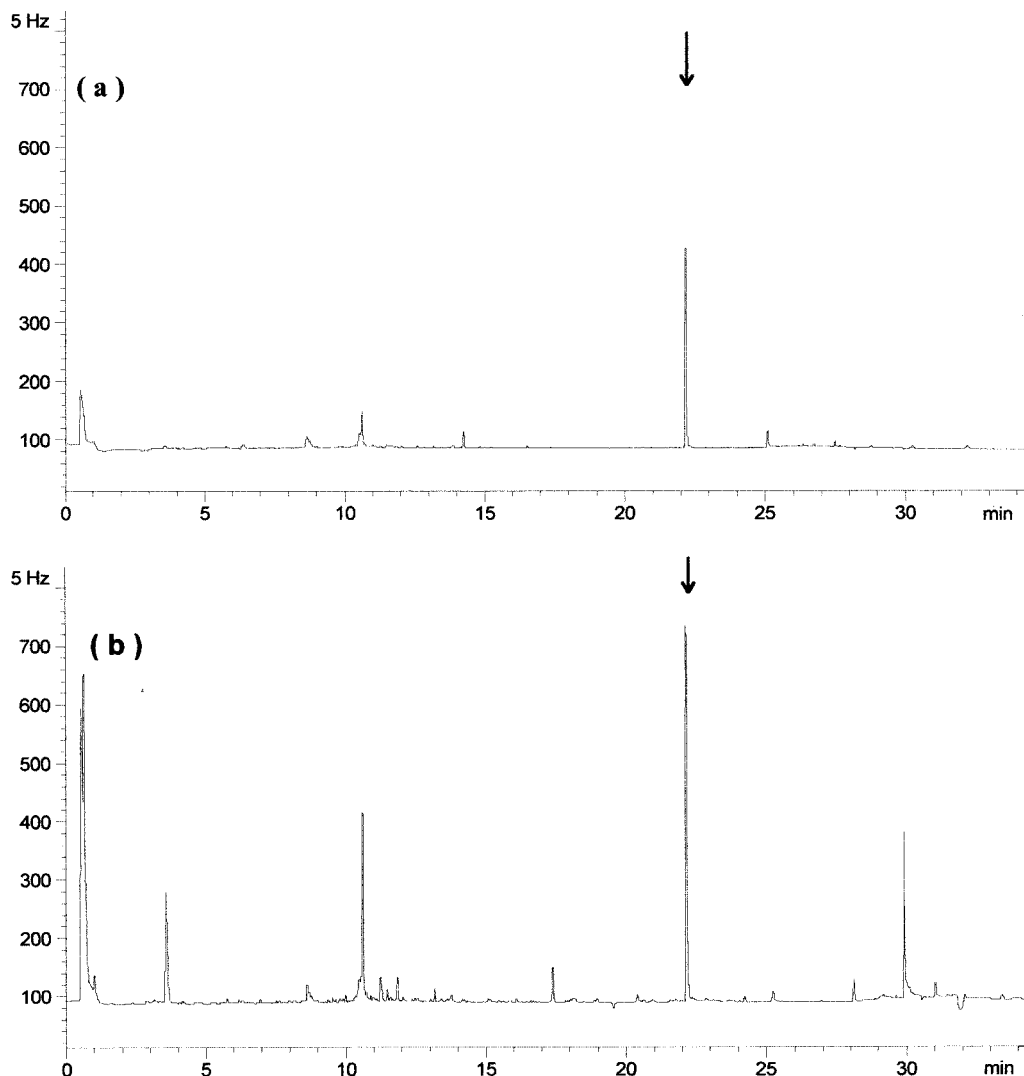


Figure 1. Gas chromatograms of (a) a standard of 0.25 ng of pendimethalin and (b) an onion extract from the treated plot (onion sample at 0.052 mg/kg).

For the confirmation of pendimethalin in the onion samples a second chromatographic analysis was performed using a 2 m × 2 mm glass column containing a mixture (1:1) of 10% OV-101 and 15% OV-210 on 80/100 Chromosorb WHP support, fitted in a Varian 3700 gas chromatograph. The temperatures of the oven, the injector, and the detector (ECD) were 200, 220, and 300 °C, respectively.

