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Cypermethrin and Deltamethrin Concentration and Contamination in Pulses from Application to Jute Sacks

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Chemicals such as malathion, fenitrothion, DDVP, EDB, BHC etc. have been used for the protection of food grains during storage (Attia 1981; Dikshit 1985) but many of these left the high concentrations and their metabolites in the commodities. Some of them were associated with undesired traits such as high persistence, carcinogenicity, deposition in tissues and development of resistance (Cogan 1982; Storey et al.1982; Hazarika and Dikshit 1992; George and Dikshit 1995). The presence of such concentrations of insecticides in the food grains assumes toxicological significance and consumption of such contaminated grains might risk the human health.

While choosing the suitable insecticides for the protection of pulses in storage, it is important to see that the insecticides have got least toxicity profile, low mammalian toxicity and wide spectrum of action. Cypermethrin and deltamethrin are highly potent synthetic pyrethroids (Pap et al.1996) with all required features as grain protectant (Rahman and Yadav 1985; Noble and Hamilton 1985; Yadav 1987; Ramzan et al. 1989; Hazarika and Dikshit 1992; George and Dikshit 1995). Laboratory studies were therefore undertaken to explore the possibility of using cypermethrin and deltamethrin as protectant for cowpea and lentil grains in storage by designing experiments to examine (i) the concentration of insecticides available in/on pulses at varied times during storage (ii) effect of decontamination to lessen the risk to humans and (iii) effect on germinability of seeds.

MATERIALS AND METHODS

The cowpea (*Vigna synensis* L. Savi ex Hassk.) and lentil (*Lens culinaris* Medik. Syn. *L. esculenta* Moench.) grains with no infestation were procured from Cooperative Stores, New Delhi. The grains were cleaned of extraneous materials, solar dried and screened through mesh to ensure uniformity. These were weighed in 2 kg lots and filled separately in jute sacks of 3 kg capacity (0.34 m x 0.30 m). The open end of the bags were stitched. Aliquots of 1 mL cypermethrin 10 EC (DE-NOCIL Crop Protection Ltd, Mumbai, India) and 3.57 mL of deltamethrin 2.8 EC (Hoechst Schering Agr Evo Ltd, Mumbai, India) were taken separately in volumetric flasks (100 mL) and diluted upto mark with distilled acetone. Both the solutions yielded a concentration of 1 mg ai mL^{-1}. From these spray solutions, 3.06 and 5.10 mL were sprayed separately on both the sides of jute sacks filled with the cowpea and lentil grains. The sprays gave an intended deposits of each insecticide @ 15 and 25 mg ai m^{-2} on sacks surface (both the sides; total area $0.204 m^2$). All the treatments were made in three replicates including control. The respective control sacks containing grains were sprayed with 3.06 and 5.10 mL of acetone. The sacks were labelled and stored in ventilated chamber for three months. Sufficient space was kept between the replicates of one treatment and the other during storage to avoid mixing.

In order to determine the concentration of insecticides and contamination in the grains at various intervals, grain samples (25 g) were drawn randomly from each treatment and replicate on 0 day (after 1 hr of treatment) and at one month interval upto three months. For withdrawing samples, each bag was opened and the grains were transferred in a tray, thoroughly mixed and then a sample of 25 g was taken. After taking samples the remaining grains were put back in the original sacks and stitched and kept at marked place.

Grain samples were ground with the help of electrical grinder and transferred to 250 mL conical flasks. To the contents, 50 mL distilled hexane-acetone (9:1) was added pand the flasks were shaken with the help of mechanical shaker for 30 min. The contents were then filtered through Whatman No.1 filter circles. The remaining materials in the flasks were again agitated with 20 mL of same solvent mixture for 5 min. The rinsate was transferred quantitatively through the same filtering system. The final volume of the extract was made to 100 mL.

