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HCH, Endosulfan, and Fluvalinate Residue Behavior in Pigeonpea (*Cajanus cajan* L. Millsp)

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Pigeonpea (Cajanus cajan L. Millsp) is one of the major pulse crop of India. The loss of pigeonpea crop due to pod and foliage pests is significant, the major pests being pod fly, hairy caterpillar, aphids, white fly, plume moth borer, leaf caterpillar and jassids. It is imperative to save every grain by chemical control methods but these toxicants should not leave unusually high residues on the edible parts. In this paper we report the residue behaviour of three different insecticides namely, hexachlorocyclohexane, endosulfan and fluvalinate on this crop.

MATERIALS AND METHODS

Pigeonpea variety UPAS-120 was grown at Indian Agricultural Research Institute, New Delhi during the summer season of 1987. Insecticides were HCH (BHC, 10% dust) @ 2.5 and 5.0 kg a.i./ha; endosulfan (Thiodan, 35 EC) @ 0.49 and 0.98 kg a.i./ha (0.07% and 0.14% @ 700 L/ha); and fluvalinate (Mavrik, 25 EC) @ 0.056 and 0.112 kg a.i./ha (0.007% and 0.014% @ 800 L/ha). Field experiment for each pesticide was performed in triplicate on three different plots and at each dose of application. A control experiment under similar conditions was also conducted.

The maximum and minimum temperatures during the crop season were 30.25°C and 10.34°C respectively with average relative humidity of 58.86%, average sunshine hours were 8.8. The crop was raised under irrigated conditions. There was no rainfall during this study.

A representative sample of green pods (50 g) collected on different intervals of time was blended three times with acetone (50 mL). The extract was concentrated under reduced pressure and diluted with saturated sodium chloride solution (150 mL). It was then partitioned three times with hexane (30 mL). The extract was cleaned-up by dropwise addition of concentrated sulphuric acid (25 mL), washed with distilled water and dried over sodium sulfate. The solution was concentrated to 10 mL and determined by gas liquid chromatography. The average recoveries for the HCH isomers viz., alpha, beta, gamma and delta ranged from 88-91%.

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At harvest time, pigeonpea grains (25 mg) were homogenized three times with acetonitrile-water (2:1, 50 mL). The extract was further partitioned into hexane and cleaned-up of coextractives as above.

The harvest time pod covers (husk, 10 g) were extracted in a Soxhlet with hexane (150 mL) for 4 hr. The extracts were subjected to clean-up in case of pods.

Fifty grams of sample of green pods were homogenized three times with isopropanol-hexane (1:3, 50 mL), and cleaned by following the procedure described by Gopal et al. (1988). Mean recoveries for endosulfan alpha, endosulfan beta and endosulfan sulfate were 97%.

At harvest time, the grains (25 g) were homogenized in a blender with acetonitrile-water (2:1, 100 mL). It was diluted with saturated solution of sodium chloride and partitioned three times with hexane (30 mL).

The dried pod covers (husks 10 g) were extracrted with hexane (100 mL) in a Soxhlet apparatus for 4 hr. The clean-up was effected as given above.

Samples of pigeonpea (green pods, 50 g) were extracted and residues quantified by gas liquid chromatography using a procedure described by Gopal et al. (1987a). Recoveries ranged from 95-97%.

Confirmation techniques were applied by making use of alternate column packing of different polarity in GLC.

The samples were analysed by gas liquid chromatography using Varian 3400 GLC fitted with an electron capture dector (Ni^{63}). The column used for the estimation of HCH, endosulfan and fluvalinate was 1.5% OV 17+1.95% OV 210 on chromosorb WHP and nitrogen flow rate maintained at 30 mL/min.

The temperatures maintained were column 175°C, injector 200°C and detector 250°C for determination of HCH residues. The limit of detection of alpha, beta, gamma and delta were 0.02, 0.014, 0.005 and 0.006 ug/g respectively.

Endosulfan samples were analysed at temperatures of column 225°C and detector 275°C. The limit of detection from fortified samples were 0.06, 0.07 and 0.01 ug/g for alpha endosulfan, beta endosulfan and endosulfan sulfate respectively.