RESULTS AND DISCUSSION

Method Efficiency. The described method of analysis of the onion samples for pendimethalin residues is relatively simple, and the cleanup of the onion extract is sufficient, as can be seen from the resulting chromatograms (Figure 1), which show very few peaks with the electron capture detector. The detector response in the investigated range of 0.10–12.50 ng presents a typical shallow curve which fit better to a second-order polynomial than to a linear relationship. With such a polynomial, the correlation coefficient for the detector response calibration curve ($n = 10$) was 0.999. Determination of pendimethalin residues in samples was done by comparing the area of pendimethalin peak in the sample chromatogram with the areas of pendimethalin standard solutions, and quantitation was by using the external standard method.

The efficiency of the method was evaluated by spiking control samples with pendimethalin at various concen-

Table 2. Mean Recovery^a and Relative Standard Deviation (RSD) for Pendimethalin at Various Fortification Levels in Onion Plants

concn (mg/kg)	recovery (%)	RSD (%)	concn (mg/kg)	recovery (%)	RSD (%)
0.05	81 ± 10	12.3	1.0	91 ± 3	3.3
0.1	84 ± 11	13.1	5.0	99 ± 3	3.0
0.5	82 ± 3	3.7			

^a Three samples for each fortification level.

tration levels. Table 2 presents the results of the recovery study. All values in this table are within the accepted range for residues determinations (Greve, 1984). The method's limit of determination, evaluated as the product of the standard deviation at the lowest validation level with the Student t value (U.S. EPA, 1984), which at 99% confidence level and for two degrees of freedom is 6.96, was found to be 0.007 mg/kg.

Disappearance of Residues in Onion. All control onion samples that were collected at various sampling dates were found to contain no detectable (i.e. <0.007 mg/kg) pendimethalin residues. Pendimethalin residues found in onions (whole plant, leaves, and bulbs) at various time intervals following application are shown in Figure 2. As shown from this figure, initial deposits of pendimethalin on whole onion plants were 0.82 mg/kg for the LRD experiment and 0.96 mg/kg for

