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PESTICIDE RESIDUES IN FOODSTUFFS IN PAKISTAN – ORGANOCHLORINE PESTICIDES IN FRUITS AND VEGETABLES

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Residue levels of organochlorine pesticides were determined in fruits and vegetables procured from the wholesale market of Karachi, during August 1982 to March 1983. A total of 141 samples were analyzed, of which only three fruits and six vegetable samples were found to contain varying amounts of different chlorinated pesticides or their metabolites. One sample of mango peel contained a residue of heptachlor, and a sample of cauliflower was found to contain aldrin, both of which were above the levels proposed by FAQ/WHO. No other residue approach the proposed maximum residue limit.

INTRODUCTION

Pesticides came into extensive use in agriculture and public health as early as 1944. They are now used on a gigantic scale. Benefits reflected in terms of enhanced farm productivity and control of vector borne diseases were so overwhelming that the real awakening to the problem of toxic residues left by pesticides came into sharp focus only around 1960. The problem of contamination of our food grains, dairy products, fruits, vegetables and our living environment by pesticides constitutes one of the most serious challenges to public health and environmental pollution. Organochlorine pesticides are persistent because of their rapid accumulation in fat and since they are not metabolised readily, their rate of excretion from the body is very low. Organophosphorus compounds, in comparison, are readily degraded and are not persistent.

The hazard of toxic residues can be considerably reduced if pesticides are used in accordance with "good agricultural practice". The information on pesticide residues occurring in food commodities is essential and should be obtained through regular monitoring procedures. Analytical surveys not only provide data on pesticide residues, but also serve to indicate whether or not the principles of "good agricultural practice" are being followed.

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. Most humans regularly ingest small amounts of chlorinated pesticides and retain them in their body fat. Moghal and Rehman [2] reported on the concentration of seven organochlorine compounds in stored fat of 60 subjects in a survey conducted in Karachi. A survey of foodstuffs in the United States [3] showed the presence of organochlorine and organophosphorus pesticides in most of the samples analysed. During a monitoring programme in Karachi in 1981 [4], pp'-DDT, pp'DDE and *gamma*-BHC were found to be present at low levels in some of the vegetables analyzed. The presence of pesticide residues in foodstuffs have also been reported by several workers elsewhere in the literature [5–8].

This work forms part of our investigations being carried out to assess the level of contamination of foodstuffs with persistent organochlorine insecticides. This paper presents the results of a survey on fruits and vegetables for organochlorine pesticide residues undertaken in Karachi between August 1982 and March 1983.

EXPERIMENTAL

Sampling: Fresh samples of fruits and vegetables were procured from the wholesale market of Karachi popularly known as Subzimandi which is responsible for the distribution of these commodities to the entire city. Generally, 1 kg of every fruit or vegetable was procured for analysis. All were random samples and drawn according to the prescribed procedure [9]. The source of supply of each sample was also found out from the wholesale dealers and is given in Tables 2 and 3.

Extraction and cleanup: For extraction and cleanup, the method of Johansson [10], slightly modified by Masud [11], was followed. For this purpose, samples of fruits and vegetables were cut into small pieces and homogenized in a high speed blender. 30 g sub-samples were taken in a conical flask and 75 ml of a mixture of

toluene and petroleum ether (3:1) were added to it. The homogenate was shaken mechanically for 3 hr, left in a deep freezer at 20° overnight and after 24 hr while cold; the clear liquid (60 ml) was immediately decanted. The extract was then evaporated to about 2 ml in a rotary vacuum evaporator at 40° and cleaned-up by 60/100-mesh Florisil in a 1.2 cm i.d. glass column using a mixture of toluene-acetone (99:1) as an elution solvent. 100 ml of the eluate was collected in each case. It was then evaporated to almost dryness and taken up in 5 ml *n*-hexane in a volumetric flask for GLC determination.

GLC determination: Pye-Panchromatograph equipped with an electron capture detector was used for GLC determination.

Operating conditions: a glass column 30 cm long x 4 mm i.d., was packed with a mixture of 7.5% QF-1 + 5% DC-200 on 80–100 mesh chromosorb W. (Phase Separations Limited; Cheshire, England). Temperatures – column oven 150°; detector oven, 175°, detector voltage, 5 volts pulsed; electrometer setting, 10^{-10} amp. full scale; nitrogen (carrier gas) flow rate, 75 ml/min., Honeywell recorder, 1mv; chart speed 8mm/min. GLC retention times of *alpha*-BHC, *beta*-BHC, *gamma*-BHC, *delta*-BHC, *Heptachlor*, Aldrin, pp′ – DDE and pp′ – DDT were found to be 0.45, 0.75, 0.50, 0.875, 0.938, 1.12, 2.875 and 5.0 min. respectively.