Fluvalinate was estimated isothermally at temperatures of column 250°C, injector 265°C and detector 300°C. The limit of detection for fluvalinate under the above stated conditions was 0.01 ug/g.

RESULTS AND DISCUSSION

The cumulative HCH residues dissipated from the crop rapidly compared to the loss of endosulfan and fluvalinate. It is pointed out that emulsifiable concentrate of endosulfan and fluvalinate were used while dust formuation of HCH was applied. The initial deposits of total HCH, endosulfan and fluvalinate were 13.19, 6.82 and 0.43 ug/g respectively at the recommended doses. The values vary greatly because of the difference in the rate of application. The loss of HCH was 97% in 15d samples while in endosulfan and fluvalinate the loss was recorded as 85% and 94% respectively in the same time period at the lower dosage of application. The initial loss of the insecticide (i.e. from 0 to 1d) was 62%, 45% and 14% in endosulfan, HCH and fluvalinate respectively.

It is evident from Table 1 and Figure 1 that alpha and gamma isomers of HCH dissipate faster than beta and delta isomers. The

Table 1. HCH residues[a] (ug/g) pigeonpea

Sampling day	Rate[b] of application	alpha	beta	gamma	delta	Total HCH	% dissipation
0(1hr)	2.5	8.17	1.76	2.35	0.91	13.19	
	5.0	23.97	3.58	6.05	1.61	35.21	
1	2.5	5.03	1.29	0.46	0.43	7.21	45.3
	5.0	14.15	2.38	1.16	1,54	19.23	45.3
3	2.5	1.63	0.63	0.05	0.12	2,43	81,4
	5.0	8.72	1,34	0.38	0.29	10.73	69.5
8	2.5	0.19	0.43	0.01	0.05	0.68	94.8
	5.0	1.95	0.87	0.03	0.12	2.97	91.5
10	2.5	0.11	0.38	0.008	0.036	0.53	95.9
	5.0	0.95	0.30	0.01	0.05	1.31	96.2
15	2.5	0.08	0.30	0.005	0.02	0.405	96.8
	5.0	0.12	0.24	0.005	0.03	0.39	98.8
Harvest	2.5	0.26	1.66	0.07	0.07	2.06	-
	Pod cover						
	Grain	0.07	0.02	0.006	0.01	0.11	-
	5.0	0.43	3.90	0.11	0.26	4.70	-
	Pod cover						
	Grain	0.07	0.05	0.008	0.04	0.16	-

[a]Average of three replicates, [b] kg a.i./ha

analytical samples of HCH isomers were obtained by repeated recrystallisation of HCH. It is apparent from the data (Table 1) that beta tends to persist with time. Till date, there is no evidence of metabolic interconversion of the isomers in the plant

