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PESTICIDE RESIDUES IN FOODSTUFFS IN PAKISTAN-ORGANOCHLORINE, ORGANOPHOSPHORUS AND PYRETHROID INSECTICIDES IN FRUITS AND VEGETABLES

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Organochlorine, organophosphorus and pyrethroid pesticides were monitored in samples of fruits and vegetables procured from the wholesale market of Karachi during July, 1988 and June, 1990. A total of 250 samples were screened out of which 93 samples were found to be contaminated with a variety of pesticides. Forty five samples have been found to contain residues above the maximum residue limits (MRL's) proposed by FAO/WHO while forty eight samples contained residues well within permissible limits. In remaining samples, no pesticide residue could be detected.

Key words: Food stuffs, Pesticide residues, Gas chromatography.

Introduction

A wide range of fruits and vegetables is grown in and around Karachi. Despite this, Karachi city, with a population of nearly 8 million, can not meet its total requirement of these commodities. For this purpose, it has to rely on supplies from other parts of Pakistan as well. Pakistan is also exporting modest quantities of fruits and vegetables to Gulf States through Karachi. These crops receive insecticidal treatment for the control of different pests. While the application of pesticides is necessary to increase crop production, its growing use poses a serious threat to public health.

In advanced countries of the world, regular and long term pesticide monitoring programmes are undertaken with a view to examine pesticide residue levels in commodities destined for consumption by humans or livestock. Egan and Weston [1] discussed the role of surveys in monitoring pesticide residues in specific foods with particular reference to food surveys in the United Kingdom. A survey of foodstuffs in the United States [2] showed the presence of organochlorine and organophosphorus pesticides in most of the samples analysed. Frank *et al.* [3] surveyed Ontario grown vegetables in Canada for pesticide residues during 1980-85. A total of 354 samples were screened. Most of the samples contained residues well within maximum residue limits (MRL) while the limits were exceeded in only a small number of samples.

Chlorinated pesticides have been found by Parveen and Masud [4-6] in samples of milk, feed and cattle drinking water drawn from Karachi Cattle Colony. Of the samples analyzed. 37, 46 and 13% samples respectively were found to be contaminated with BHC isomers, p,p'-DDT, p,p'-DDE, heptachlor epoxide, aldrin and dieldrin. The most frequently occuring pesticide was gamma-BHC. According to Aleksei Yablokov [7], nearly 50% of all foodstuffs in some parts of the Soviet Union were badly contaminated with pesticides. 1987 data showed that 30% of all food in Leningrad was dangerous to health, and 42% of the milk supply nationwide was polluted with pesticides.

Since sufficient data on pesticide residue levels in food commodities is not available in Pakistan, this work forms part of our investigations being carried out to determine the level of contamination of foodstuffs with persistent organochlorine, organophosphorus and pyrethroid pesticides. This paper presents results of a 2 year pesticide monitoring programme carried out on samples of fruits and vegetables obtained from Karachi wholesale market during July 1988 and June 1990. Overall, the data indicate if pesticide residues were present in these commodities and whether these residues were in voilation of maximum residue limits (MRL) permitted by FAO/WHO [8].

Material and Methods

Sampling. Samples of fresh fruits and vegetables were procured from the wholesale market of Karachi. Generally, each composite sample consisted of 0.5kg. All were random sample and drawn according to the prescribed procedure [9].

Sample preparation and extraction. Fruits and vegetable were sliced and composited into small pieces. Sub-samples were then taken for analysis. For extraction, method of Johansson [10] modified by Masud [11] was followed. According to the procedure, the sample (30g) was finely homogenized in a high speed blender using a mixture of 75 ml toluene + n-hexane (3:1). The homogenate was put on an electrical shaker for 3 hrs and then left in a deep freezer at 20° overnight. After 24 hrs, the clear solution was quickly decanted and extract was concentrated to about 2ml in a rotary vacuum evaporator at 60°.

Clean-up. Method of Masud [11] has been adapted after slight modification. The modification is the addition of 0.5g activated charcoal (Merck Art No.2183) to Florisil at the column cleanup stage. All other steps are similar to the

described procedure. In each case, 100 ml eluate was collected. Toluene-acetone (99:1) was employed as a mobile phase. The eluate was evaporated to almost dryness and takenup in 5 ml n-hexane in a volumetric flask for GLC determination.

