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Dissipation of Deltamethrin and Fenvalerate Residues in Green Gram (*Vigna radiata* (L.) Wilczek) under Indian Climatic Condition

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Green gram (Vigna radiata) (L.) Wilczek is an important food crop in Indian agriculture and considered to be one of the major sources of protein. It is widely used in India and is frequently damaged mainly by pod borers (Heiothes armigera Hb.), cut worms (Agrotis ipsilon Huf.) and stem fly (Melanagromyza phaseoli Coquilett.). The pod borers rank among most destructive insect pests of green gram and their control necessitates efficient pesticide application schedule. For controlling these pests, delta-methrin [(S)-α-cyano-3-phenoxybenzyl-(1R, Cis)-2-2-dimethyl-3-2(2,2-dibromovinyl) cyclopropane carboxylate] and fenvalerate [S,R)- α -cyano-3-phenoxybenzyl-(S,R)-2-(4-chlorophenyl)-3-methyl butyrate] are widely used during the cultivation of this crop. Studies on the persistence and degradation of these two insecticides in different plants in different climatic conditions have been reported (Awasthi 1989; Gupta et al. 1990, Kumar and Agnihotri 1991; Raha et al. 1993; Sukul and Handa 1987). However, data on the persistence of deltamethrin and fenvalerate in green gram are inadequate. Since these two insecticides are highly toxic and used at flowering and pod formation stage, toxic residues may remain in the crop including grains and pose hazards to the consumers. Therefore, it was felt necessary to study their dissipation pattern in green gram in Indian climatic condition to find the safe waiting period (T_{MRL}) and half-life values ($T_{\frac{1}{2}}$). An attempt was also made to evaluate the extent of residue level in soil which may be the ultimate sink of pesticides.

MATERIALS AND METHODS

Green gram (PS-16) was grown on sandy loam soil of IARI Farm at New Delhi (Sand 60%, Silt 26%, clay 14%, pH 8.2; Organic Carbon 0.46%) during the summer season in randomised block design with 4 replications for each treatment. Deltamethrin (2.8 EC) and fenvalerate (20 EC) were separately applied twice as foliar spray (0.02%) @ 700 lit/ha; 140 g ai/ha) at the flowering stage and 20 days later at the pod formation stage. For the control, water was sprayed @ 700 lit/ha. The details of the management practices are given as below :

Net plot size	:	10.24 sq m
Rows in each plot	:	14

Length of each row	:	3.20 m
Row to row distance	:	20 cm
Plant to plant distance	:	5 cm
Net seed rate	:	70 kg/ha
Maximum temperature	:	42° C
Minimum temperature	:	23° C
Relative humidity	:	43-95%
Rainfall	:	Traces
Fertilizer applied	:	N(10 kg/ha), P(40 kg/ha) and K(20 kg/ha)

In the present investigation, commercial formulations of deltamethrin (2.8 EC) and fenvalerate (20 EC) were analysed by converting organic chlorine and cyanide present in synthetic pyrethroids into inorganic chloride and cyanide by nascent hydrogen liberated by sodium and isopropyl alcohol. The supplied formulations were found to contain 2.55% for deltamethrin and 18.88% for fenvalerate. Thus for field application, the dilution of deltamethrin & fenvalerate was made on the basis of determined values.

Foliage samples from each replication were drawn separately at 0 (1 hr after spray), 5, 10 and 15 days after first application. Pod samples were collected at 0, 5, 7, 10 and 12 days after the second spraying, seeds, straw and pod cover samples at harvest. Soil samples were drawn at 0, and 20th day of first spray, 0 day of second spray and at harvest time with the help of a soil auger from a depth of 0-12 cm at different spots in each plot and representative sample of 25 g was taken by quatering.

25 g foliage and pod samples were chopped into small pieces and extracted with 100 mL acetone in a Waring blender for 2 min. The contents were filtered through Buchner funnel. The remnants were transferred back to the blender, re-extracted with 50 mL acetone and the contents were filtered again under suction. The filtrates were combined and concentrated to 20 mL in a Kuderna-Danish evaporator. The concentrated acetone extract was quantitatively transferred to a separatory funnel with acetone rinse, diluted with 200 mL of saturated aqueous solution of NaCl and re-extracted with n-hexane (3 x 50 mL). The n-hexane fractions were concentrated and dried over anhydrous sodium sulphate. The concentrated extracts of the samples were cleaned up by preparative thin layer chromatography using silica-gel plates of 1 mm thickness, K MnO_4-H_2So_4(100 mg K MnO_4 dissolved in 20 mL 50% H_2So_4) as chromogenic reagent and n-hexane-acetone (9:1), as the developing solvent. Seed, dry pod cover, straw and soil samples, after grinding to a coarse powder were extracted with n-hexane in soxhlet apparatus, refluxing over a waterbath at 80°C for 12 hr. In each case, the extracts were cleaned up by the acetonitrile partition technique (Jones and Riddick, 1952) followed by a second clean-up using thin layer chromatography. Pod samples with 0 day residues were washed and boiled separately to see the possibility of mitigation of residues by washing and boiling.