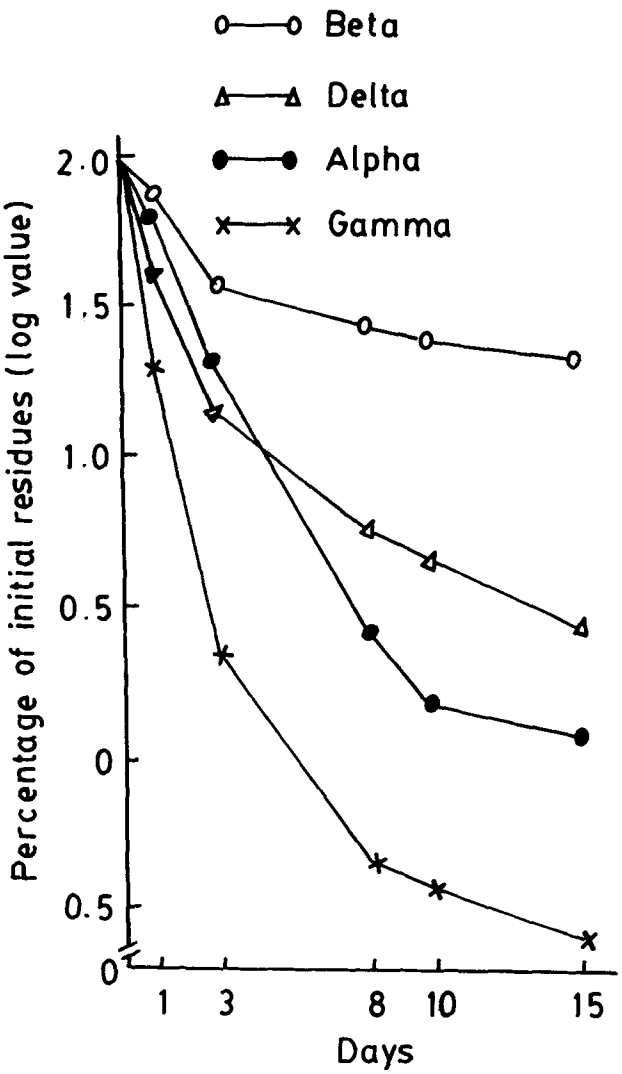

Figure 1. Decline of HCH isomers on pigeonpea

according to Kalra et al. (1988). The waiting period of total HCH on pigeonpea cannot yet be suggested as its Maximum Residue Limit has not yet been documented.

Endosulfan is an effective cyclodiene insecticide against pod borers and has been recommended by All India Coordinated Research Project on Pulses. It is evident from the work reported by Santharam (1981) that endosulfan has been found to be more

effective against pod borers as compared to biological control by nuclear polyherosis virus (NPV).

The data in Table 2 reveals that endosulfan sulfate, a toxic metabolite of endosulfan appears in the 2d samples, builds up in

Table 2. Endosulfan residues[a] (ug/g) in pigeonpea

Sampling day	Rate[b] of application	alpha	beta	alpha +	Endosulfan sulfate	Total endosulfan	%Dissipation
0(1hr)	0.49	0.04	2.78	6.82	-	6.82	-
	0.98	7.53	6.16	13.69	-	13.69	-
2	0.49	1.06	1.48	2.54	0.06	2.60	61.87
	0.98	2.24	2.92	5.16	0.10	5.26	61.58
5	0.49	0.53	1.13	1.66	0.11	1.77	74.05
	0.98	0.91	1.76	2.67	0.21	2.89	78.89
9	0.49	0.41	1.02	1.43	0.07	1.50	78.00
	0.98	0.47	1.13	1.60	0.14	1.74	87.23
15	0.49	0.21	0.63	0.84	0.05	0.89	86.95
	0.98	0.36	0.90	1.26	0.11	1.37	89.99
Harvest grains	0.49	0.06	0.08	0.14	0.01	0.15	-
	0.98	0.25	0.14	0.39	0.03	0.42	-

a Average of three replicates, lb kg a.i./ha

the 5d samples and thereafter declines gradually. Similar observation was reported by Estesen (1979) on cotton in 3d samples. However, Mackneil et al. (1979) did not detect any endosulfan sulfate on pears, pea and grapes till the 6th day. Endosulfan sulfate was prepared in the laboratory by potassium permanganate oxidation of alpha endosulfan in presence of acetic acid.

Figure 2 also illustrates that the loss of alpha isomer is fast as compared to the rate of decline of the beta isomer. The method of clean-up of endosulfan followed in this experiment has been simplified as compared to that followed by Estesen (1979), where the crop was extracted with benzene and clean-up affected with florisil.

The persistence pattern of fluvalinate has been studied on a number of other crops viz., on tobacco (Chopra, 1977), cotton (Agnihotri, 1986) and tea (Gopal, 1987b). Fluvalinate has been reported (Rajakulendran, 1982) to be less toxic to the predator in tobacco budworm. It has been shown to be safer than flucythrinate and permethrin (Rajakulendren, 1982). The data (Table 3) indicate the rate of dissipation of fluvalinate from