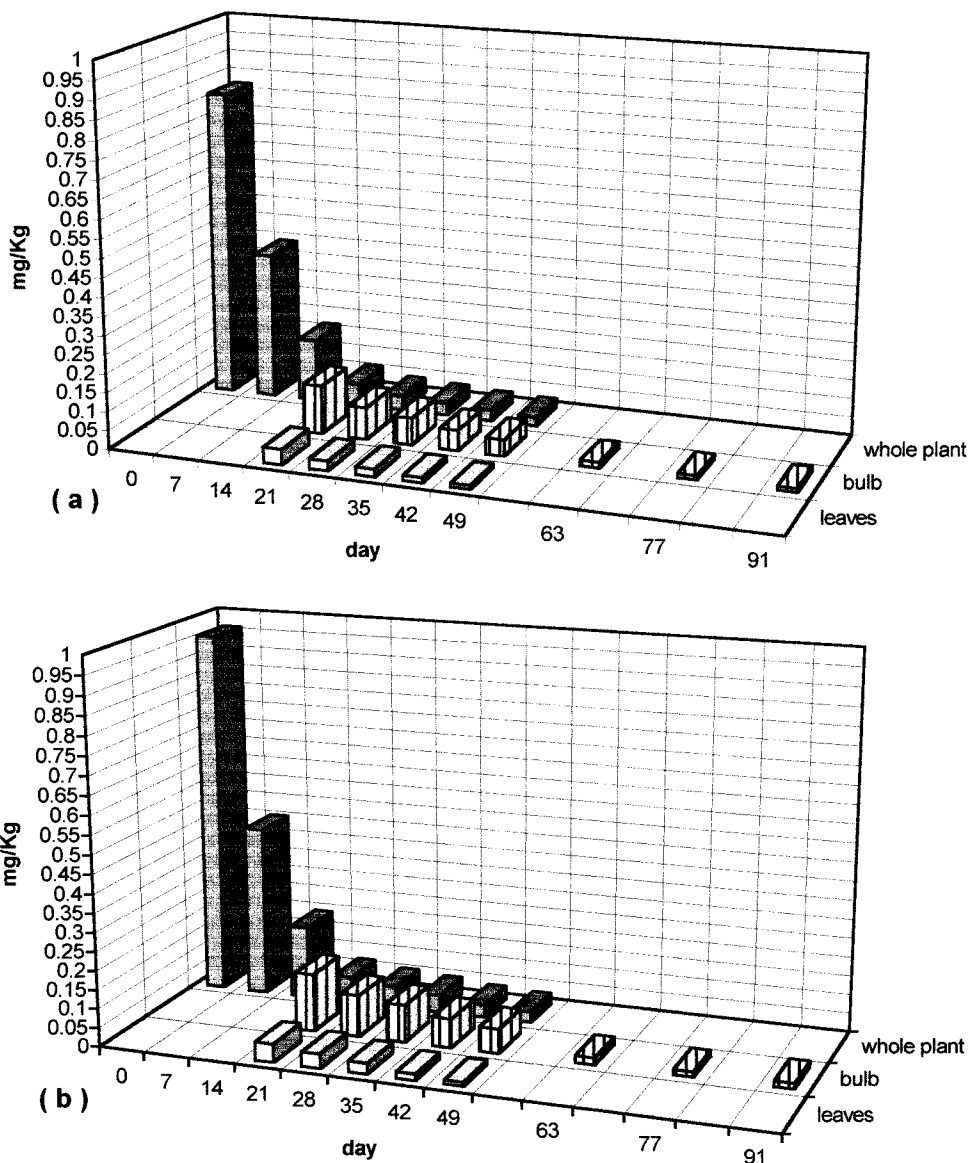


Figure 2. Pendimethalin residues (milligrams per kilogram) in onions at various time intervals following application: (a) LRD (1.32 kg of ai/ha); (b) HRD (2.00 kg of ai/ha). The residues in whole onion plant for the experimental period from the 21st until 49th days was estimated by considering pendimethalin residues in the leaves and the bulb and their mass ratio.

the HRD experiment. Thereafter, a rapid diminution of residues was observed, until the 21st day following application, when the residue found was $\approx 7\%$ of the initial concentrations for the both doses. Pendimethalin concentration, 7 days following application, was found to be approximately half of the initial concentrations for both cases. The losses seem to be primarily due to dilution effect (as the rate of growth of onion plant is important) and secondarily to the removal by heat or chemical decomposition. After the 21st day, the residues in the whole onion plant declined relatively slowly with time, and this seems to be due to the minor growth rate of the plant. At the 49th day following application, pendimethalin concentration in onion plants was estimated to be only $\sim 3\%$ of the initial concentrations at both application doses.

Concerning the partition of pendimethalin in the bulb and in the leaves, it should be noted that, as shown in Figure 2, at the investigated period (21st until 49th day after application) the concentration of the ai is higher (about 3 times) in the bulb than in the leaves for both application doses. This could be explained by the fact

that the residues in the bulb are affected both by pendimethalin chemical decomposition and by adsorption of pendimethalin molecules from the soil solution, while in the leaves they are affected only by decomposition of initial deposits of pendimethalin, as it is a nonsystemic herbicide.

According to our study pendimethalin residues on the dry onion at harvest time, for both cases (low and high application doses), were clearly below the lowest of the previously mentioned permissible MRLs set by European countries. This is in discord with the results of a study in India (Sharma and Mehta, 1989) in transplanting onion cultivation, when at harvest (115 days after application) much higher residue concentrations were observed, i.e., 0.103 ppm for the dose of 2.0 kg/ha. It seems that in our field experimental conditions dissipation of pendimethalin residues was faster. As for the residues found in the spring onions at harvest time, they were < 0.05 mg/kg for treatment at the LRD but were slightly > 0.05 mg/kg (i.e. 0.054 mg/kg) in the case of the HRD. In this case it seems preferable to apply pendimethalin earlier and a PHI should be established.

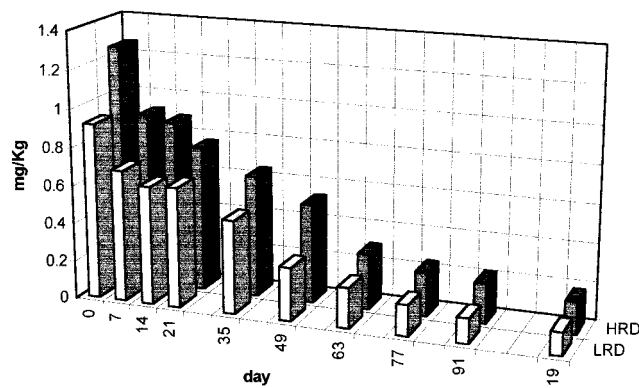


Figure 3. Pendimethalin residues (milligrams per kilogram) in onion planting soil at various time intervals following application: (a) LRD (1.32 kg of ai/ha); (b) HRD (2.00 kg of ai/ha).

