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Persistence and Dissipation Kinetics of Deltamethrin on Chili in Different Agro-Climatic Zones of India

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Abstract Multi-location supervised field trials were conducted at four different agro climatic locations in India to evaluate the dissipation pattern of deltamethrin on chili. Deltamethrin 10 EC was applied on chili @17.5 and 35 g a.i. ha^{-1}, samples of green chili were drawn at different time intervals and that of red chili and soil at harvest time and quantified by gas liquid chromatography equipped with electron capture detector. The identity of residues were confirmed by Gas Chromatograph–Mass Spectrophotometer in selective ion monitoring mode in mass range 181, 253 m/z. Limit of quantification of the method was found to be 0.01 mg kg^{-1}. Half-life of deltamethrin at application rate of 17.5 g a.i. ha^{-1} varied from 0.36 to 1.99 days and at double the application rate was found to range from 0.38 to 2.06 days. Residues of deltamethrin were found below its determination limit of 0.01 mg kg^{-1} in red chili and soil. On the basis of the data generated, Deltamethrin 10 EC has been registered for use on chili in India and its Maximum Residue Limit has been fixed as 0.05 μg/g.

Keywords Chili · Deltamethrin residues · Gas Chromatograph · Dissipation · Half life

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Chili (*Capsicum annuum* L.; *Capsicum frutescene* L.), also known red pepper, is an important cash crop in India and is grown for its pungent fruits, which are used both green and ripe red (in the dried form) to impart pungency to the food. As a condiment, it has become indispensable to every Indian home. The pungency is due to the active, 'capsicin' contained in the skin and septa of the fruit. The increased availability of oleoresins and spice oils of chili has also enhanced its consumption in various food preparations. India is the largest producer of chilies in the world but its production pattern is highly erratic (Thamburaj and Singh 2005).

Deltamethrin, [(S)-cyano-(3-phenyl) methyl] (1R, 3R)-3-(2, 2- dibromomethylcyclopropane-1- carboxylate, a pyrethroid insecticide, is used for the control of lepidopterous pests on various vegetable crops (Hirano, 1989). It has been recommended for foliar application on various vegetables and field crops. It also provides protection to grains during storage. When used at recommended doses, deltamethrin presents no hazards to honey bees and other pollinators. This is because deltamethrin is effective in controlling a wide range of insect pests in agriculture at very low application rates (Deo and Krishnakumari 1991). The presence of residues on crops is a matter of serious concern; therefore, it becomes mandatory to assess the impact of use of this insecticide from residues point of

view for the safety of the consumers. However, no information is available on persistence of deltamethrin on chilli in different agro climatic zones of India. Therefore, multilocation supervised field trials were undertaken in different agro climatic zones of India to generate data on the persistence and dissipation kinetics of deltamethrin residues in chili fruit and harvest time residue in soil.

Materials and Methods

The supervised field trials were conducted at four different locations in India viz., Anand Agricultural University, Anand (Gujarat) (Location I); Acharya NG Ranga Agricultural University, Hyderabad (Andhra Pradesh) (Location II); Bidhan Chandra Krishi Viswavidyalaya (West Bengal) (Location III) and Punjab Agricultural University, Ludhiana (Punjab) (Location IV). The field trials were laid out with chili in randomized block design (RBD) with three replications during the year 2008–2009. The crop varieties used were Chili Palio, LCA-334, Pusa Jwala and CH-1 at locations I, II, III and IV, respectively. The weather data during the period of experimentation for each location is presented in Table 1. Deltamethrin 10 EC was applied three times at weekly intervals @ 17.5 (T_1) and 35 g.a.i. ha^{-1} (T_2). In control plot only water was sprayed (T_0).

Green chili samples (500 g) were drawn from each replicate treatment after last application of the insecticide at 0 (2 h), 1, 3, 5, 7, 10 and 15 days and red chili and soil samples were drawn at harvest time which varied at each location. It took 52 days for conversion of green chili to red at locations I and II while red chili was formed after 40 and 30 days at locations III and IV. This variation might be due to different agro-climatic conditions at these locations (Table 1).

A representative 50 g sample of chopped and macerated chili was dipped overnight into 100 mL acetone in an Erlenmeyer flask. The extract was filtered into 1 L separatory funnel, diluted with 600 mL brine solution, partitioned the contents into dichloromethane (2 × 75 mL) and hexane (2 × 75 mL). Combined hexane and dichloromethane fractions were dried over anhydrous sodium sulfate and treated with 500 mg activated charcoal powder for 2–3 h at room temperature. The clear extract so obtained was filtered through Whatman filter paper No. 1, concentrated to near dryness and again added 20 mL acetone and concentrated using rotary evaporator at 30 °C. Repeated the process to completely evaporate dichloromethane and the final volume was reconstituted to about 5 mL with acetone. A representive 50 g soil sample was also processed in the similar manner as for chili.

