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MONITORING OF MULTIPLE PESTICIDE RESIDUES IN COTTON SEEDS DURING THREE CROP SEASONS

ZAHIDA PARVEEN, IRSHAD A. K. AFRIDI,* S. Z. MASUD AND M. M. H. BAIG

Pesticide Research Laboratory, Tropical Agricultural Research Institute,Karachi University Campus, Old Block Nos. 09 and 10, Karachi-75270, Pakistan

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After having established proper analytical methodology for multiple pesticide residues, major cotton growing areas of Pakistan were surveyed extensively and 250 samples of cotton seeds were drawn from progressive farmers' fields and different ginning factories during three crop seasons (June, 1986-January, 1989). Laboratory investigation of these samples showed contamination in 73.6 % samples with 24 different pesticides/metabolites. The results indicated that out of 24 pesticides, 9 were organochlorine, 8 organophosphorus and 7 synthetic pyrethroid compounds. MRLs exceeded in 40.6% samples. The most frequently occuring pesticides were cyhalothrin, dimethoate, DDT and its metabolites, endosulfan and monocrotophos.

Key words: Monitoring, Pesticide residues, Cotton seeds.

Introduction

Information on pesticide residue levels in agricultural commodities intended for human consumption is essential for marketing and human safety. Such information is scanty in Pakistan and other underdeveloped countries. The efforts to organize research in this area from academic, economic and health perspectives were, therefore, initiated by carryingout studies using cotton seed as a model. It is estimated that 80 % of the total pesticides, consumed in Pakistan, are used for the protection of cotton crop. Most of the compounds are lipophilic in nature and their undesirable contamination of cotton seeds, due to excessive use of these pesticides, would pose potential risk to human health.

Widespread use of pesticides has resulted in their presence and persistence in various crops and their occurrence in food and feed products. The residue of aldrin was reported in cotton seed and in its oil, 75 days after treatment of cotton field [1]. The total toxic aldicarb residue was also investigated in soil, cotton seed and cotton lint [2]. Chawla and Kakkar evaluated the residues of endosulfan, fenitrothion, quinalphos and carbaryl in cotton seeds and found quite low quantities which offered no problem despite their six applications during the flowering and boll formation stage [3]. Numerous other references of similar work are available elsewhere in the literature [4-7].

This realization caused intensive research for detection and determination of toxic chemicals like chlorinated hydrocarbons (OCs), organophosphates (OPs) and synthetic pyrethroids (SPs) which threaten lives and health of people by contaminating crops and polluting the environment. This paper includes agricultural commodities with OC,OP, and SP pesticides and also presents the results of three years monitoring programme carried out on cotton seed samples. The data presented herein also indicate whether pesticides, if any, are in violation of maximum residue limits (MRLs) presented by FAO/WHO [8].

*Department of Chemistry, University of Karachi, Karachi-75270, Pakistan

Materials and Methods

Sampling. For the determination of pesticide residues of a commodity, it is necessary to have representative sample for analysis. Therefore, as far as possible, recommendations of Codex Committee on Pesticide Residues from FAO/WHO [9] were followed. For this purpose, a detailed map of cotton growing areas in Pakistan was obtained from Pakistan Central Cotton Committee. Since sampling from each farmer's land was not possible, it was decided to draw samples from progressive farmers and ginning factories who were aware of the products used in a particular geographical locality. 127 samples from Punjab and 123 samples from Sindh were collected during three crop seasons, from June 1986 to January 1989. Owners of ginning factories, pesticide suppliers and progressive farmers were interviewed to collect information about the pattern of sale and use of pesticides in the sampling area. The final samples (0.5 kg) were packed in polythene bags, sealed and labelled after sub-sampling and frozen at--20°C for subsequent residue analyses.

Determination of pesticide residues. Reference grade pesticides were supplied by the manufacturers for this study.

Analytical reagent grade chemicals were used. All solvents were redistilled in an all glass system before use.

Samples were analyzed in accordance with described procedures [10]. Each sample (5 g) was extracted with successive (50+15+10ml) portions of extraction mixture (distilled water + acetonitrile, 1:4). The combined extract was partitioned with n-Hexane three times. All the three layers of n-Hexane were combined and concentrated to approx. 2 ml and poured on a column of silica gel plus activated charcoal. The column was eluted with 15% ethyl ether in n-hexane and 250 ml eluate was collected for each sample. The cleaned up extracts were evaporated to dryness in a rotary vacuum evaporator and taken up in 2-5 ml n-hexane for gas chromatographic determination (GLC). GLC was equipped with ^{63}Ni electron capture and thermionic specific detection systems employing 2m x 2mm i.d. glass columns packed with 1.5% OV-17+1.95% OV-210 and 3% OV-17 on 18/100 mesh chromosorb W-HP respectively.