Deltamethrin and fenvalerate residues were measured by gas-liquid

chromatography, using Tracor MT 220 with Ni^{63} electron capture detector. Aliquots (1-10 µL size) of residue extracts were injected with U-shaped glass column 180 cm x 6.25 mm i.d. packed with 3% OV-17 stationary phase on 80-100 mesh chromosorb-W at a column temperature 255°C. The injection and detector temperature were 275°C each. The flow of the carrier-gas N_2 was 90 mL/min.

The efficiency of the extraction, clean-up and estimation procedures was checked from recovery experiments for deltamethrin and fenvalerate by fortifying the respective samples. The recovery values of deltamethrin and fenvalerate treated leaves, pods, seeds and soil ranged from 85 to 90%.and soil ranged from 85 to 90%. The rate of dissipation of deltamethrin and fenvalerate residues was worked out by determining the $T_{\frac{1}{2}}$ value. The residue data were further tested statistically to work out T_{MRL} values for obtaining the waiting period (Hoskins, 1961).

RESULTS AND DISCUSSION

The retention time values of deltamethrin and fenvalerate were 1.2 and 2.4 min. respectively. The response in both cases was linear in the range 1.0-2.0 ng.

The initial deposits of deltamethrin and fenvalerate on foliage collected 1 hr after spray after 14.1 and 13.1 ppm, respectively (Table 1). After 5 days the corresponding residue came down to 4.4 and 6.8 ppm, representing a loss of 68.7 and 47.9%. After 15 days deltamethrin and fenvalerate residues represented a loss of 95.4 and 86.8% respectively. Sharp fall in deltamethrin and fenvalerate residues in the first 5 days could be attributed to the physical removal by the weathering in view of their poor contact with plant material (Gunther and Blinn, 1955). The deposits of deltamethrin and fenvalerate on pods after the second spray were 0.9 and 1.1 ppm respectively (Table 2). The residue on pods were much less than those on leaves during the first spray, probably because of the smaller surface area of pods as compared to leaves and partial cover provided by the leaves during spraying of the toxicant on the crop.

Whenlog of ppm residues of deltamethrin and fenvalerate on leaves (Fig. 1) and pods (Fig. 2) were plotted against the number of days, a straight line was obtained, indicating that the rate of their dissipation followed a first order reaction. The residue data were also subjected to statistical analysis. So far no MRL of deltamethrin and fenvalerate has been assigned on green gram. On the basis of MRL of deltamethrin as assigned by FAO (1980) on pea (0.05 ppm) and of fenvalerate on beans (1.0 ppm), T_{MRL} for delta - methrin and fenvalerate has been worked out and suggested that deltamethrin and fenvalerate treated green gram pods may be used for consumption as green vegetables after 10.7 and 1.5 days, respectively.

Pods with initial deposits of 0.9 ppm deltamethrin and 1.1 ppm fenvalerate were washed with running water and boiled separately, the reduction of residues were 30 and 50%, respectively. Cooking

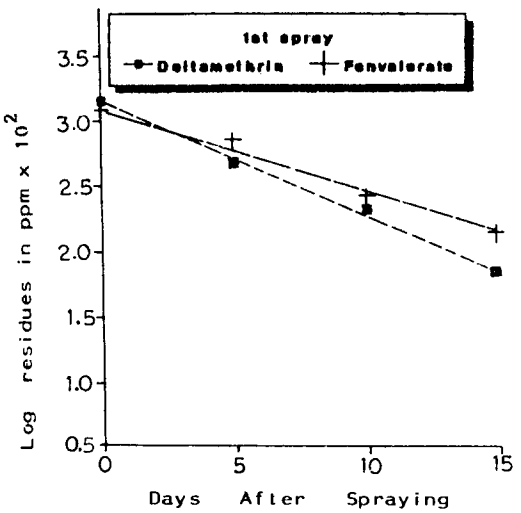

Fig. 1 Linear plot for first order reaction of deltamethrin and fenvalerate in/on green gram foliage after first spraying