The residues of deltamethrin were estimated on gas chromatograph (Shimadzu 2010) equipped with electron capture detector (ECD), capillary column DB-5, 30 m length, 0.25 mm internal diameter and 0.25 µm film thickness. The temperature of column, injector and detector was maintained at 280, 290 and 310 °C, respectively. The residues of deltamethrin were estimated by comparison of peak height of standard and that of the unknown samples run under identical conditions. Fairly good response was observed by injecting 0.1 ng of deltamethrin. When chili/soil sample (50 g) was processed and final volume constituted to 5 mL was injected into the instrument, there was no base line noise. Therefore, the limit of quantification (LOQ) was observed to be 0.01 mg kg^{-1} for both the substrates. The identities of residues in treated samples were confirmed by Gas Chromatograph–Mass Spectrophotometer in selective ion monitoring (SIM) mode in mass range 181, 253 m/z.

Chili and soil samples were spiked with deltamethrin at different levels and analysed as per methodology described above. The percent recoveries obtained at the various locations are presented in Table 2. The results have been reported without applying any correction factor.

Results and Discussion

The recovery of deltamethrin from chili fruits and soil samples spiked at 0.01, 0.05 and 0.10 mg kg^{-1} levels from all the four locations after following standardized analytical methodology was found to be quite consistent and more than 80 percent. The results have been reported as such without applying any correction factor. Average initial deposits of deltamethrin following application @17.5 g.i. ha^{-1} were found to be 0.49, 0.44, 0.21 and 0.21 mg kg^{-1},

Table 1 Weather parameters during experimental period on chili

Sr. No.	Weather parameter	I	II	III	IV
1.	Average minimum temperature (°C)	17.86	15.5	16.1	25.7
2.	Average maximum temperature (°C)	31.75	31.7	29.0	32.8
3.	Average minimum relative humidity (%)	42.03	33	53.95	75
4.	Average maximum relative humidity (%)	81.65	84	93.85	87
5.	Rainfall (mm)	375.20	Nil	58.3	170.6

Table 2 Recovery of deltamethrin at various spiking levels in chili and soil from different locations

Sr No.	Substrate	Fortification level	% Recovery, Mean ± SD[a]			
			I	II	III	IV
1.	Chili	0.01	82.72 ± 6.19	87.66 ± 3.06	81.67 ± 3.64	91.25 ± 2.33
		0.05	83.40 ± 3.30	84.64 ± 4.24	89.33 ± 2.93	94.09 ± 5.99
		0.10	82.82 ± 2.88	84.33 ± 2.52	88.00 ± 3.17	89.53 ± 3.19
2.	Soil	0.01	84.97 ± 2.76	86.33 ± 5.03	81.67 ± 4.92	85.85 ± 4.61
		0.05	86.62 ± 6.62	85.44 ± 4.26	89.33 ± 1.94	87.88 ± 3.15
		0.10	85.50 ± 3.50	85.33 ± 3.79	85.33 ± 3.71	91.25 ± 2.33

[a] Mean ± SD of three determinations

Table 3 Residues of deltamethrin on chili fruits after application of deltamethrin @ 17.5 g a.i. ha^{-1} from different locations

Days after application	Residues of deltamethrin (mg kg^{-1})			
	I	II	III	IV
Before application	BDL	BDL	BDL	BDL
0	0.49[a]	0.44	0.21	0.21
1	0.18 (63.27)	0.11(75.00)	0.15 (28.58)	0.03 (85.71)
3	0.04 (91.84)	0.05(88.89)	0.09 (57.14)	0.02 (90.48)
5	0.02 (95.92)	BDL	0.04 (80.95)	BDL
7	0.01 (97.96)	BDL	BDL	BDL
10	BDL	BDL	BDL	BDL
15	BDL	BDL	BDL	BDL
Red chili (At harvest)	BDL	BDL	BDL	BDL
Soil (At harvest)	BDL	BDL	BDL	BDL
$t_{1/2}$	0.69	0.61	1.99	0.36

Figures in parentheses indicate percent dissipation

[a] Mean of three replicates

*BDL b*elow determination limit of 0.01 mg kg^{-1}

Table 4 Residues of deltamethrin on chili fruits after application of deltamethrin @ 35 g a.i. ha^{-1} from different locations

Days after application	Residues of deltamethrin (mg kg^{-1})			
	I	II	III	IV
Before application	BDL	BDL	BDL	BDL
0	0.64*	0.69	0.39	0.37
1	0.34 (46.88)	0.18 (73.91)	0.26 (33.33)	0.06 (83.78)
3	0.10 (84.34)	0.08 (88.41)	0.12 (69.23)	0.03 (91.89)
5	0.08 (87.50)	0.01 (98.55)	0.07 (82.05)	BDL
7	0.07 (89.06)	BDL	0.04 (94.20)	BDL
10	0.04 (93.75)	BDL	BDL	BDL
15	BDL	BDL	BDL	BDL
Red Chili (At harvest)	BDL	BDL	BDL	BDL
Soil (At harvest)	BDL	BDL	BDL	BDL
$t_{1/2}$	1.14	0.70	2.06	0.38

