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STUDY OF FRUITS AND VEGETABLES IN NWFP, ISLAMABAD AND BALOCHISTAN FOR ORGANOCHLORINE, ORGANOPHOSPHORUS AND PYRETHROID PESTICIDES RESIDUES

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Samples of fruits and vegetables procured from the growers' fields and main selling points of North West Frontier Province, Islamabad and Quetta/Pishin districts of Balochistan during Dec.1990 and Sep. 1992, were monitored for organochlorine, organophosphorus and pyrethroid pesticides. Among the 300 samples screened, 121 samples contained a variety of pesticides. Thirty-eight samples contained pesticide residues above maximum residue limits (MRLs) proposed by FAO/WHO, while for several samples, no MRL was available for detected pesticides but high amounts of residues were found to be present in certain commodities. The remaining samples did not contain detectable pesticide residues.

Key words: Pesticide residues, Gas chromatography, Maximum residue limits.

Introduction

With increasing insistence in recent years by importing countries on food shipments being free from insect infestation, insecticides and fumigants are being widely used for pest control in countries of foodstuffs origin. Fruits and vegetables abundantly grown in Pakistan are also exported in modest quantities to different countries. In order to ensure quality of these commodities, it is necessary that they should be free from pest infestation. These crops are, therefore, sprayed with different pesticides for pest control. Pesticides are essential for boosting agricultural production but their growing mis-use also poses a serious threat to public health, livestock and poultry etc. It is, therefore, essential to regularly monitor pesticides in commodities destined for consumption by humans and other animals.

The importance of surveys in monitoring pesticide residues in foodstuffs has been discussed by Egan and Weston [1]. Organochlorine pesticides have been monitored in fruits and vegetables during a survey (1982-83) conducted in Karachi by Masud and Shamim [2]. In a similar survey, conducted in Karachi wholesale market during 1988-90 by Masud and Nusrat [3], nearly 40% samples were found to contain either organochlorine, organophosphate or pyrethroid pesticides, while 20% contained pesticides above maximum residue limits (MRL) proposed by FAO/WHO. Zahida and Masud [4-6] generated useful data in the year 1984 after their survey of Karachi Cattle Colony for organochlorine pesticides in milk, cattle feed and drinking water. 40, 46 and 13% samples of the three commodities respectively were found contaminated. Gamma-BHC was frequently monitored while some of the samples also contained residues of banned pesticides like aldrin and dieldrin.

In order to generate pesticide residue data on different crops in Pakistan, the Pesticide Residue Laboratory of Pakistan Agriculture Research Council has embarked upon an elaborate programme of monitoring of fruits, vegetables and other agricultural crops for the presence of organophosphorus, organochlorine and pyrethroid pesticides. This paper presents results of surveys of fruits and vegetables from NWFP, Islamabad and some parts of Balochistan province for pesticide residues. Three hundred samples were screened between Dec. 1990 and Sep. 1992. As far as possible, the data also indicates whether pesticide residues present in any of the tested commodities are in excess of maximum residue limits permitted by FAO/WHO.

Materials and Methods

Sampling. Samples of fresh fruits and vegetables were procured from growers' fields and main selling points of selected areas of NWFP, Islamabad and Quetta/Pishin districts of Balochistan. All samples were drawn in a random manner according to the prescribed procedure [7]. Atleast three primary samples were drawn from each selected grower's field/consignment which were then combined by mixing into a bulk sample. The bulk sample was suitably reduced to yeild a final representative sample for analysis.

Residue analysis. Samples were extracted according to the method of Masud [8], cleaned up and quantitatively ana-

lyzed by gas liquid chromatography according to the procedures described by Masud and Nusrat [3]. These methods are breifly described hereunder:

Extraction and cleanup. The samples were cut into small pieces, composited and sub-samples were taken for analysis. Sample (30 g) was homogenized in a blender using a 3:1 mixture of toluene and *n*-hexane (75 ml). The homogenate was shaken on an electrical shaker for 3 hr and frozen at -20°C overnight. After 24 hr the clear solution was quickly decanted and the extract was concentrated to approx. 2 ml in a rotary vacuum evaporator. The extract was then cleaned up on a Florisil / Charcoal column using toluene-acetone (99:1) as a mobile phase. 100 ml eluate was collected in each case. The eluate was evaporated to dryness and taken-up in 5 ml *n*-hexane for GLC determination.