Gas chromatographic determination. Pye-Unicam Series-204 gas-liquid chromatograph, equipped with ^{63}Ni electron capture and flame ionization detectors, was employed with the respective operating parameters.

Organophosphorus pesticides. Glass colum 1 meter long x 4 mm i.d. packed with 3% OV-101 on 100-120 mesh chrom WAW, DMCS treated. Temperatures: Injector 250°, column oven 180°, detector (FID) 250°, attenuation 64, Range 1, nitrogen carrier gas 30ml/min., Hydrogen 28ml/min. and air 300ml/min. The detector was linear in the range of 0.01, -2.0 ng for detected pesticides.

Synthetic pyrethroids. Similar to organophosphorus pesticides except for the column oven temperature. It was 220° in the case. The detector was linear in the range of 0.01-2.0 ng.

Organochlorine pesticides. Glass column 1 meter long x 4mm i.d. packed with a mixture of 1.5% SP-2250 + 1.95% SP-2401 on 100-120 mesh Supelcoport. Temperatures: Injector 250°C, column oven 180°, Detector (ECD) 250°, current 8V., Attenuation 64, nitrogen (carrier) 30ml/min. The detector was linear in the range of 0.01-1.0 ng for detected pesticides.

Servoscribe strip chart recorder (Kelvin Electronics Co. Ltd., England) with a speed of 120 mm/hr. was employed with the gas chromatograph.

Prior to use, each packed column was conditioned for 24 hrs under a slow stream of nitrogen at temperatures 50° higher than their working temperatures.

GLC retention times and detection limits of pesticides under the above operating parameters are given in Table 1.

Each cleanedup sample extract was gas chromatographed thrice alongwith the relevant insecticide standard (Analytical grade supplied by the manufacturers) in *n*-hexane using 0.1-0.2 µl injection. The amount of insecticide in each sample extract was calculated by comparing its peak height with that of the standard. Peak height was calculated by measuring the vertical distance from the peak apex to a line forming the base-line of the peak. Typical gas chromatogram of cleaned-up extract of coriander is presented in Fig.1.

Thin-layer chromatography. Extracts of samples found to contain pesticides were also screened for further confirmation of identity by thin layer chromatography on 20/20 cm silica gel coated glass plates (Merck Art No.5715) using toluene-acetone (10:2) as a mobile phase. The plates were evaluated by employing a mixture of 10% zinc chloride and 20% diphenyl amine in acetone as chromogenic reagents [12].

Results and Discussion

Since the treatment history of the produce was unknown, surveillance was designed to check for as many pesticides as possible. For this purpose. multi-residue procedures were applied to determine organochlorine, organophosphorus and pyrethroid pesticides in samples of fruits and vegetables. Multiresidue procedures could also detect other pesticides that were not recommended but may have been present through non-registered use, residue carry-over from the past use or drift from other treatments in nearby fields. It was not possible to examine sampled commodities for all the registered pesti-

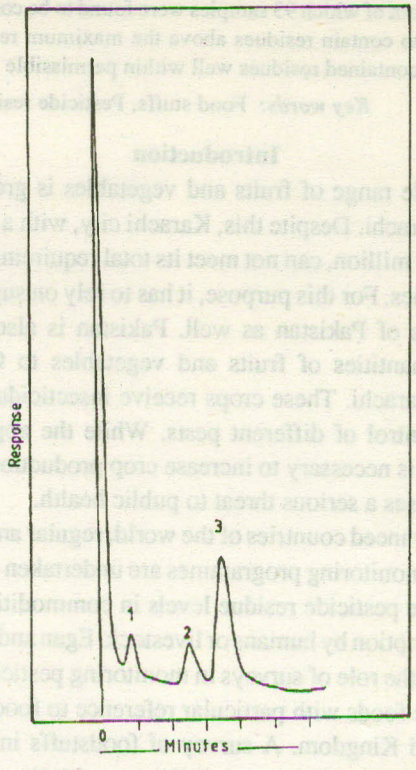

Fig. 1. Gas chromatogram of pesticides detected in coriander. (1). Cypermethrin. (2). Gamma-BHC. (3). Malathion .

