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Dissipation of Pendimethalin in the Garlic (*Allium sativum* L.) under Subtropical Condition

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Pendimethalin is the common name of N-(1-ethylpropyl)-3,4-dimethyl-2,6-dinitrobenzenamine, a dinitroaniline herbicide that is used widely for selective control of most annual grasses and many annual broad-leaved weeds in crop fields such as rice, peanut, soybean, cabbage, garlic, onion, radish, tomato, pea, and tobacco in Taiwan. Field dissipation studies have revealed that pendimethalin is persistent (Walker and Bond, 1977; Zimdalh et al., 1984; Smith et al., 1995). Walker and Bond (1977) found that the half-life of pendimethalin in a sandy soil, with the moisture at 75% field capacity, is 98 days at 30°C and 409 days at 10°C. The half-life of pendimethalin in a sandy loam soil treated with 1.5 kg a.i./ha in wheat crops in the tropical climate of India ranges from 58 to 63 days (Kulshrestha and Yaduraju, 1987). Singh et al. (2002) have also found that the dissipation of pendimethalin in soil has a half-life of 74 days. Pendimethalin degrades more rapidly in anaerobic soil than in aerobic soil conditions. The $T_{1/2}$ values of pendimethalin in anaerobic and aerobic soils are 33 and 52 days, respectively (Kulshrestha and Singh, 1992). However, field studies conducted in Greece show that DT_{50} of pendimethalin in onion fields range from 37 to 39 days (Nicholas and George, 1998). Furthermore, the half-lives of Pendimethalin in cabbage fields with the application rates of 1 kg a.i./ha and 2 kg a.i./ha are 15 and 17 days, respectively (Arora and Gopal, 2004). Besides persistence, the mobility and leaching ability are also important in the environmental study of pesticides. Pendimethalin is classified as a non-leaching compound (Cooper et al., 1994). The field persistence of residues of pendimethalin in soil and garlic (*Allium sativum* L.) plants in the subtropical conditions of Taiwan have not been examined. This study measures the dissipation and mobility of pendimethalin in a garlic field by the model ecosystem. Additionally, the movement and degradation of pendimethalin in garlic plants are investigated.

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Materials and Methods

The experiments were performed at Wufeng (N 24° 01′ 16″, E 120° 40′ 55″), Taiwan, using a model ecosystem containing six sets of plots, set in an open-sided greenhouse fitted with a clear plastic roof to protect it from rain. Each plot had an inner cell (2.8 m × 0.8 m × 0.45 m) and an outer cell (4.0 m × 2.0 m × 0.6 m). The inner cell was filled with soil (Fig. 1). The plots contained a sandy loam soil (sand 70%, silt 20%, and clay 10%) with a pH of 6.60, a cation exchange capacity (CEC) of 5.45 cmol/kg, and an organic C content of 2.13%. Garlic (*Allium sativum* L.) plants were planted in two rows per plot and ten plants per row. The ecosystems were managed according to field usage.

Pendimethalin (34% EC, from Cyanamid Taiwan Corporation) was applied to the soil surface at rates of 1.19 kg a.i./ha (recommended dose) and 2.38 kg a.i./ha (twice the recommended dose) one week after sowing the garlic. Each treatment was duplicated. The remaining two plots were not sprayed with pendimethalin, and thus were control plots. The soil was sampled with a soil auger (5.5 cm inner diameter) at 0 (three hours after application), 2, 7, 15, 28, 42, and 63 days after the application. Five cores of sub-samples were taken randomly at each plot, each core consisting of surface soil (0–10 cm deep) and bottom soil

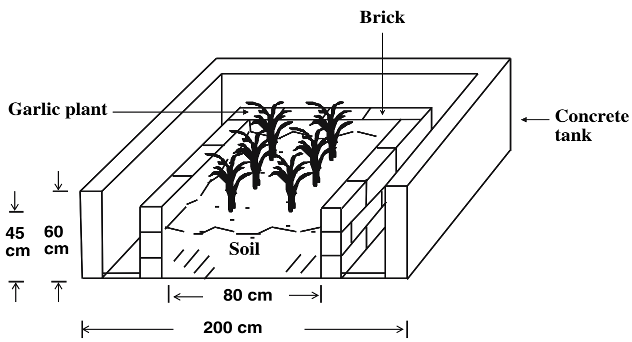

Fig. 1 Sideview of a model ecosystem

(10–20 cm deep). The surface and bottom soil sub-samples of each plot were mixed in one sample. Garlic plants were sampled at intervals of seven days after 28 days of pendimethalin application.

To analyze the pendimethalin residue in soil, 10 g of soil was extracted twice with 100 mL and 50 mL acetone by shaking with an end-over-end shaker (amplitude 2.5 cm, 200 rpm for 30 minutes). The extract was collected and filtered with 0.2 μm polytetrafluoroethylene (PTFE) filter paper. The extract was dehydrated with anhydrous sodium sulfate, and concentrated to near dryness, then re-dissolved in 5 mL acetonitrile for high-performance liquid chromatography (HPLC)analysis. Table 1 lists the operation conditions for HPLC. A homogeneous garlic sample (20 g) was macerated in 100 mL acetone for 1 minute with a homogenizer. The extract was separated from plant fiber by filtration, and transferred into a 500 mL separatory funnel. 100 mL of aqueous NaCl solution (50 g/L) was then added, and extracted with 100 mL and 50 mL dichloromethane. The dichloromethane extract was dehydrated and concentrated to near dryness, and then re-dissolved in 5 mL acetonitrile and cleaned up with a Florisil column (1000 mg, Merck). The column eluate was concentrated and redissolved in 1 mL *n*-hexane for gas-liquid chromatography (GLC) analysis. Table 2 shows the GLC operation conditions. The degree of recovery was tested by spiking 10 g soil and/or 20 g garlic plant blank samples with 1 μg of pendimethalin, respectively. The recovery rates were 96.5% for the soil, and 73% for the garlic plant. The detection limits were 0.04 μg/g and 0.02 μg/g for the soil and garlic plant, respectively.