Residues in Soil. Air-dry soil samples (20 g) from the untreated plot were spiked with pendimethalin solution at 0.1, 0.5, 1.0, and 1.5 mg/kg and analyzed following the procedure described above. The average recoveries obtained from four replicates varied from 88 to 101% with the relative standard deviation ranging from 4 to 8%. The results obtained from the soil samples, which were taken from the onion planting at various time intervals following pendimethalin application, are summarized in Figure 3. The initial deposits were 0.92 mg/kg for the LRD experiment and 1.26 mg/kg for the HRD experiment. At the first week important losses of 25% and 28%, respectively, were observed, which may be attributed to volatilization and photodecomposition during the first days following application and to removal by chemical and biological ways, which seem to be the principal factors for pendimethalin degradation in soil during the experimental period. The half-lives of pendimethalin in the onion planting soil, as evaluated from the degradation lines for the investigated period, were found to be approximately 37 days for the LRD experiment and 39 days for the HRD experiment. This indicates an independence of the degradation rate from the application dose, which is consistent with other papers (Zimdahl et al., 1984; Walker and Bond, 1977). The lower half-life of pendimethalin in soil found in our study compared to other studies (Zimdahl et al., 1984; Walker and Bond, 1977) may be due to differences in the experimental conditions, such as soil temperature and moisture, and to the fact that the herbicide was not incorporated in the soil

and was therefore more susceptible to the environmental factors. At the spring onion harvest time it was estimated that 52% of the initial deposits remained in the soil, while at the bulb onion harvest time the corresponding number was $\approx 14\%$ for both application doses.

The analysis of soil control samples indicated concentrations of pendimethalin < 0.03 mg/kg, although Stomp was not used in this plot for the previous year. This may be possibly attributed to drift deposition from neighboring fields.

LITERATURE CITED

- British Crop Protection Council and Royal Society of Chemistry. *The Pesticide Manual*, 10th ed.; BCPC and RSC: London, U.K., 1994.
- FAO/WHO. Recommended method of sampling for the determination of pesticide residues. *Codex Alimentarius Commission of the Joint FAO/WHO Food Standards Programme*, 2nd ed.; Food and Agricultural Organization/World Health Organization: Rome, 1986; Vol. XIII, Part VI.
- Greve, P. A. Good Laboratory Practice in Pesticide Residue Analysis. In *Pesticide Residue Analysis*; Ambrus, A., Greenhalgh, R., Eds; Proceedings of a Joint WHO/FAO Course; WHO/FAO: Rome, 1984; p 281.
- Ministry of Welfare, Health and Cultural Affairs. *Analytical Methods for Residues of Pesticides in Foodstuffs*; Greve, P. A., Ed.; Rijswijk, Netherlands, 1988; Part I, p 8.
- Sánchez-Brunete, C.; Martínez, L.; Tadeo, J. L. Determination of Corn Herbicides by GC-MS and GC-NPD in Environmental Samples. *J. Agric. Food Chem.* **1994**, *42*, 2210–2214.
- Savage, K. E.; Jordan, T. N. Persistence of three dinitroaniline herbicides on the soil surface. *Weed Sci.* **1980**, *28*, 105–110.
- Sharma, R.; Mehta, H. M. Studies on pendimethalin and fluchloralin residues in soil and onion. *Indian J. Agron.* **1989**, *34* (2), 245–247.
- Smith, A. E.; Aubin, A. J.; McIntosh, T. C. Field persistence studies with emulsifiable concentrate and granular formulations of the herbicide pendimethalin in Saskatchewan. *J. Agric. Food Chem.* **1995**, *43*, 2988–2991.
- U.S. EPA. *Fed. Regist.* **1984**, *49* (209), 198.
- Walker, A.; Bond, W. Persistence of the herbicide AC 92,553, N-(1-ethylpropyl)-2,6-dinitro-3,4-xylidine, in soils. *Pestic. Sci.* **1977**, *8*, 359–365.
- Zimdahl, R. L.; Catizone, P.; Butcher, A. C. Degradation of pendimethalin in soil. *Weed Sci.* **1984**, *32*, 408–412.

Received for review August 18, 1997. Revised manuscript received November 14, 1997. Accepted November 16, 1997.

JF970712H