Results and Discussion

Analytical data of pesticide residues in cotton seeds are summarized and presented in Tables 1-3. A total of 250 samples belonging to three crop seasons were screened.

Amongst all individual pesticides determined quantitatively in cotton seeds, DDT occurred most frequently. 40 samples belonging to 1986-1987 crop, were found contaminated with DDT and its metabolites (Table 1). Highly hazardous organochlorine (OC) pesticides dieldrin and aldrin (WHO/FAO), were present in 12 and 11 samples respectively and amongst organophosphates (OP), 27 samples contained various levels of different compounds. Methamidophos, a highly hazardous OP (WHO/FAO), was detected in 7 samples while monocrotophos was found in only 2 samples. Residues of three synthetic pyrethroids (SP), cypermethrin, flucythrinate and cyfluthrin were detected in 6,3 and 2 cotton seed samples, respectively. Cyfluthrin and cypermethrin exceeded MRL in 1 and 2 samples respectively, while flucythrinate, a highly hazardous pesticide (WHO/FAO), was found within limits.

Accordingly 67.1% of samples were found to be contaminated with various levels of pesticide residues and 31.4% exceeded MRL (Fig.1). As stated earlier, the most frequently occurring group of pesticides was OC compounds which are highly persistent and lipophilic in nature. Parathion-methyl, which was detected in 6 samples to be exceeding MRL, is also extremely hazardous for the applicators (WHO/FAO). Our findings indicate that aldrin and dieldrin, which have been banned in Pakistan since 1980's are still being used to some extent probably from the remaining old stock.

Table 2 presents pesticide monitoring data of 1987-88 crop in cotton seed samples. Amongst the organochlorine compounds, 63 samples were found contaminated, while organo-

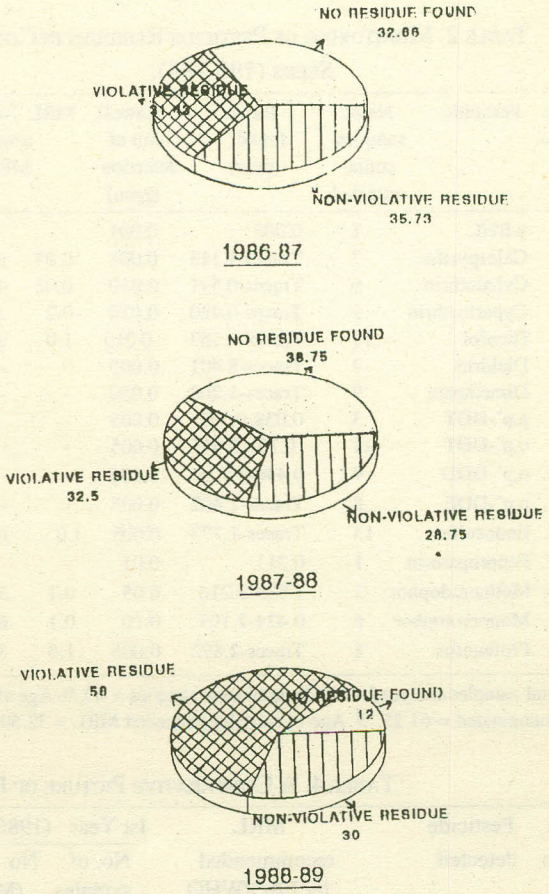

Fig. 1. Summary of 3 years monitoring studies on cotton seeds for pesticide residues.

TABLE 1. MONITORING OF PESTICIDE RESIDUES IN COTTON SEEDS (1986-87).

Sl. No.	Pesticide	No.of samples contaminated	Range found (ppm)	Lowest limit of detection (ppm)	MRL	No. above MRL	No. below MRL
1.	Aldrin	11	0.031-2.214	0.001	-	-	-
2.	γ-BHC	10	0.004-1.225	0.001	-	-	-
3.	Chlorpyrifos	3	0.480-1.115	0.010	0.05	3	-
4.	Cyfluthrin	2	Traces-0.393	0.100	0.05	1	1
5.	Cypermethrin	6	Traces-0.544	0.010	0.20	2	4
6.	Dicofol	5	Traces-2.560	0.010	1.0	2	3
7.	Dieldrin	12	0.008-5.945	0.005	-	-	-
8.	Dimethoate	4	0.399-0.864	0.050	-	-	-
9.	p,p'-DDT	7	0.028-0.457	0.005	-	-	-
10.	o,p'-DDT	13	0.054-2.289	0.005	-	-	-
11.	o,p'-DDD	7	Traces-1.020	0.005	-	-	-
12.	o,p'-DDE	13	0.027-1.717	0.005	-	-	-
13.	Endosulfan	8	Traces-1.438	0.005	1.0	2	4
14.	Flucythrinate	3	Traces	0.050	0.1	-	3
15.	Methamidophos	7	0.146-1.299	0.050	0.1	7	-
16.	Monocrotophos	2	1.810-2.211	0.100	0.1	2	-
17.	Parathionmethyl	6	0.167-3.179	0.050	0.05	6	-
18.	Pirimiphosmethyl	2	0.303-0.469	0.005	-	-	-
19.	Profenofos	5	0.035-2.067	0.005	1.0	1	4