Gas chromatography. Pye-Unicam Series-204 gas-liquid chromatograph, equipped with ^{63}Ni electron capture and flame ionization detectors, was employed for the determination of organochlorine, organophosphorus and pyrethriod pesticides. All GLC analyses were performed according to the described operating parameters for the three pesticides groups [3]. Each cleaned up sample extract was gas chromatographed thrice alongwith the relevant insecticide standard (Analytical grade insecticides supplied by the manufacturers). Quantitation of gas chromatograms was done by the peak height method, i.e., by comparing the peak height of the sample extract with that of the relevant insecticide standard.

Thin layer chromatography. Further confirmation of identity of pesticides detected in contaminated samples was done by thin layer chromatography in accordance with described procedures [3,9].

Results and Discussion

Since no maximum residue limit (MRL) has so far been fixed for any pesticide in fruits, vegetables and other food commodities in Pakistan, we have to compare our results with existing standards proposed by FAO/WHO [10]. In the present study, samples were collected from main selling points as well as from growers' fields of NWFP, Islamabad and Quetta/ Pishin districts of Balochistan. The object of including growers' fields in the study was to find out the history of pesticide usage in the area. 300 samples were screened for organochlorine, organophosphorus and pyrethroid pesticides. Multi-residue procedures were applied for this purpose. Extraction, cleanup, GLC and TLC procedures employed in the monitoring procedures were all developed by the authors earlier. The cleaned up extracts were quite clear and free from plant colouring matter and no interferring peak was observed in any of the cleaned up extracts when injected into GLC. The methods are reliable, efficient and sensitive down to picogram levels. It was not possible to screen sampled commodities from main selling points for all the pesticides registered for use in the country but efforts have been made to cover as many pesticides as possible. For samples from growers' fields,

TABLE 1. FRUIT AND VEGETABLE SAMPLES ANALYZED FROM N.W.F.P.

S. No.	Commodity	No. of samples		Pesticides detected	No. of samples	Quantity (ppm)	MRL
		Analysed	Contaminated				
1.	Radish	9	2	(i) p,p'-DDT	1	0.8	1.0
				(ii) Lindane	2	0.12, 0.65	1.0
2.	Coriander	1	1	(i) Lindane	1	1.5	2,0
				(ii) Malathion	1	3.2	3.0
3.	Turnip	7	2	(i) p,p'-DDT	1	6.2	1.0
				(ii) o,p'-DDT	2	0.8, 0.2	1.0
				(iii) p,p'-DDE	1	2.1	1.0
				(iv) Lindane	2	3.8, 0.03	1.0
				(v) Malathion	1	2.0	3.0
4.	Cauliflower	6	3	(i) p,p'-DDT	1	0.85	1.0
				(ii) Lindane	2	0.8, 0.12	0.5
				(iii) Malathion	2	0.1, 3.0	0.5
5.	Brinjal	8	2	(i) p,p'-DDT	2	0.16, 0.85	1.0
				(ii) o,p'-DDT	1	Traces	1.0
				(iii) p,p'-DDE	1	Traces	1.0
6.	Spinach	3	2	(i) Lindane	1	0.15	2.0
				(ii) Methyl parathion	1	0.15	N.A

(Continued)

(Table 1, continued)