The dissipation rate constant of pendimethalin in soil was determined by linear regression from the transformed first-order rate equation $\ln C = \ln C_0 - Kt$, where C denotes the pendimethalin concentration as a function of time in days (t). C_0 denotes the highest pendimethalin concentration, and K is the degradation rate constant. The time for dissipation of 50% (DT_{50}) of the highest concentration was derived from the equation $DT_{50} = \ln 2/K$.

Table 1 Operating conditions of HPLC for determination of pendimethalin

Instrument	HP 1100		
Detector	UV detector (240 nm)		
Column	Merck LiChroshpher 100 Select - B		
Eluent	Minutes	CH_3CN (%)	H_2O (%)
	0	80	20
	7	80	20
	16	100	0
Post time (min)	3		
Run time (min)	16		
Flow rate (mL/min)	1		
Injection vol. (μL)	10		

Table 2 Operating conditions of GLC for determination of pendimethalin

Instrument	HP 6890		
Detector	Electron capture detector (ECD)		
Column	DB-608		
Oven temp. (°C)	°C/min	°C	Min
	Initial	170	5
	2	210	5
	20	250	10
Inlet temp. (°C)	250		
Detector temp. (°C)	300		
Column flow rate (mL/min)	mL/min	mL/min	Min
	Initial	8	10
	–1	3	15
	+2	10	
Makeup flow (mL/min)	60		
Anode flow (mL/min)	5		

Results and Discussion

Table 3 summarizes the dissipation of pendimethalin in soil and garlic. The highest residue of pendimethalin in soil, found three hours after application, was 1.29 and 2.35 μg/g for application rates of 1.19 kg a.i./ha and 2.38 kg a.i./ha, respectively. Pendimethalin dissipated under the experimental conditions. The residue level in soil decreased as the day-after-application (DAA) increased. For an application rate of 1.19 kg a.i./ha, the residue in soil was 1.06 μg/g on 2 DAA, then dissipated to < 0.04 μg/g on 63 DAA. For an application rate of 2.38 kg a.i./ha, the residue in soil was 1.99 μg/g on 2 DAA, which dissipated to 0.27 μg/g on 63 DAA (Table 3).

The rate of dissipation of pendimethalin in soil was measured in terms of first-order kinetics, and the DT_{50} was calculated to 14 days at 1.19 kg a.i./ha, and 21 days at 2.38 kg a.i./ha (Table 3). Several authors have reported that photodecomposition, biodegradation, and chemical decomposi-

Table 3 Dissipation of pendimethalin in soil and garlic (*Allium sativum* L.) plants at different application rates

DAA(day)	Residues in soil (μg/g)*		Residues in garlic plant (μg/g)	
	1.19 kg a.i./ha	2.38 kg a.i./ha	1.19 kg a.i./ha	1.38 kg a.i./ha
0**	1.29 ± 0.10***	2.35 ± 0.28	–	–
2	1.06 ± 0.08	1.99 ± 0.45	–	–
7	0.59 ± 0.14	1.54 ± 0.20	–	–
15	0.46 ± 0.02	1.26 ± 0.36	–	–
28	0.34 ± 0.08	0.83 ± 0	0.16 ± 0	0.21 ± 0.06
42	0.12 ± 0.01	0.61 ± 0.09	ND****	ND
63	<0.04	0.27 ± 0	ND	ND
DT_{50} (day)	14	21	–	–

* Surface soil (0 – 10 cm in depth)

** Three hours after application

*** Data are means ± standard deviations

****Non-detectable, the detection limit was 0.02 μg/g

tion can accelerate the dissipation of pendimethalim in soil (Parochetti and Dec, 1978; Savage and Jordan, 1980; Barua et al., 1990). The half-life of pendimethalin varied from 13 to 17 days in tropical and Mediterranean plan field conditions (Cooper et al., 1994). Moreover, the DT_{50} was 6.4 days under the subtropical conditions of Malaysia (Ismail and Kalithasan, 1997). These findings reveal that pendimethalin dissipates more rapidly under subtropical and tropical conditions than in temperate conditions.

Pendimethalin residues were found only in the surface soil (0–10 cm deep) at both application rates during the experimental periods (Table 3), conforming that pendimethalin cannot leach to the layer below 10 cm deep in the soil. Pendimethalin has low water solubility and high adsorption characteristics. This herbicide has been predicted to be a non-leaching compound with the Gustafson model (Cooper et al., 1994). Walker and Bond (1977) found that pendimethalin is a low-mobility herbicide. The experimental results of Lee (2000) also indicated pendimethalin had low-runoff and leaching properties in turf soil in Korea. The experimental results of this study demonstrate that pendimethalin is a slightly persistent, low-mobility herbicide under the experimental conditions.

Pendimethalin was found in garlic plants on 28 DAA. The residues of pendimethalin were 0.16 μg/g and 0.21 μg/g at application rates of 1.19 kg a.i./ha and 2.38 kg a.i./ha, respectively. However, two weeks later (on 42 DAA) the residues were undetectable in garlic plants for both treatments (Table 3). This result indicates pendimethalin was transported from the soil to the garlic plant, and was degraded in the garlic plant.

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