The extracts were concentrated to 5 mL and passed through glass columns (35 cm x 2 cm id) packed with 10 g activated neutral alumina over 5 g anhydrous sodium sulphate. The elution was done with 100 mL of the same solvent mixture. The eluates obtained were concentrated by a rotary flash evaporator and transferred quantitatively to 25 mL volumetric flasks. The volume was made up to the mark with the same solvent mixture.

The cleaned extracts were analysed by gas liquid chromatography (Hewlett Packard 5890 A) equipped with Ni^{63} detector. The GLC conditions were: glass column (1m x 2 mm id) packed with 3% OV-17 coated with Chromosorb; column temperature 270°C; injector and detector temperature 300°C; N_2 flow 30 mL min^{-1}.

The efficiency of extraction, cleanup and determinative steps was checked by fortifying the cowpea and lentil grains. Untreated grains (25 g) were spiked with 25 µg of cypermethrin and deltamethrin separately and kept 24 hr. Next day foritfied samples were extracted, cleaned up using neutral alumina (10 g), charcoal (0.5 g) and Florisil (10 g) and analysed the insecticides as before.

The effect of some simple decontamination processes like washing and washing plus steaming of the contaminated grains in mitigating the concentration of insecticides was monitored on 0 day (1 hr after treatment) and 2 months time. The pulse samples (50 g) were drawn from each treatment and replicate as described earlier.

The samples were divided into two parts. In the first case 25 g grains were washed two times with water (2 x 50 mL), dried, extracted, cleaned up and quantified the concentrations of the insecticides left. In the second, the grains were washed two times with water (2 x 50 mL) and steamed till grains became soft. These steamed grains were allowed to reach room temperature, crushed and extracted two times with acetone (2 x 100 mL) by agitation in a mechanical shaker. Supernatants were concentrated to 10 mL in a rotary flash evaporator and transferred quantitatively in a separatory funnel, diluted with water and partitioned three times with n-hexane (3 x 50 mL). The hexane extract was concentrated, cleaned up and quantified as before.

The effect of cypermethrin and deltamethrin treatments on the germination of cowpea and lentil grains was also seen.

RESULTS AND DISCUSSION

The analytical data on the recovery of insecticides from spiked grains extracted with hexane-acetone (9:1) followed by clean up using alumina, charcoal and Florisil is given in Table 1.

Table 1. Recovery of insecticides from fortified pulses

Adsorbent	Pulse	Amount recovered (μg)	
		Cypermethrin	Deltamethrin
Alumina	Cowpea	23.01 (92.0)	23.60 (94.4)
	Lentil	22.60 (90.4)	23.32 (93.3)
Charcoal	Cowpea	18.84 (75.4)	20.00 (80.0)
	Lentil	18.30 (73.2)	19.30 (77.2)
Florisil	Cowpea	24.10 (96.4)	24.50 (98.0)
	Lentil	23.60 (94.4)	23.84 (95.4)

25 g grains were fortified with 25 μg of insecticides. Figures in parentheses are percent recovery

Cypermethrin was recovered to the extent 92, 75.4 and 96.4%, respectively by using alumina, charcoal and Florisil from fortified cowpea grains whereas recoveries of deltamehrin were 94.4, 80 and 98%. It is seen from the data that the recoveries were little more in the case of deltamethrin from all the adsorbents as compared to that of cypermethrin irrespective of cowpea or lentil. However recoveries of deltamethrin were lower in case of lentil as compared to cowpea and the same was true for cypermethrin also. The performance of Florisil was better than the other two adsorbents for both the insecticides and from both the pulses. Charcoal gave the lowest recoveries whereas alumina ranked second and differences between alumina and Florisil were marginal (about 2 to 4%).

The better recoveries by Florisil may possibly be due to the fact that it is more inert than alumina in retaining both the insecticides whereas low recoveries from charcoal were due to its high adsorptive power. Further, little higher recoveries of deltamethrin to that of cypermethrin may be attributed that it is more polar than cypermethrin and due to high coloured pigments lentil showed less recoveries for both the insecticides. Florisil is costlier and less available, therefore, experimental samples were cleaned up by using alumina. Based on the recovery values, a necessary correction in the data was incorporated.