7.	Lady's finger	10	8	(i)	p,p'-DDT	3	3.1, 8.10, 2.70	1.0
				(ii)	Lindane	4	0.15, 2.10, 4.30, 0.13	0.1
				(iii)	Malathion	4	2.30, 7.29, 6.54, 10.31	8.0
				(iv)	Methamidophos	3	0.21, 1.83, 0.24	1.0
				(v)	Methyl parathion	4	1.89, 2.83, 1.83, 2.31	N.A
				(vi)	Cypermethrin	4	1.71, 1.23, 1.12, 3.43	0.1
				(vii)	Deltamethrin	1	1.7	N.A
8.	Pumpkin	5	2	(i)	p,p'-DDT	1	Traces	1.0
				(ii)	Lindane	1	0.12	0.5
				(iii)	Cypermethrin	1	0.11	N.A
9.	Bitter gourd	4	3	(i)	Lindane	2	0.15, 0.11	1.0
				(ii)	Triazophos	1	2.11	N.A
				(iii)	Cypermethrin	1	1.5	N.A
				(iv)	Deltamethrin	1	1.7	N.A
10.	Cucumber	4	3	(i)	Lindane	2	2.10, 2.09	2.0
				(ii)	Cypermethrin	2	0.16, 1.80	0.22
				(iii)	Deltamethrin	1	0.13	NA
11.	Tomato	12	5	(i)	p,p'-DDT	1	0.15	1.0
				(ii)	Lindane	1	1.16	2.0
				(iii)	Malathion	3	2.0, 10.0, 8.14	3.0
				(iv)	Fenvalerate	2	1.17, 2.13	1.0
				(v)	Deltamethrin	1	0.91	N.A
12.	Peach	3	1	(i)	p,p'-DDT	1	0.85	0.5
				(ii)	Lindane	1	0.24	1.0
13.	Apricot	4	1	(i)	p,p'-DDT	1	Traces	1.0
				(ii)	Lindane	1	0.17	N.A
14.	Beet sugar	2	1		Lindane	1	0.19	0.1
15.	Pear	3	1		Lindane	1	Traces	0.5
16.	Mango	2	2	(i)	Lindane	1	0.11	0.5
				(ii)	Methamidophos	1	2.20	1
				(iii)	Fenvalerate	1	1.13	N.A
				(iv)	Cypermethrin	1	0.10	N.A
17.	White gourd (Tinda)	9	2	(i)	Lindane	1	0.11	N.A
				(ii)	Fenitrothion	1	0.18	N.A
				(iii)	Cypermethrin	1	1.20	N.A
18.	Long cucumber	3	1	(i)	Fenvalerate	1	0.12	0.2
19.	Onion	10	3	(i)	Methamidophos	2	4.61, 0.17	0.5
				(ii)	Malathion	1	8.52	0.5
				(iii)	Methyl parathion	3	3.15, 1.09, 1.81	N.A
				(iv)	Cypermethrin	1	1.23	0.1
				(v)	Fenvalerate	1	2.21	0.05
20.	Plum	12	2	(i)	Triazophos	1	1.4	N.A
				(ii)	Deltamethrin	2	1.31, 1.90	N.A
21.	Mint	3	2	(i)	p,p'-DDT	2	1.60, 0.19	1.0
				(ii)	Lindane	2	Traces, Traces	N.A
22.	Potato	7	1	(i)	p,p'-DDT	1	Traces	1.0
				(ii)	Lindane	1	Traces	0.05
23.	Water melon	2	–		N.D*	–	–	–

(Continued)

(Table 1, continued)

24.	Green pepper	2	–	N.D*	–	–	–
25.	Orange	8	-	N.D	–	–	–
26.	Sugar cane	1	-	N.D	–	–	–
27.	Lemon	1	–	N.D	–	–	–
28.	Apple	2	–	N.D	–	–	–
29.	Guava	1	–	N.D	–	–	–
30.	Pomegranate	1	–	N.D	–	–	–
31.	Carrot	2	–	N.D	–	–	–
32.	Peas	1	–	N.D	–	–	–
33.	Garlic	5	–	N.D	–	–	–
34.	Grapes	1	–	N.D	–	–	–
35.	Luffa (Turi)	1	–	N.D	–	–	–

*N.D = None detected.

TABLE 2. FRUIT AND VEGETABLE SAMPLES ANALYZED FROM ISLAMABAD.