Total samples analyzed = 70, Contaminated samples = 47, % Age of samples contaminated = 67.14, % Age of samples exceeded MRL = 31.43.

TABLE 2. MONITORING OF PESTICIDE RESIDUES IN COTTON SEEDS (1987-88).

Sl. No.	Pesticide	No.of samples conta-minated	Range found (ppm)	Lowest limit of detection (ppm)	MRL	No. above MRL	No. below MRL
1.	γ-BHC	1	0.003	0.001	-	-	-
2.	Chlorpyrifos	7	Traces-1.113	0.001	0.05	6	1
3.	Cyhalothrin	6	Traces-0.591	0.010	0.02	4	2
4.	Cypermethrin	5	Traces-0.420	0.010	0.2	2	3
5.	Dicofol	11	Traces-3.167	0.010	1.0	2	7
6.	Dieldrin	7	Traces-8.401	0.005	-	-	-
7.	Dimethoate	9	Traces-1.203	0.050	-	-	-
8.	p,p'-DDT	3	0.038-0.532	0.005	-	-	-
9.	o,p'-DDT	11	0.701-5.045	0.005	-	-	-
10.	o,p'-DDD	9	0.446-3.775	0.005	-	-	-
11.	o,p'-DDE	8	Traces-1.402	0.005	-	-	-
12.	Endosulfan	13	Traces-1.773	0.005	1.0	6	7
13.	Fenpropathrin	1	0.211	0.01	-	-	-
14.	Methamidophos	3	1.039-3.216	0.05	0.1	3	-
15.	Monocrotophos	6	0.424-2.193	0.10	0.1	6	-
16.	Profenofos	8	Traces-2.892	0.005	1.0	3	5

Total samples analyzed = 80, Contaminated samples = 49, % Age of samples contaminated = 61.25, % Age of samples exceeded MRL = 32.50.

TABLE 3. MONITORING OF PESTICIDE RESIDUES IN COTTON SEEDS (1988-89).

Sl. No.	Pesticide	No.of samples conta-minated	Range found (ppm)	Lowest limit of detection (ppm)	MRL	No. above MRL	No. below MRL
1.	Bifenthrin	4	Traces-0.075	0.010	-	-	-
2.	Chlorpyrifos	9	Traces-0.650	0.001	0.05	3	5
3.	Cyfluthrin	4	0.256-6.501	0.100	0.05	4	-
4.	Cyhalothrin	39	Traces-8.403	0.010	0.02	36	3
5.	Cypermethrin	15	Traces-1.908	0.010	0.2	8	7
6.	Diazinon	1	0.308	0.100	0.1	1	-
7.	Dicofol	9	0.572-6.230	0.010	1.0	6	3
8.	Dimethoate	41	0.070-5.320	0.050	-	-	-
9.	p,p'-DDT	2	0.048,0.467	0.005	-	-	-
10.	o,p'-DDT	2	0.006, 0.238	0.005	-	-	-
11.	o,'p-DDD	6	0.027=0.186	0.005	-	-	-
12.	o,p'-DDE	7	0.015-0.092	0.005	-	-	-
13.	Endosulfan	30	0.009-0.930	0.005	1.0	-	30
14.	Fenvalerate	1	0.064	0.050	0.02	1	-
15.	Flucythrinate	1	Traces	0.050	0.1	-	1
16.	Methamidophos	12	0.079-2.050	0.050	0.1	11	1
17.	Monocrotophos	18	0.070-6.912	0.100	0.1	17	1
18.	Profenofos	15	0.004-2.010	0.005	1.0	2	1

Total samples analyzed = 100, Contaminated samples = 88, % Age of samples contaminated = 88, %Age of samples exceeded MRL = 58.

TABLE 4. A COMPARATIVE PICTURE OF PESTICIDE RESIDUES DETECTED IN COTTON SEEDS (1986-88).