TABLE 1. GLC RETENTION TIMES AND MINIMUM DETECTION LIMITS OF COMPOUNDS MONITORED IN FRUITS AND VEGETABLES.

Pesticide group	Pesticide	Retention time (min)	Detection limit (mg/kg)
Organochlorine	Lindane	5.2	0.001
	p,p'-DDT	10.6	0.01
	op-DDT	7.0	0.01
	p,p'DDE	5.6	0.005
Organophos-phorus	Malathion	7.2	0.05
	Methyl parathion	6.0	0.005
	Methamidophos	1.25	0.008
	Thiometon	1.75	0.01
Pyrethroid	Fenvalerate	3.5	0.009
	Cypermenthrin	1.7	0.007

TABLE 2. SUMMARY OF VEGETABLE AND FRUIT SAMPLES ANALYZED, NUMBER OF CONTAMINATED SAMPLES, PESTICIDES DETECTED WITH QUANTITIES AND PROPOSED MAXIMUM RESIDUE LIMITS (MRL's).

S. No.	Commodity	No. of sample analyzed	No. of contaminated samples	Pesticides detected	No. of samples	Quantity/sample Mg/kg	MRL
Vegetables:							
1.	Luffa (Turi)	7	–	–	–	–	–
2.	Pumpkin	6	1	Lindane (gamma -BHC	1	0.03 ppm	0.5
3.	Cauliflower	6	5	(i) p,p'-DDT	4	0.8, 2.0, 10.3, 8.4	1.0
				(ii) o,p-DDT	2	Traces, 0.3	1.0
				(iii) Lindane	1	0.66	0.5
				(iv) Methyl parathion	1	2.5 ppm	0.2
				(v) Thiometon	1	1.0	0.5
				(vi) Malathion	1	2.5 ppm	0.5
				(vii) Methamidophos	1	2.60	1.0
				(viii) Fenvalerate	1	0.10	5.0
				(ix) Cypermethrin	1	0.1	N.A
4.	Spinach	7	5	(i) p,p' -DDT	3	0.04, 1.0, 1.0	1
				(ii) p,p' -DDE	1	Traces	1
				(iii) Lindane	2	Traces, 1.5	2
				(iv) Malathion	3	1.7, 5.0, 4.0	8
				(v) Cypermethrin	1	Traces	2
5.	White gaurd (Tinda)	5	–	–	–	–	–
6.	Coriander	6	6	(i) p,p' -DDT	3	0.8, Traces, 1.0	1.0
				(ii) o,p -DDT	2	Traces, 0.04	1.0
				(iii) Lindane	3	0.5, 0.2, 0.3	2.0
				(iv) Methyl parathion	1	1.5	0.2
				(v) Thiometon	1	0.4	0.5
				(vi) Malathion	2	7.5, 3.0	3.0
				(vii) Methamidophos	1	2.6	1
				(viii) Fenvalerate	1	Traces	0.1
				(ix) Cypermethrin	1	0.3	0.5
7.	Cucumber	6	1	p,p' -DDT	1	4.6	1
8.	Bitter gourd	5	3	(i) Lindane	1	0.02	1
				(ii) Methyl parathion	1	4.0	0.2
				(iii) Malathion	2	2.0, 2.0	8
				(iv) Methamidophos	1	Traces	1
9.	Fenugreek	5	2	(i) p,p' -DDT	1	Traces	1.0
				(ii) Methyl parathion	1	0.5	0.2
				(iii) Malathion	1	1.8	8.0
10.	Lettuce	5	4	(i) p,p' -DDT	1	8.2	1.0
				(ii) Lindane	2	1.5, Traces	2.0
				(iii) Malathion	1	7.5	8
				(iv) Methamidophos	1	1.2	1.0
				(v) Cypermethrin	1	0.09	2.0
11.	Brinjal	10	5	(i) p,p' -DDT	1	1.0	1.0
				(ii) p,p' -DDE	1	Traces	1.0
				(iii) Lindane	3	0.15, Traces, 0.14	0.5
				(iv) Malathion	2	10.5, 2.5	8.0
12.	Onion (Green)	4	1	(i) o,p -DDT	1	0.04	1.0
				(ii) Cypermethrin	1	1.8	0.1
13.	Turnip	6	6	(i) p,p' -DDT	2	Traces, 0.04	1.0
				(ii) Malathion	2	0.15, Traces	3.0
				(iii) Fenvalerate	4	0.10,0.10, 2.0, Traces	0.1
				(iv) Cypermethrin		3.0, 0.05	0.1
14.	Sweet potato	1	–	–	–	–	–
15.	Tomato	7	4	(i) Lindane	2	0.13, 0.06	2.0
				(ii) Malathion	1	0.27	3.0