S. No.	Commodity	No. of samples		Pesticides detected	No. of samples	Quantity (ppm)	MRL
		Analysed	Contaminated				
1.	Coriander	3	2	(i) p,p'-DDT	1	0.16	1.0
				(ii) o,p'-DDT	1	Traces	1.0
				(iii) Lindane	1	1.3	2.0
				(iv) Malathion	1	2.5	3.0
				(v) Cypermethrin	1	0.17	1.0
2.	Cabbage	2	2	(i) p,p'-DDT	1	0.18	1.0
				(ii) Lindane	2	0.14, 0.15	0.5
				(iii) Malathion	2	Traces, 5.11	8.0
				(iv) Cypermethrin	1	3.1	N.A
3.	Brinjal	8	6	(i) p,p'-DDT	2	0.13, 4.5	1.0
				(ii) Lindane	2	0.18, 0.19	0.5
				(iii) Malathion	2	3.5, 2.71	8.0
4.	Turnip	5	4	(i) p,p'-DDT	3	0.3, 0.2, 0.4	1.0
				(ii) Lindane	3	0.14, 0.09, 0.07	1.0
				(iii) Cypermethrin	4	0.10, 0.05, 0.08, 0.08	0.1
5.	Cauliflower	2	2	(i) o,p'-DDT	2	Traces, Traces	1.0
				(ii) Cypermethrin	2	0.8, 0.6	1.0
6.	Fenugreek	2	2	p,p'-DDT	2	Traces, Traces	1.0
7.	Carrot	3	2	(i) p,p'-DDT	2	2.3, 2.35	1.0
				(ii) Lindane	2	0.3, 3.38	0.2
8.	Spinach	6	6	(i) p,p'-DDT	1	1.0	1.0
				(ii) Lindane	2	0.5, 0.5	2.0
				(iii) Malathion	6	2.0, 3.2, 3.2, 2.0 4.2, 8.6	8.0
9.	Tomato	8	5	(i) Lindane	2	2.18, 0.17	2.0
				(ii) Malathion	3	2.32, 0.21, 0.28,	3.0
				(iii) Cypermethrin	1	0.15	0.5
				(iv) Fenvalerate	3	0.19, 0.13, 2.25	1.0
10.	Lady's finger	8	8	(i) p,p'-DDT	3	3.42, 2.90, 1.61	1.0
				(ii) Lindane	1	2.13	0.02
				(iii) Malathion	7	6.11, 8.31, 4.10, 3.19 0.26, 3.6, 9.10	8.0
				(iv) Methamidophos	3	1.32, 1.22, 0.26	1.0
				(v) Fenvalerate	1	0.20	1.0

(Continued)

(Table 2, continued)

11.	Bitter gourd	3	3	(i)	Lindane	2	0.12, 0.14	0.2
				(ii)	Malalthion	2	3.47, 1.30	8.0
				(iii)	Deltamethrin	1	1.12	N.A
12.	Lettuce	3	1		p,p'-DDT	1	1.8	1.0
13.	Mint	1	1	(i)	Lindane	1	1.40	2.0
				(ii)	Cypermethrin	1	0.14	2.0
14.	Beet sugar	1	1		Cypermethrin	1	0.10	N.A
15.	Pumpkin	1	1		Cypermethrin	1	Traces	N.A
16.	White gourd	2	2	(i)	Lindane	1	2.18	N.A
				(ii)	Cypermethrin	2	0.15, 0.11	N.A
				(iii)	Fenvalerate	1	0.16	N.A
17.	Luffa (Turi)	1	1	(i)	Lindane	1	4.21	N.A
				(ii)	Cypermethrin	1	1.63	N.A
				(iii)	Methamidophos	1	2.11	0.1
				(iv)	Methyl parathion	1	1.71	N.A
18.	Mango	2	1		Methamidophos	1	2.30	N.A
19.	Capsicum	1	1	(i)	Lindane	1	1.31	N.A
				(ii)	Fenvalerate	1	3.23	0.5
				(iii)	Malathion	1	2.50	N.A
20.	Cucumber	1	-		N.D*	–	–	–
21.	Musk melon	1	-		N.D	–	–	–
22.	Orange	1	-		N.D	–	–	–
23.	Apple	2	-		N.D	–	–	–
24.	Dates	1	-		N.D	–	–	–
25.	Plum	1	-		N.D	–	–	–
26.	Cheeko	1	-		N.D	–	–	–
27.	Apricot	1	-		N.D	–	–	–
28.	Green pepper	3	-		N.D	–	–	–
29.	Peas	1	-		N.D	–	–	–
30.	Garlic	3	-		N.D	–	–	–
31.	Radish	3	-		N.D	–	–	–
32.	Guava	1	-		N.D	–	–	–
33.	Lemon	4	-		N.D	–	–	–
34.	Potato	2	-		N.D	–	–	–
35.	Pomegranate	1	-		N.D	–	–	–
36.	Onion	4	-		N.D	–	–	–
37.	Ginger	1	-		N.D	–	–	–
38.	Long cucumber	1	-		N.D	–	–	–

*N.D = None detected.

Table 3. Fruit and Vegetable Samples Analyzed from Quetta/Pishin Districts.

