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Behavior of Lindane and Endosulfan on Cowpea

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Cowpea is one of the major pulse crop durinq the (Kharif season July-September) in India. It is infested by all the major pests of pulses, namely pod borers, aphids and hairy caterpillar, which cause reduction in yield. Till recently HCH (hexachlorocyclohexane) was beinq used (Mukherjee eta1.1992) for the control of the insect pests in pulses. HCH dust was popular among the farmers inspite of its containinq the other inactive isomers of HCH, viz., alpha, beta and delta which did not possess insecticidal activity. The use of these unwanted isomers led to their accumulation which is responsible for bioaccumulation in the food chain. This led to the introduction of the active isomer of HCH, lindane in the country and made another orqanochlorine insecticide, endosulfan, which is relatively less persistent (Gopal and Mukherjee 1993a), amonq the existinq orqanochlorines, an insecticides of choice in farmers field.

The introduction of lindane EC and dust formulation of endosulfan prompted us to evaluate the residue behavior of lindane and endosulfan on cowpea crop.

MATERIALS AND METHODS

Cowpea crop, variety Ganqa Safed 2 was qrown at Indian Agricultural Research Institute, New Delhi durinq the Kharif season of 1996. Insecticides applied were lindane dust (Hemalin - 20, 20 EC) @ 250 and 500 g a.i./ha 10.05 and 0.1% @ 500 L/ha) and endosulfan dust (Thiodan-2, 2% dust) @ 350 and 700 g a.i./ha. The field layout was randomised block desiqn. The experiment was performed in triplicate for each pesticide on three different plots and at each dose of application. A control experiment under similar conditions was also conducted. The insecticides were applied at 50% pod formation staqe.

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The maximum and minimum temperatures durinq the crop season were 33.26°C and 24.52°C, respectively with averaqe relative humidity of 72.52%., average sunshine hours were 8.19. The crop was raised under irriqated conditions. The total1 rainfall durinq the study was 3.98 mm.

A representative sample of cowpea pods (25g) collected on different intervals of time was blended three times with acetone (50 mL) in a Warinq blender. The extract was concentrated under reduced pressure and diluted with saturated sodium chloride solution (150 mL). It was then partitioned into hexane (30mL). 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 qas liquid chromatoqraphv. At harvest time, cowpea qrains were homoqenized three times with acetonitrile water (2:l. 50mL). The extract was partitioned into hexane and cleaned-up of co-extractives as above.

The harvest time pod covers (husk, 10g) and qrains (powdered. 25g) were extracted in a Soxhlet extractor with hexane-acetone (150 mL) for 6 hr. The extracts were subjected to clean-up as in case of pods.

The endosulfan residues were extracted from cowpea pods (25g) by homoqenizinq three times with isopropanol-hexane 11:3, 50mL) and cleaned by followinq the procedure described by Gopal etal. (1988). At harvest time, the qrains were qrinded in a Wiley Mill, and 25 g sample was extracted in a Soxhlet extractor for 6 hr with hexane-acetone 11:l. 250 mL). The extract was concentrated and made up in hexane-acetone 19:1, 100 mL) and subjected to charcoal clean up as above.

The residues of lindane and endosulfan were quantified by gas liquid chromatoqraphy usinq an electron capture detector (Ni^{63}) in Hewlett Packard 5890 Series I. The column used for the determination was 3% OV-17 (qlass, 2m lona and 2mm ID) on chromosorb WHP. The carrier qas, nitroqen flow was maintained at 30 mL/min. The temperatures maintained were column 220° C injection port 250°C and detector 300°C. The sensitivity for lindane was 0.001 ug, 0.005 ug for alpha endosulfan and beta endosulfan and 0.06 ug for endosulfan sulfate.

A recent review (Mukherjee and Gopa1,1996aj lists various column packinqs and temperature conditions that can be used to confirm the identity of the orqanochlorine insecticides usinq an alternate column polarity.

RESULTS AND DISCUSSION

The percent recovery of lindane and total endosulfan from cowpea pods ranqed from 88-91. The cumulative residues of lindane dissipated from the crop faster than endosulfan. The percent dissipation by day-16 for is lindane is about 98, while that of endosulfan is only 76 (Table 1 and 2).

