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Evaluation of pendimethalin residues in garlic

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ABSTRACT

A field experiment was conducted to study the persistence and accumulation of pendimethalin residues in garlic. Pendimethalin was applied as pre-emergence treatment at three different doses, *viz.* 0.75, 1.5 and 3.0 kg/ha. Mature garlic bulbs were collected at crop harvest and soil samples were collected at 0, 15, 30, 45, 60, 75, 90, 120 days after herbicide application and at crop harvest. These samples were analyzed for pendimethalin residues by a validated Gas Liquid Chromatography (GLC) method with an accepted recovery of 79.1–88.2%. The analysis showed that pendimethalin did not leave any residues in soil beyond harvest of the crop at any of the applied dose. On the other hand, garlic bulbs collected at harvest showed 0.004 µg/g pendimethalin residues at a dose of 3.0 kg/ha and below detectable limit (BDL) at 0.75 and 1.5 kg/ha.

Key words: Garlic, Pendimethalin, Persistence, Residues

Garlic (*Allium sativum)* is an important bulbous vegetable crop, cultivated commercially throughout tropical and subtropical belt of the world. It is very slow to germinate and grow in the initial stages. Weed infestation in garlic is one of the major factors for bulb yield loss to the tune of 79-89% (Ahmed 1991). Garlic is a long-duration crop and the aggravated labour problem in agriculture is a limitation. Therefore, it is necessary to rely on herbicides for an effective and timely weed control. The most important consideration in chemical weed control is persistence of herbicides in soil and their residues in crop produce. Pendimethalin [N-(1-ethylpropyl)-3, 4 dimethyl 2, 6 dinitrobenze-namine], a selective pre-emergence herbicide has wide spread use for control of a wide variety of grasses and broadleaf weeds (Sinha *et al.* 1996 and Bhowmick and Ghosh 2002) in crops like peas (*Pisum sativum* L.), rice (*Oryza sativa* L.), wheat (*Triticum aestivum* L.), soybean (*Glycine max* L. *merr.*) and several other vegetable crops including garlic (*Allium sativum* L.). This herbicide is soil-applied, moderate in persistence and relatively immobile in nature (Tsiropoulos and Miliadis 1998 and Triantafyllidis *et al.* 2009). The most likely route of herbicide dissipation is soil binding. Field studies on persistence and accumulation of pendimethalin residues in garlic crop are meager. Thus, the present investigation was undertaken to study the persistence and accumulation of pendimethalin residues in garlic.

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MATERIALS AND METHODS

A field experiment was conducted at the Research Farm of Department of Agronomy, CSK HPKV, Palampur in a randomized block design with three replications. Residue analysis was conducted in the residue laboratory of Department of Agronomy, CSK HPKV, Palampur. Pendimethalin was sprayed at three different doses *i.e.* 0.75, 1.5 and 3.0 kg/ha in garlic crop as pre emergence herbicide. Five soil cores were randomly taken from each of the treated and untreated plot using auger upto the depth of 15cm at 0, 15, 30, 45, 60, 75, 90 and 120 days after herbicide application. These cores were bulked together, air dried, powdered and passed through a 2 mm sieve to achieve uniform mixing. Garlic bulbs were collected at the maturity of the crop from pendimethalin treated and untreated plots.

Pendimethalin residues were extracted as described by Sondhia and Dubey (2006). Pendimethalin reference analytical standard was obtained from Accu Standard Inc., USA. All the other chemicals and solvents used in the study were analytical grade reagents. The gas liquid chromatography (Clarus-500, Model Perkin Elmer) equipped with Ni^{63} electron capture detector (ECD) and fitted with a column RTx 5 (30 m x 0.25 mm i.d.) under oven isothermal conditions of 210 ^{o}C. The injector and detector were maintained at 240 ^{o}C and 350 ^{o}C respectively. Nitrogen was used as a carrier gas with a flow of 30 ml/min. The injection volume of standard solution and sample was 1 µl for analysis.

Garlic bulbs were cut into small pieces and homogenized with acetone. Homogenized garlic bulbs and soil samples were extracted with 50 ml acetone on a horizontal shaker for two hours. The contents were filtered and the collected filtrate was dried using vacuum rotary evaporator. The residues were dissolved in 50 ml dichloromethane and taken in a 500 ml separating funnel followed by the addition of 100 ml of 10% sodium chloride (hexane washed). The contents were shaken vigorously for 15-20 minutes and the layers were allowed to separate. The organic layer was collected and the aqueous layer was further extracted with 20 ml of dichloromethane 2-3 times. The dichloromethane fractions were pooled and passed through AR grade anhydrous sodium sulphate and was dried using rotary flash evaporator at 40°C. The final volume was made upto 5 ml using distilled hexane in 10% acetone. However, clean up procedure was required for garlic bulbs. A glass column was packed with 6 g of activated florisil and in between two layers of anhydrous sodium sulphate and activated charcoal were added. Concentrated extracts of garlic samples were loaded on the top of column and eluted with 75 ml hexane. The eluted hexane was collected and concentrated using flash evaporator.