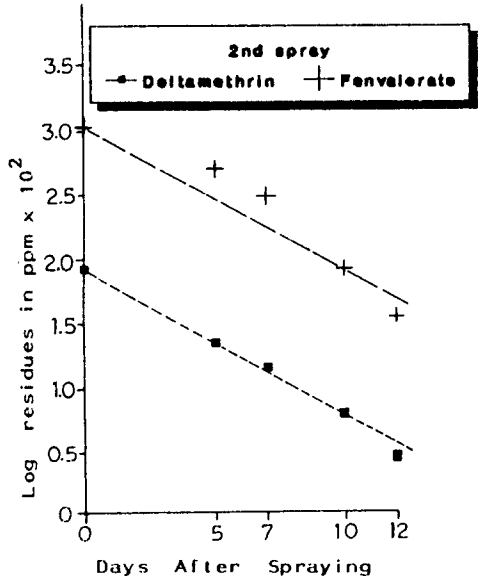

Fig. 2 Linear plot for first order reaction of deltamethrin and fenvalerate in/on green gram pods after second spraying

was found to be more effective than washing in reducing residues of insecticides. It is assumed that temperature played an important role in degrading insecticide residues and the portion which entered inside the pods through translocation was also subjected to degradation by cooking.

At final harvest, residues of deltamethrin and fenvalerate in straw, dry pod cover and seed samples were estimated (Table 2) and residues in gains were found to be below tolerance limit. In other experiments, when fenvalerate and deltamethrin were applied in chickpea at the same concentration as in the present investigation, the terminal residues in chickpea grains were also below tolerance limit (Sukul and Handa 1984; 1987). Lipoid solubility of fenvalerate is said to be one of the major factors in translocation of the toxicant from the treated plants to plant products.

Table - 1. Residues of deltamethrin & fenvalerate in/on green gram foliage after first spraying

Days after treatment	Deltamethrin residues (ppm)*	Progressive residues (%)	Fenvalerate residue (ppm)*	Progressive reduction (%)
0	14.1±1.1	-	13.1±0.6	-
5	4.4±0.6	68.7	6.8±0.2	47.9
10	2.0±0.1	85.8	2.6±0.3	79.9
15	0.6±0.1	95.4	1.7±0.3	86.8
Regression Equation	Y = 3.16-0.09 X		Y = 3.12-0.06 X	
$T_{\frac{1}{2}}$ (days)	3.3		5.0	
T_{MRL} (days)	27.3		18.7	

* Mean of 4 replications

Table - 2. Residues of deltamethrin and fenvalerate in/on green gram pod, after second spraying and at harvest in dry pod cover, straw and seeds

Days after treatment	Deltamethrin residues (ppm)*	Progressive reduction (%)	Fenvalerate residues (ppm)*	Progressive reduction (%)
0	0.9±0.2	-	1.1±0.0	-
5	0.2±0.0	73.5	0.5±0.2	55.4
7	0.2±0.0	81.6	0.3±0.1	72.2
10	0.1±0.0	91.9	0.1±0.0	92.4
12	-	-	-	-
Regression Equation	Y = 2.99-0.12 X		Y = 2.18-0.12 X	
$T_{\frac{1}{2}}$ (days)	2.5		2.5	
T_{MRL} (days)	10.7		1.5	
At harvest				
Straw	0.8±0.1		0.6±0.1	
Dry pod cover	0.8±0.1		0.6±0.1	
Seed	N.D.		-	

* Mean of 4 replications N.D. = Not detectable

Table - 3. Residues of deltamethrin and fenvalerate in green gram cropped soil at different intervals

Insecticide	Residues (ppm)*			
	0 day of first spray	20th day of first stray	0 day of 2nd spray	At harvest 30th day of 2nd spray
Deltamethrin	0.1	-	0.1	-
Fenvalerate	0.1	0.1	0.1	0.1

* Mean of 4 replications

Though soil was not directly treated with insecticides, it was found to contain traces of deltamethrin and fenvalerate (Table 3). This may be due to the fact of direct fall of insecticides from stem and foliage to the soil while applying, wash-off by rainfall and other mechanisms of physical removal of insecticides.

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