Table 1. Residues of Lindane (ug g^{-1}) in Cowpea Pods

Samplinq day	Rate[a] of application	Averaqe[b] residues	% Dissipation
0(1hr)	250	0.250	
	500	0.510	
1	250	0.093	62.8
	500	0.188	63.13
3	250	0.077	69.2
	500	0.162	68.2
5	250	0.042	83.2
	500	0.089	82.5
7	250	0.028	88.8
	500	0.077	84.9
10	250	0.017	93.2
	500	0.035	93.1
16	250	0.005	98.0
	500	0.017	96.6
Harvest	250	0.001 or Trace	-
Pod covers	500	0.006	-
Grains	250	ND	-
	500	0.003	-

Replicates, [a], g a.i. ha^{-1}: [b], Averaqe of three replicates
ND - Non detectable ≤ 0.001 ug g^{-1}

In the samples analysed for lindane no other HCH isomers were detected indicatinq that lindane is not interconverted to other isomers of HCH, namely alpha. beta and delta. This is also evident when lindane EC was sprayed on chickpea crop (Gopal and Mukherjee. 1993b). In comparinq the application of HCH dust on chickpea and pigeonpea the dissipation pattern of gamma isomer,it was found similar to as in this study (Mukherjee etal. 1989).

The dissipation pattern of endosulfan (Table 2) shows that endosulfan, which is a mixture of two stereoisomers alpha and beta, appears on day-0 and slowlv dissipates with time. Alpha isomer of endosulfan dissipates to 72 percent by day-16 while beta isomer dissipates by

81 percent in the same period of time, at both the concentrations of application. Endosulfan sulfate, a toxic metabolite was first detected in day-5 samples. which then peaked on day-10 and then sraduallv declined by day-16 in the samples (Mukherjee etal. 1993a). The other deqradative metabolites endosulfan lactone. endosulfan ether,endosulfan diol were not determined as they are non toxic to mammals. The alpha endosulfan is known to undergo interconversion in plants to beta endosulfan as observed by Mukherjee and Gopa1,1994a when pure emulsifiable concentrate of alpha isomer and beta isomer were applied separately on chickpea crop. The data (Table 21 shows that alpha isomer dissipates from 15.6 percent on day-l to 72.6 in day-16.in contrast to the dissipation rate of beta endosulfan which is 51 percent by day-1 and reaches a maximum of 83 percent by day-16. The data reveals the rate of loss is 57 percent in alpha, whereas it is only 32 percent in case of beta isomer, indicating that alpha degrades faster with time while beta degrades slowly and tends to accumulate. This may be due to interconversion of alpha isomer into betaisomer as is evident by the report of Mukherjee and Gopal (1994a). Although beta enosulfan is known to persist it has been very effectively degraded by *Asperigillus* niger(Mukherjee etal. 1994b). No endosulfan sulfate is detected in

Table 2 Persistence of Endosulfan on Cowpea Pods

Samplina day	Rate[a] of application	Average[a] Residues (ug g^{-1}) alpha	beta	endosulfan sulfate	Total	%Dissipation
0	350	0.74	0.40		1.15	
	700	1.95	0.96		2.91	
1	350	0.62	0.24		0.86	29.6
	700	1.74	0.63		2.37	18.2
5	350	0.45	0.16	0.01	0.63	48.5
	700	1.24	0.37	0.053	1.66	42.7
10	350	0.32	0.16	0.021	0.50	59.0
	700	0.85	0.26	0.052	1.17	59.8
16	350	0.20	0.08	0.005	0.29	76.4
	700	0.53	0.18	0.008	0.72	75.1
Harvest	350	0.09	0.001	-	0.09	
Pod cover	700	0.16	0.003	-	0.17	
Grains	350	0.007	0.024	-	0.03	
	700	0.009	0.051	-	0.06	

[a], ga.i.ha-L: [b], averaqe of three replicates

harvest grains, but the percent of beta isomer is more than the alpha isomer in the grains.

Table-3 Half Life and Regression Equation

Pesticide	Treatment g a-i. ha^{-1}	RL$_{50}$ (day)	Regression Equation y=
Lindane	250	3	2.18 -0.09x
	500	4	2.47 -0.09x
Endosulfan	350	8	0.085-0.04x
	700	8	0.463-0.04x

The half life of lindane was 3 days and that of endosulfan was 8 days at the recommended rate of application (Table 4).The regression equation is also given in the table. The waiting period of lindane and endosulfan on cowpea cannot be proposed as the Maximum residue limit (MRL) of both lindane and endosulfan is not yet documented by FAO/WHO.During a monitoring experiment conducted in the market samples residues of both these insecticides were detected (Mukherjee and Gopa1,1996b) in vegetables ,pulses and other commodities.It is therefore imperative to establish the MRL of these insecticides on pulses. This work was a part of the programme under All India Coordinated Project on Pesticides Residues.

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