Validation of the method was performed in terms of recovery experiment before analysis of unknown samples. Different known concentrations of pendimethalin (0.01, 0.1, 0.5, 1.0, 5.0 and 10 ppm) were prepared in n-hexane by diluting the stock solution. One micro liter of standard solution was injected in gas liquid chromatography (GLC), the peak area measured and standard curve was prepared. The recovery study was conducted with soil and garlic bulbs. One ml of pendimethalin was added uniformly on the surface matrix and mixed well before adding extraction solvent. The extraction and cleanup process was performed as described in methodology. The results are presented in Table 1. Quantification of pendimethalin residues in soil and garlic was accomplished by comparing the peak response for samples with peak area of standards.

RESULTS AND DISCUSSION

Under described conditions of GC, pendimethalin was eluted as a single sharp peak at 7.6 minutes (Fig.1.) The standard curve for reference pendimethalin showed linearity and the detector showed good sensitivity for the pendimethalin residues up to 0.05 µg/ml. The recovery experiment conducted with soil and garlic bulbs showed that recovery percentage for soil varied from 79.3-83.8%; however, it varied between 79.1 and 88.2% in the case of garlic bulbs at fortification level of 0.5 and 1.0 µg/g of pendimethalin, respectively (Table 1). The recoveries of pendimethalin at different concentration levels were satisfactory within the range 79.1–88.2%, confirming a good repeatability of the method. The equation of analytical calibration graphs, obtained by plotting peak areas in the *y* -axis against concentrations of pendimethalin in the *x* -axis within the range of 0.05 to 10 µg/ml, was $y = 82723\ x + 316449$, which showed good linearity, and the value of correlation coefficient was 0.99. Pendimethalin residues and their per cent dissipation data in different matrices at different time intervals as detected by GLC are presented in Table 2. The initial deposits of pendimethalin in soil immediately after application of pendimethalin 0.75, 1.50 and 3.00 kg/ha were found to be 0.301, 0.668 and 1.439 mg/kg, respectively which after 120 days of herbicide application reached to below detectable levels, 0.001 and 0.08 mg/kg, respectively. Thus, the corresponding percent losses of pendimethalin were 100, 99.85 and 99.44%, respectively. The data on per cent dissipation revealed that dissipation rate was faster during first 15 days and thereafter dissipation occurred at constant rate. More than 80-90% of pendimethalin 0.75, 1.50 and 3.00 kg/ha dissipated within 75 days after application. The dissipation of pendimethalin on 75th day after application was 98.7, 95.6 and 87.9% for pendimethalin 0.75, 1.50 and 3.00 kg/ha, respectively indicating that only 1.30, 4.35 and 12.1% of applied pendimethalin remained in soil at 75th day. Pendimethalin residue data (Table 2) at three application rates *i.e.* 0.75, 1.50 and 3.00 kg/ha also revealed that herbicide in soil persisted upto 90 days at a dose of 0.75 kg/ha and 120 days at 1.50 and 3.00 kg/ha. This indicates that pendimethalin at higher doses per-

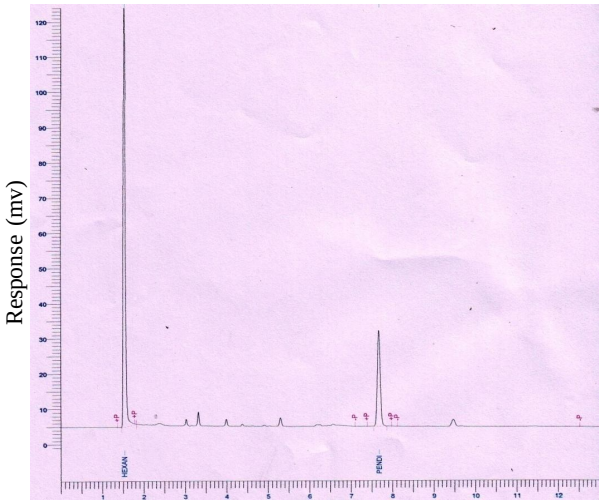

Fig. 1. Rt value of pendimethalin

Table 1. Recoveries of pendimethalin from soil and garlic fortified with known amount of herbicide