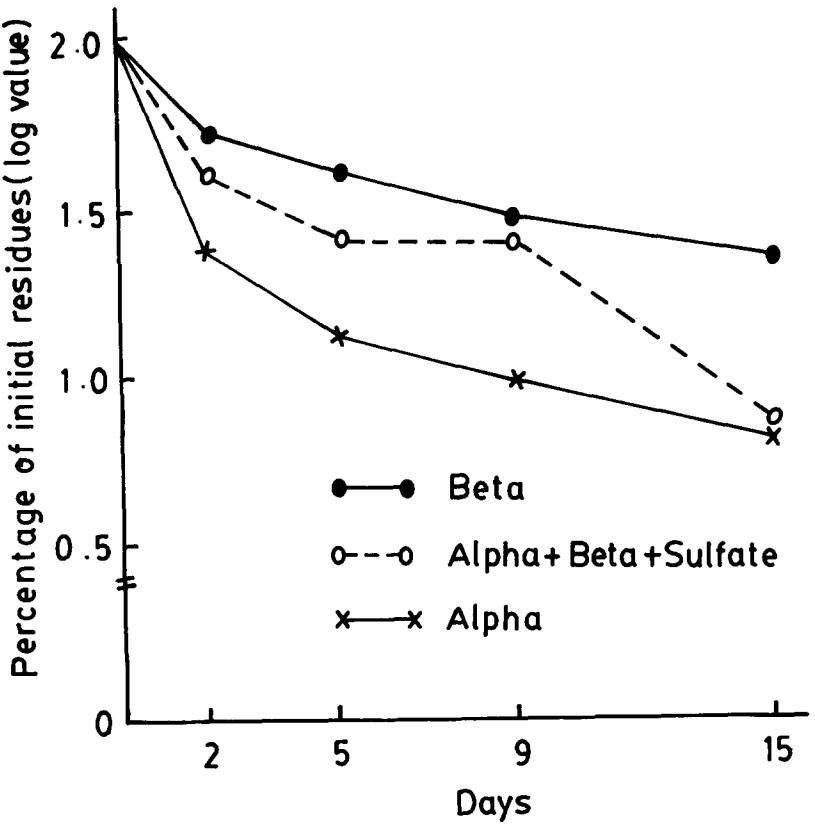

Figure 2. Decline of endosulfan isomers and its metabolites on pigeonpea

the crop. At harvest time the residues of fluvalinate were not detected in the seeds. This is the first report of the persistence of fluvalinate on a pulse crop namely pigeonpea. The tolerance level of fluvalinate on pulses has yet to be established, the residues data generated may help in proposing the MRL of fluvalinate.

The half lives of gamma HCH, total HCH, endosulfan, fluvalinate are given in Table 4. HCH and endosulfan persist in pod covers in more amounts as compared to fluvalinate at the harvest time. While HCH and endosulfan were recorded in the harvest grains, fluvalinate was not present in harvest grain samples. This reinforces the view that the newer pesticides especially the synthetic pyrethroids have an edge over the other pesticides due to their enhanced activity even at lower dosages of application.

Table 3. Fluvalinate residues[a] (ug/g) in pigeonpea

Sampling	Rate[b] of application	Average residues	%Dissipation
0(1hr)	0.056	0.43	-
	0.112	0.88	-
1	0.056	0.37	14.1
	0.112	0.58	34.0
4	0.056	0.28	33.8
	0.112	0.30	65.8
7	0.056	0.08	80.5
	0.112	0.24	72.8
10	0.056	0.06	85.2
	0.112	0.13	85.0
15	0.056	0.02	94.4
	0.112	0.05	94.3
Harvest	0.056	ND	-
Grains	0.112	ND	-

A Average of three replicates, b kg a.i./ha
ND - not detectable

Table 4. Half life, waiting period and regression equation

Pesticide	Rate of application (kg a.i. per ha)	Half Life RL_{50} (days)	Waiting period (days)	Regression equation Y =
HCH	2.6	2	1	2.74-0.16x
(gamma isomer)	5.0	2	3	2,90-0.02x
Total HCH	2.5	3	-	2.87-0.10x
	5.0	3	-	3.41-0.13x
Endosulfan	0.49	7	8	2.67-0.04x
(alpha+beta+ sulfate)	0.98	5	10	2.94-0.06x
	0.056	4	-	1.65-0.08x
Fluvalinate	0.112	4	-	1.82-0.07x

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