Table 2. Amount of insecticides on pulses resulting from external spray on sacks

Time (month)	Treatment ($mg\ m^{-2}$)	Amount of insecticide ($mg\ kg^{-1}$)			
		Cypermethrin		Deltamethrin	
		Cowpea	Lentil	Cowpea	Lentil
0 day (1 hr)	15	0.058	0.060	0.070	0.074
	25	0.070	0.080	0.076	0.086
1	15	0.046 (20.68)	0.050 (16.66)	0.059 (15.71)	0.061 (17.56)
	25	0.055 (21.42)	0.062 (22.50)	0.062 (18.48)	0.067 (22.09)
2	15	0.021 (63.79)	0.026 (56.66)	0.040 (42.85)	0.032 (56.75)
	25	0.032 (54.28)	0.042 (47.50)	0.039 (48.68)	0.044 (48.43)
3	15	ND (100.00)	ND (100.00)	ND (100.00)	ND (100.00)
	25	ND (100.00)	ND (100.00)	ND (100.00)	ND (100.00)

ND, not detectable; Figures in parentheses are percent cumulative loss

Initial penetration of cypermethrin was 0.058 and 0.070 mg kg^{-1} in cowpea grains after 1 hr of spray treatment from both the rates of application (Table 2). The contamination levels decreased with time phase and reached to non detectable value in a period of 3 months. Lentil had little higher amounts of cypermethrin throughout and its contamination dislodged by 47.50 to 56.66% in two months as compared to 54.28 to 63.79% from cowpea. The grains did not show the presence of either of the insecticides in 3 months time.

The response of deltamethrin was always found higher for both cowpea and lentil to that of cypermethrin. In this case also lentil grains possessed more amount of deltamethrin than cowpea (Table 2). Observation of the records showed that both the insecticides disappeared faster in cowpea and retained more in lentil. This observation can be attributed to the fact that the effects of most insecticides appear to be connected due to their lipophilicity and the dynamic function of seed membrane or seed coat and pigments present in the substrates. Partition studies indicate that membrane fluidity and insecticide structure are main parameters affecting pesticide incorporation and toxicity. Possibly less moisture, high pigments present in lentil and lipophilicity of the two insecticides caused more retentation. This fact is again supplemented by less recovery of cypermethrin and deltamethrin in lentil to that of cowpea (Table 1) due to above parameters.

The maximum residue limits of these insecticides have not been fixed for cowpea and lentil in India. The FAO/WHO (1993) has fixed the Maximum Residue Limits (MRL) of 0.05 mg kg^{-1} on beans and peas for cypermethrin and 1 mg kg^{-1} for beans and lentil for deltamethrin. If these values are adopted for cowpea and lentil in India, it would be seen that the deltamethrin treatments were safe but cypermethrin contaminated grains will pose hazards if offered for consumption upto one month of application. However after one month the concentrations in the grains were lower than the MRL values.

The reported concentrations obtained may be connected to health hazards and hence decontamination was studied in mitigating the insecticides. Contaminated cowpea grains obtained after 1 hr of treatment, when washed with water, reduced the concentration of cypermethrin from 0.058 and 0.070 mg kg^{-1} to 0.034 and 0.037mg kg^{-1} from both the rates of application and dislodged 41.4 and 47.1% cypermethrin. Lentil grains when washed with water dislodged 45 to 46.2% cypermethrin. Almost similar reductions were noticed in case of cowpea (40 to 47.3%) and lentil (45.9 to 47.7%) contaminated with deltamethrin. Thus the contaminated grains were found safe when washed with water. The process of washing followed by steaming of contaminated grains in open container rendered the pulses free from hazards and ensured further safety. The insecticidal treatments did not cause any significant difference in germination, visual change in quality and colour of the grains when compared with control.

To conclude, deltamethrin can safely be used on jute sacks filled with pulses without causing appreciable contamination in the grains whereas cypermethrin required one month allowance. However, the decontamination process discussed as above ensured safety.

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