Figures in parentheses indicate percent dissipation

[a] Mean of three replicates

*BDL b*elow determination limit of 0.01 mg kg^{-1}

respectively, at locations I, II, III and IV (Table 3). Low initial deposit at centre IV may be due to high average temperature but the same at location III may be due to different crop variety employed for the purpose. Residues of deltamethrin reached below determination limit of 0.01 mg kg^{-1} after 5 days at location II and IV and it took

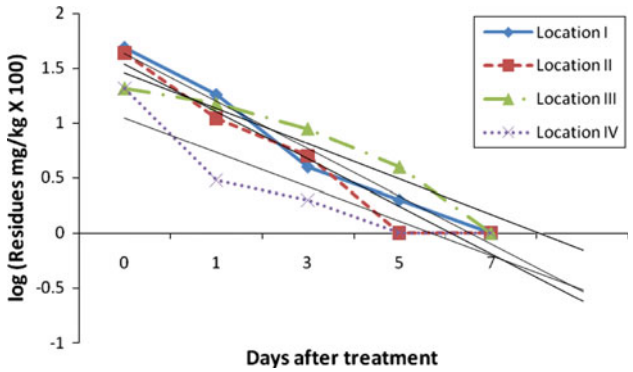

Fig. 1 Semi-logarithm graph (single dose) showing dissipation kinetics of deltamethrin on chili. Regression equation: *Location I* −0.436x + 1.72; *Location II* −0.099x + 0.417; *Location III* −0.1509x + 2.3422; *Location IV* −1.94x + 1.356

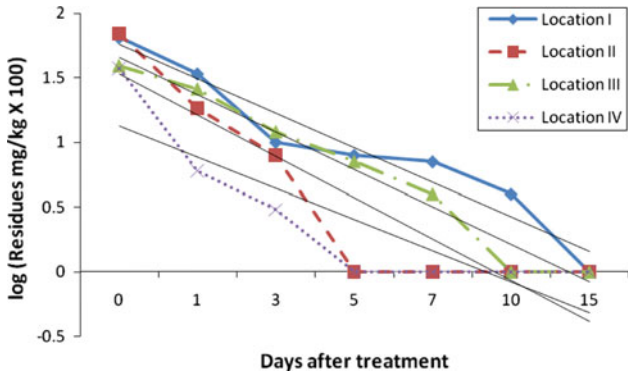

Fig. 2 Semi-logarithm graph (double dose) showing dissipation kinetics of deltamethrin on chili. Regression equation: *Location I* − 0.265x + 2.018; *Location II* −0.494x + 2.282; *Location III* − 0.1456 + 2.5599; *Location IV* −1.82x + 1.368

7 days for location III and 10 days for location I (Table 3). Similarly when deltamethrin was applied at double the dose, the average deposits at four locations were observed to be 0.64, 0.69, 0.39 and 0.37 mg kg^{-1}, respectively, at location I, II, III and IV (Table 4). These residues of deltamethrin declined to below determination limit of 0.01 mg kg^{-1} after 5, 7, 10 and 15 days, respectively, at locations IV, II, III and I (Table 4). The dissipation followed the first order kinetics at both the dosages at all the locations (Figs. 1, 2).

Half-life ($t_{1/2}$) of deltamethrin following application at 17.5 g.a.i. ha^{-1} at the four locations was found to be 0.69, 0.61, 1.19 and 0.36 days, respectively, at locations I, II, III and IV. The corresponding values of half-life ($t_{1/2}$) at double the dosages were observed to be 1.14, 0.70, 2.06 and 0.38 days, respectively, at locations I, II, III and IV. Red chili samples collected from all the four locations at harvest time did not show the presence of deltamethrin residues at determination limit of 0.01 mg kg^{-1}.

The persistence of deltamethrin has also been studied on tomato (Singh et al. 1989); cotton, cauliflower (Singh et al. 1990a, b); cabbage (Singh et al. 1992); gerbera (Hatzilazarou et al. 2004); sesame (Battu et al. 1992); brinjal (Singh and Kalra 1992); chick pea (*Cicer aerietinum* L.) during storage (Lal and Dikshit 2000); moongbean (Srivastava and Sehgal 2001); two varieties of wheat grains. WH-147 and HD-2687 during storage under laboratory conditions (Rani et al. 2006); rice grains (Rahula and Shah 2008); and the residues of deltamethrin dissipated below detectable limit at harvest. Therefore, the recommended use of this insecticide does not constitute any residue hazards to the consumers.

On the basis of the data generated, the Deltamethrin 10 EC has been registered for use on chili by Central Insecticide Board and Registration Committee, Ministry of Agriculture, Government of India and the MRL has been fixed by Food Safety and standard authority of India, Ministry of Health and Family Welfare, Government of India under Prevention of Food and Adulteration as 0.05 μg/g.

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