(Contd. Table 2)

(Table 2, Continue)

				(iii) Cypermethrin	1	Traces	0.5
16.	Lady's finger	8	6	(i) p,p'-DDT	2	0.75, 0.51	1.0
				(ii) p,p' -DDE	1	Traces	1.0
				(iii) Lindane	1	0.02	1.0
				(iv) Malathion	1	0.17	8.0
				(v) Fenvalerate	1	0.10	0.1
				(vi) Cypermethrin	2	1.4, 0.3	0.1
17.	Cabbage	6	3	(i) p,p' -DDT	2	8.6, 8.2	1.0
				(ii) Lindane	2	0.13, 0.1	0.5
				(iii) Methamidophos	1	3.1	1.0
				(iv) Cypermethrin	2	3.3, 1.1	N.A
18.	Potato	4	–	–	–	–	–
19.	Green papper	4	–	–	–	–	–
20.	Capsicum	5	–	–	–	–	–
21.	Mint	5	2	(i) Malation	2	5.5, 3.0	8.0
				(ii) Cypermethrin	1	2.5	N.A
22.	Wild cerely (Soya)	5	5	(i) p,p' -DDT	1	0.04	1.0
				(ii) o,p -DDT	2	0.07, 0.5	1.0
				(iii) Malathion	3	1.13, 0.3, 2.1	8.0
				(iv) Methamidophos	1	Trces	1.0
				(v) Cypermethrin	1	1.2	N.A
23.	Beet sugar	6	2	Malathion	2	1.5, 4.3	0.5
24.	Carrot	5	4	(i) p,p' -DDT	1	3.2	1.0
				(ii) Malathion	2	1.2, 1.5	0.5
				(iii) Fenvalerate	1	0.2	0.5
				(iv) Cypermethrin	3	3.0, 0.05, 0.04	0.1
25.	Radish	10	4	(i) p,p' -DDT	2	0.08, 1.4	1.0
				(ii) Malathion	2	1.5, 2.0	0.5
				(iii) Fenvalerate	1	0.05	1.0
26.	Garlic	3	–	–	–	–	–
27.	Peas	3	–	–	–	–	–
28.	French beans	3	–	–	–	–	–
29.	Mustard	1	–	–	–	–	–
30.	Ginger	5	1	(i) p,p' -DDT	1	Traces	1.0
				(ii) o,p -DDT	1	Traces	1.0
				(iii) p,p' -DDE	1	Traces	1.0
31.	Arum	6	–	–	–	–	–
32.	Gourd	2	–	–	–	–	–
33.	Cow pea	2	–	–	–	–	–
34.	Lambs quarter (Bathwa)	4	2	(i) p,p' -DDT	2	Traces, 0.05	1.0
				(ii) Lindane	2	0.03, 0.02	2.0
				(iii) Cypermethrin	1	Traces	2.0
35.	Seeds of radish (Mongray)	2	1	(i) p,p' DDT	1	0.05	1.0
				(ii) Fenvalerate	1	0.05	0.05
36.	Parselay	1	–	–	–	–	–
37.	Long cucumber (Kakry)	3	–	–	–	–	–
38.	Green grams	1	1	Cypermethrin	1	1.1	0.05
39.	Lemon	1	–	–	–	–	–
40.	Cluster bean	1	–	–	–	–	–
Fruits							
41.	Mango	12	9	(i) p,p' -DDT	5	1.0, 0.2, 1.5, 0.07, 0.8	1.0
				(ii) o,p -DDT	2	0.25, 0.8, 0.07, 0.8	
				(iii) p,p' -DDE	3	Traces, Traces, Traces	1.0
				(iv) Lindane	1	Traces	0.5
				(v) Malathion	2	3.4, 4.1	8

(Contd. Table 2)

(Table 2, Continue)