One to five microlitre quantities of fruit and vegetable extracts in *n*-hexane and relevant standard insecticides were injected separately into the gas chromatograph using a 10μl syringe. The response of the detector was linear over the range tried. The peak height method was used for the quantitative determination. Typical gas chromatograms of pesticides found in mango peel and cauliflower are presented in Fig. 1.

RESULTS AND DISCUSSION

In order to derive some inference, it is desirable to compare our results with the existing standards. 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 MRLs proposed by the FAO/WHO [12]. The pesticides included in the survey, together with analytical limits of determination and the maximum residue limits, are given in Table 1.

An important prerequisite for pesticide residue analyses is the use of clean glassware/equipments in order to avoid cross contamination. It was, therefore, ensured that all the equipment used in the present investigations was thoroughly cleaned and made pesticide-free before proceeding with residue determination.

A total of 140 samples were examined. These samples belonged to 19 and 28 different fruits and vegetables respectively. Three samples from each lot of fruit or vegetable were drawn and each sample was analyzed in triplicate in order to check the reproducibility of the results. Analytical data for fruits and vegetables are presented in Tables 2 and 3 respectively. Each figure is the mean of three replicates.

It is evident from the Tables that out of the samples analyzed, only three fruits and six vegetables were found to contain varying amounts of different chlorinated pesticides. Usually, the edible part of each fruit or vegetable was analyzed, but in the case of mangoes and peaches,

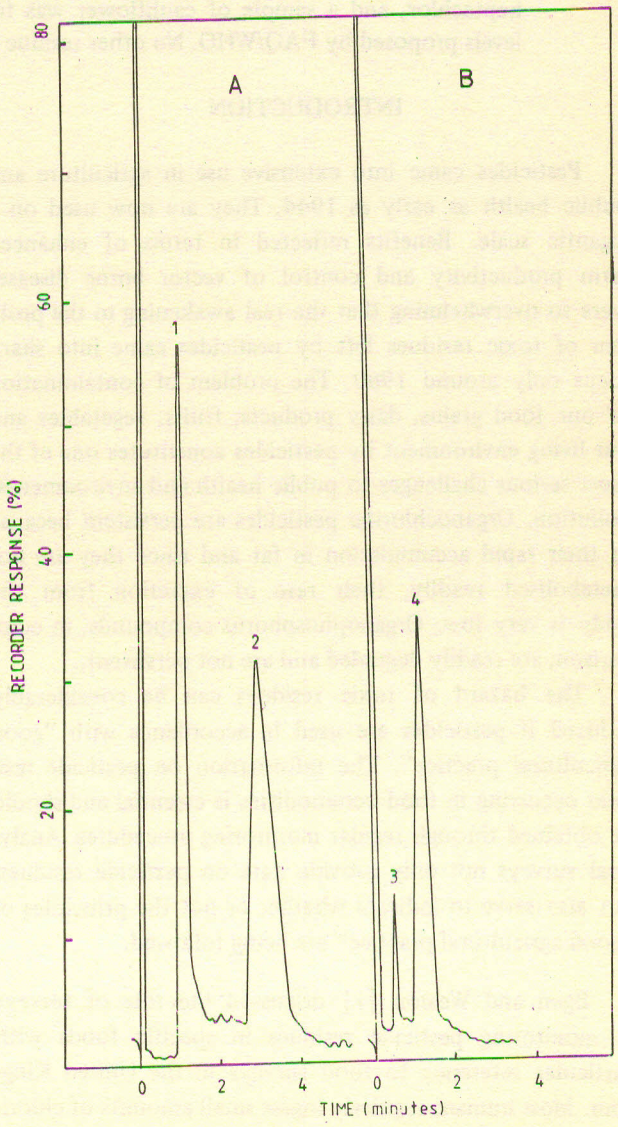

Fig. 1. Gas chromatograms of cleaned-up extracts. A Mango peel and B. Cauliflower 1. heptachlor, 2-*p,p*′-DDE, 3-α-BHC and 4-aldrin.

both peel and its pulp were examined. It is interesting to note that, while the pulp of both fruits were found to be free from any pesticide residue, the peel in each case was found to contain 0.32 mg kg^{-1} heptachlor, 0.96 mg kg^{-1} pp' – DDE and 0.10 mg kg^{-1} heptachlor respectively.