Sl. No.	Pesticide detected	MRL recommended by FAO/WHO (ppm)	Ist Year (1986-87)		2nd Year (1987-88)		3rd Year (1988-89)		Remarks
			No. of samples conta-minated	No. above (MRL)	No. of samples conta-minated	No. above (MRL)	No. of samples conta-minated	No. above (MRL)	Hazardous to human beings (FAO/WHO)
1.	Aldrin	ND	11	0	ND	0	ND	0	Highly
2.	γ-BHC	ND	10	0	1	0	ND	0	Moderately
3.	Bifenthrin	ND	ND	0	ND	0	4	0	"
4.	Chlorpyrifos	0.05	3	3	7	6	9	3	"
5.	Cyfluthrin	0.05T	2	1	0	0	4	4	"
6.	Cyhalothrin	0.02	ND	0	6	4	39	36	"
7.	Cypermethrin	0.2	6	2	5	2	15	8	"
8.	Diazinon	0.1	0	0	0	0	1	1	"
9.	Dicofol	1.0	5	2	11	2	9	6	Slightly
10.	Dieldrin	ND	12	0	7	0	0	0	Highly
11.	Dimethoate	ND	4	0	9	0	41	0	Moderately
12.	p,p'-DDT	ND	7	0	3	0	2	0	"
13.	o,p'-DDT	ND	13	0	11	0	2	0	"
14.	o,p'-DDD	ND	7	0	9	0	6	0	"
15.	op'-DDE	ND	13	0	8	0	7	0	"
16.	Endosulfan	1.0	8	2	13	6	30	0	"
17.	Fenpropathrin	N.D.	0	0	1	0	0	0	"
18.	Fenvalerate	0.02	0	0	0	0	1	1	"
19.	Flucythrinate	0.1	3	0	0	0	1	0	Highly
20.	Methamidophos	0.1	7	7	3	3	12	11	"
21.	Monocrotophos	0.1	2	2	6	6	18	17	"
22.	Parathionmethyl	0.05	6	6	0	0	0	0	Extremely
23.	Primiphosmethyl	N.D.	2	0	0	0	0	0	Slightly
24.	Profenofos	1.0T	5	1	8	3	15	2	Moderately

Total no. of samples analyzed = 250, Total No. of samples contaminated = 184, %Age of samples contaminated = 73.6, %Age of samples exceeded MRL = 40.6.

phosphates and synthetic pyrethroid pesticides were confirmed in 33 and 12 samples respectively. The pesticide residues were found in about 61.3% cotton seed samples during 1987-88 survey, out of which, 32.5% samples had pesticide residues greater than the maximum residue limits (Fig.1). The residues detected most frequently were those of endosulfan,DDT and its metabolites, dicofol, dimethoate and profenofos. As in the previous case, organochlorine pesticide residues were most frequent in cotton seeds.

During the third monitoring year, 1988-89, floods caused damage to the standing crop of cotton in the provinces of Punjab and Sindh. Compared with the previous two years data, a higher number of cotton seed samples were found to contain pesticide residues (Table-3 and Fig.1). The organochlorine compounds were detected in 56 samples. No MRL for DDT and its metabolites in cotton seed has yet been established. Organophosphates contaminated 96 samples while synthetic pyrethroids were present in 64 samples. No MRL for bifenthrin and dimethoate has so far been fixed. The most frequently occurring pesticides during the crop year (1988-89) were cyhalothrin, dimethoate and endosulfan. It is important to emphasize here that the OP pesticides, methamidophos and monocrotophos were found in 12 and 18 samples, and that out of these, 11 and 17 samples exceeded the MRLs recommended by FAO/WHO respectively. Similar results were observed for the synthetic pyrethroid pesticide, cyhalothrin; 36 out of 39 samples exceeded MRLs. All of the selected OC, OP and SP pesticides were also detected in the third year of these monitoring studies.

A comparative picture of analytical data for three years' cotton seed samples is given in Table 4. It is likely that chlorpyrifos, cypermethrin, dicofol, dimethoate, DDT and its metabolites, endosulfan, methamidophos, monocrotophos, and profenofos were used by farmers throughout the three crop seasons. The main reasons may be the easy availability in the local market, lesser market price and better results. It may also be concluded that decomposition rate of some of the above mentioned compounds is slow under the environmental conditions in cotton growing regions. The presence of methamidophos and monocrotophos residues throughout the three years study presents a serious situation as approximately all the samples crossed the MRLs. Parathion-methyl was detected in 6 samples in the first year of the study and was found to contain residues higher than the recommended MRL. This three years' monitoring study shows the extent of contamination of cotton seeds with 24 different OC, OP and SP pesticides and their metabolites. The use of these compounds is relatively high in tropical countries where greater pest activity prevails due to long summer and short winter. Therefore, regular monitoring of the pesticides in these regions is essential from human health point of view.

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