				(vi) Methamidophos	5	1.8, Traces, 1.5, 2.0 2.1	1.0
42.	Peach	5	4	(i) p,p' -DDT	1	Traces	1.0
				(ii) o,p -DDT	1	Traces	1.0
				(iii) p,p' -DDE	1	Traces	1.0
				(iv) Lindane	2	0.4, 0.3	0.5
				(v) Methamidophos	2	Traces, 3.4	1.0
43.	Apple	7	1	(i) p,p' -DDT	1	Traces	1.0
				(ii) Lindane	1	0.83	0.5
44.	Parsimon (Amlok)	2	–	–	–	–	–
45.	Banana	2	–	–	–	–	–
46.	Pomegrenate	2	–	–	–	–	–
47.	Grapes	2	–	–	–	–	–
48.	Musk melon	7	–	–	–	–	–
49.	Orange	6	–	–	–	–	–
50.	Grape fruit	1	–	–	–	–	–
51.	Papaya	5	–	–	–	–	–
52.	Guava	6	3	(i) p,p' -DDT	2	Traces, 2.0	1.0
				(ii) o,p-DDT	1	Traces	1.0
				(iii) Lindane	2	0.03, 0.04	0.5
				(iv) Methamidophos	1	2.65	1.0
				(v) Cypermethrin	1	4.0	1.0
53.	Sepota	2	–	–	–	–	–
54.	Ziziphus	2	–	–	–	–	–
55.	Cherry	2	–	–	–	–	–
56.	Plum	2	–	–	–	–	–
57.	Apricot	2	1	(i) Malathion	1	Traces	6.0
				(ii) Methamidophos	1	0.7	1.0
58.	Pear	1	–	–	–	–	–
59.	Dates	1	1	(i) p,p'-DDT	1	Traces	1.0
				(ii) Cypermethrin	1	1.4	1.0

N.A. = Not available.

TABLE 3. NUMBER OF SAMPLES OF VEGETABLES AND FRUITS CONTAINING PESTICIDE RESIDUES BELOW AND ABOVE MRL.

Pesticide	No. of samples containing pesticides	No. below MRL	No. above MRL
Lindane (gamma-BHC)	26	24	2
p,p' -DDT	38	28	10
p-p' -DDE	8	8	–
op-DDT	12	12	–
Malathion	30	21	9
Methyl parathion	4	–	4
Methamidophos	15	5	10
Thiometan	2	1	1
Fenvalerate	10	9	1
Cypermethrin	22*	9	8

*NMR of cypermethrin for 5 vegetables are not available.; However, 4 such vegetables contained high amounts of cypermethrin.

cides but efforts have been made to cover as many pesticides as possible.

For clean-up of sample extracts, the method of Masud [11] was slightly modified. The addition of 0.5g activated charcoal to a slurry of Florisil for the column cleanup of extracts helped to remove chlorophyl and other plant colouring materials from sample extracts thus prolonging the life of gas chromatographic stationary phases in the GC column and giving results free from interference. Gas chromatography of extracts revealed the efficiency of extraction and cleanup methods. No interferring peak was observed in any of the samples.

Pesticide monitoring studies gave us an idea of the level of its residues present in or on food commodity and enabled us to adopt precautionary measures accordingly. Since no MRL has so far been fixed for any pesticide on fruits and vegetables and other food commodities in Pakistan, it would be desirable to compare our results with internationally accepted Codex Limits [8].

Out of a total of 250 samples of fruits and vegetables analyzed, 93 samples were found to contain different organochlorine, organophosphate and pyrethroid pesticides in varying amounts. Results of contaminated samples are presented in Table 2 and are compared with MRL's of detected compounds as far as possible. For some of the compounds, no MRL could be found in the literature. This means that either the MRL has

not so far been fixed for such compounds or they are not approved for use on fruits and vegetables. It is evident from this table that in 45 out of 93 contaminated samples, the quantities of detected compounds exceeded the maximum residue limits [8]. In other words, it can be said that these samples could pose pesticide hazards to the consumer. A summary of contaminated samples found to contain residues below and above MRL is presented in Table 3.

Conclusion

In view of the above findings, it has become essential to impart education to the farming community about proper use and the dangers involved in the mis-use of pesticides. Pesticides would pay dividends only if used in accordance with "good agricultural practice" and would become a curse if mis used.

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