S. No.	Commodity	No. of samples Analysed	Contaminated	Pesticides detected	No. of samples	Quantity (ppm)	MRL
1.	Apple (Amri)	4	2	(i) Azinphos methyl	2	0.19, 0.9	N.A
				(ii) Methidathion	1	Traces	N.A
2.	Apple (Golden delecious)	4	3	(i) Azinphos methyl	3	0.14, 0.13, 0.09	N.A
				(ii) Methidathion	1	0.05	N.A
3.	Apple (Mashhadi)	4	3	(i) Azinphos methyl	1	0.12	N.A
				(ii) Methidathion	3	0.02, Traces, 0.08	N.A

(Continued)

(Table 3, continued)

4.	Apple (Red delecious)	3	1	Azinphos methyl	1	0.10	N.A
5.	Apple (Summer qand)	3	1	Methidathion	1	0.05	N.A
6.	Apple (White Kulu)	4	2	Methidathion	2	0.03, 0.08	N.A
7.	Apple (Special Kalat)	3	1	Methidathion	1	Traces	N.A
8.	Apple	5	2	Azinphos methyl	2	0.11, 0.03	N.A
9.	Turnip	2	1	(i) BHC	1	0.04	N.A
				(ii) Malathion	1	2.6	3.0
				(iii) Fenvalerate	1	0.10	0.1
10.	Lady's finger	2	1	(i) BHC	1	1.0	1.0
				(ii) Cypermethrin	1	2.2	0.1
11.	Cucumber	5	1	BHC	1	0.8	N.A
12.	Arum	3	1	BHC	1	0.12	N.A
13.	Capsicum	2	–	N.D*	–	–	–
14.	Luffa (Turi)	2	–	N.D	–	–	–
15.	Green pepper	2	–	N.D	–	–	–
16.	Tomato	2	–	N.D	–	–	–

*N.D = None detected.

TABLE 4. NUMBER OF SAMPLES OF VEGETABLES AND FRUITS CONTAINING PESTICIDE RESIDUES BELOW AND ABOVE MRL.

S. No.	Pesticide	No. of samples containing pesticides	No. of dedected pesticides below MRL	No. of detected pesticides aboveMRL
1.	Lindane	52	37	15
2.	p, p'-DDT	32	18	14
3.	o, p'-DDT	6	6	–
4.	p, p'-DDE	2	1	1
5.	Malathion	37	28	9
6.	Methyl parathion	9	2	7
7.	Methamidophos	11	4	7
8.	Azinphos methyl	9	9	–
9.	Fenvalerate	12	6	6
10.	Cypermethrin	27	17	10
11.	Deltamethrin	7	7	–
12.	Methidathion	9	9	–

screening for pesticides was mostly limited to treatment history obtained from farmers.

A total of 300 samples, i.e., 155, 95 and 50 samples from NWFP, Islamabad and Quetta/Pishin districts respectively, were screened for pesticides. 50, 52 and 19 samples from the above mentioned three places respectively were found to contain varying amounts of organochlorine, organophosphate and pyrethroid pesticides.

Results are presented in Tables 1-3 and are compared with MRLs of detected compounds as far as possible. It is evident from the three tables that a total of 38 samples exceeded the maximum residue limits (MRLs) of detected pesticides, i.e., 21 from NWFP, 16 from Islamabad and only one from Quetta/ Pishin districts. Samples with high MRLs can be hazardous and can have various long and short term side effects. No MRL could be found in the available literature for detected pesticides in 49 samples (21 from NWFP, 10 from Islamabad and 18 from Quetta/Pishin districts) but 22 of them contained considerably high quantities of pesticides (15 from NWFP and 7 from Islamabad) which in the opinion the of authors, may also pose a health hazard to the consumers.

Samples from growers fields generally followed the pattern of treatment history. It is interesting to note that from Quetta/Pishin districts, only one sample containing cypermethrin exceeded the MRL but overall, the quantities of detected pesticides were low and within limits. A summary of contaminated samples containing pesticides above MRL is presented in Table 4.

Conclusion

Pesticide usage in Pakistan is rapidly increasing and cases of mis-use or over-use of pesticides are simultaneously on the increase. In the backdrop of such a situation, it is essential to impart proper education to the farming community about hazards involved in the misuse of toxic/persistent pesticides and the Agriculture Pesticides Ordinance of 1971 should be rigidly enforced. In this way, risks to human beings, livestock, poultry etc. can be minimized considerably. Furthermore, periodical monitoring of food commodities for pesticides is essential to assess the level of their contamination.

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