Herbicide	Amount added (µg/g)	*Amount recovered (µg/g)	Average recovery (%)
Soil	0.5	0.419 ± 0.05	83.8
	1.0	0.793 ± 0.026	79.3
Garlic	0.5	0.441 ± 0. 013	88.2
	1.0	0.791 ± 0.018	79.1

*Values are average of three replications

Table 2. Residues (mg/kg) of pendimethalin in soil (0-15 cm depth) treated at different doses

Days after herbicide application	Rates of pendimethalin application (kg/ha)		
	0.75	1.50	3.00
0	0.301 (0)	0.668 (0)	1.439(0)
15	0.119 (60.5)	0.389 (50.8)	1.048 (27.1)
30	0.052 (82.8)	0.245 (63.3)	0.864 (39.9)
45	0.018 (94.0)	0.160 (76.0)	0.587 (59.2)
60	0.011 (96.3)	0.068 (89.9)	0.336 (76.6)
75	0.004 (98.7)	0.029 (95.6)	0.174 (87.9)
90	0.001 (-)	0.009 (98.6)	0.133 (92.5)
120	BDL (-)	0.001 (99.8)	0.08 (94.4)
Harvest	BDL (-)	BDL (-)	BDL (-)

*The values given in the parentheses are % dissipation

Table 3. Slope of curve, rate constant and half life values of pendimethalin residues in soil

Pendimethalin (kg/ha)	Slope of curve (b)	Rate constant (K)	Half life (days)	Correlation coefficient	Regression equation
0.75	0.026	0.059	11. 9	0.99	Y= - 0.026 x + 2.494
1.50	0.020	0.046	15.0	0.99	Y= - 0.020 x + 2.938
3.0	0.14	0.032	21.5	0.96	Y= - 0.014 x + 1.318

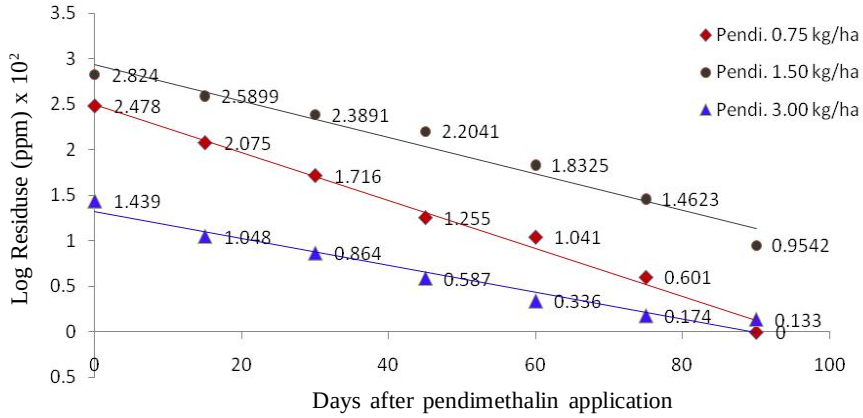

Fig. 2. First order dissipation curve of pendimethalin in soil

sisted in the soil for longer duration than lower doses. Pendimethalin did not leave residues in soil beyond harvest of the crop at any of the applied doses. Similar observations have been reported by Sinha *et al.* (1996) where pendimethalin persisted for over 75 days at the application rate of 2.0 kg/ha. The logarithmic plots of herbicides residue vs time are presented in Fig. 2. These plots indicated that dissipation of pendimethalin at all three levels of application, *viz.* 0.75, 1.50 and 3.00 kg/ha fitted first order kinetics decay curve and is in line with the findings of Tandon (2008). The slope of the curve, correlation coefficient, rate constant and half life of herbicide along with the regression equations are summarized in Table 3. Half life for pendimethalin

at 0.75, 1.50 and 3.00 kg/ha were 11.9, 15 and 21.5 days, respectively. These findings are in agreement with that of Alister *et al.* (2009) who also reported the half life of pendimethalin varied from 10.5 to 31.5 days. This may be due to combined effect of soil physico-chemical properties including high organic carbon and comparatively low temperature (Raj *et al.* 1999). Pendimethalin residues in garlic bulbs were below the detectable level in case of pendimethalin 0.75 and 1.50 kg/ha and 0.004 mg/g in pendimethalin 3.00 kg/ha. From the data regarding residues of pendimethalin in garlic bulbs collected at the harvest of crop, it was evident that residues of pendimethalin were below maximum residue limit set by WHO/ FAO (0.5 mg/ kg). It indicates that the use of pendimethalin in garlic could be considered safe.

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