BHC isomers and DDT metabolites were also studied. The results indicate that organochlorine pesticides, if present, are in low concentrations and well within the FAO/WHO prescribed limits except in two cases. For instance, mango peel contained 0.32 mg kg^{-1} heptachlor against the

Table 1. Pesticides to be determined, analytical limits of determination and the proposed FAO/WHO Maximum Residue Limits (MRL)

Pesticide	Limit of Determination (mg kg^{-1})	MRL (mg kg^{-1})		Remarks
		Fruits	Vegetables	
Aldrin/Dieldrin	0.03	0.05	0.2	Limits are for aldrin/dieldrin separately or for their sum expressed as dieldrin if both are present.
BHC (mixture of isomers)	Alpha-BHC = 0.005 Beta-BHC = 0.05 Gamma-BHC = 0.001 Delta-BHC = 0.01	No ADI	No ADI	––
DDT	pp'-DDT = 0.02 pp'-DDE = 0.01 DDD = 0.1	3.5	1.0	These limits apply to DDT, DDD and DDE singly or in combination.
Endosulfan	0.5	2.0	2.0 (except root vegetables) 0.2 (Root vegetables)	––
Endrin	0.02	0.02	No ADI	Limits are for the sum of endrin plus delta-keto endrin.
Heptachlor	0.008	0.01	No ADI	Residues of hepachlor and its epoxide to be determined separately and sum to be expressed as heptachlor.
Lindane	0.001	3	3	––

Table 2. Organochlorine pesticide residues in fruits belonging to different places

S. No.	Common English name	Botanical name	Source	Date of sampling	Pesticides found	
					Pesticides	Quantity* mg kg^{-1}
1.	Mango	*Mangifera indica*	Multan	27.08.82	Peel:Heptachlor pp'-DDE Pulp:Nil	0.32, 0.33, 0.32 0.88, 0.96, 1.04 Nil
2.	Peach	*Prunus persica*	Quetta	27.08.82	Peel:Heptachlor Pulp:Nil	0.10, 0.08, 0.10 Nil
3.	Grape	*Vitis vinifera*	Kabul (Afghanistan)	07.09.82	Nil	Nil
4.	Apple	*Pyrus malus*	Swat	15.09.82	Nil	Nil
5.	Apple	*Pyrus malus*	Quetta	15.09.82	Nil	Nil
6.	Banana	*Musa sapienlum*	Karachi	03.10.82	Nil	Nil
7.	Grape fruit	*Citrus paradisi*	Quetta	09.10.82	Nil	Nil
8.	Papaya	*Carica papaya*	Karachi	09.10.82	Nil	Nil
9.	Porsion	*Diospyras kaki*	Multan	07.11.82	Nil	Nil
10.	Guava	*Psidium guajava*	Karachi	14.11.82	Nil	Nil
11.	Guava	*Psidium guajava*	Larkana	14.11.82	Nil	Nil
12.	Orange Fruit	*Citrus aurantium*	Mirpurkhas	14.11.82	Nil	Nil
13.	Sepota	*Achrus sepota*	Karachi	14.11.82	Nil	Nil
14.	Melon	*Cucumis melo*	Karachi	12.12.82	Nil	Nil
15.	Plum	*Prunus domestica*	Hyderabad	21.03.83	pp'DDT	0.10, 0.15, 0.08
16.	Pomegrenate	*Punica granatum*	Kandhar (Afghanistan)	21.03.83	Nil	Nil
17.	Raspberry	*Rubus idaeus*	Karachi	21.03.83	Nil	Nil
18.	Watermelon	*Citrulus vulgaris*	Karachi	25.03.83	Nil	Nil
19.	Dates	*Phoenix doctylifera*	Sukkur	28.03.83	Nil	Nil

* Three samples were drawn from every lot for analysis and each figure in this column is the mean of three replicates.

proposed MRL of 0.01 mg kg^{-1}. Similarly, 0.75 mg kg^{-1} aldrin was present in a sample of cauliflower against 0.2 mg kg^{-1} proposed by FAO/WHO. The sample of carrot contained 0.009 mg kg^{-1} heptachlor (besides lindane) and some of the vegetables have also been found to contain residues of BHC isomers, although no acceptable daily intakes (ADI) have been fixed for these compounds in vegetables in view of their presistence. Endosulfan could not be detected in any of the samples studied.

Organochlorine pesticides are persistent and several of them have been found to possess carcinogenic, mutagenic and teratogenic effects. For this reason, they have either been phased out of use in America, Britain and in several other countries or their use has been greatly restricted.

In Pakistan, organochlorine pesticides have not been approved for use on fruits and vegetables but more recently the Government have allowed restricted use of BHC on citrus, mango and almond trees. The farmer, being uneducated, generally uses any pesticide which he can get easily and at a cheaper rate of eradicating pest infestation. It has, therefore, been observed that many organochlorine pesticides are being freely used by the farmer in the field.

Table 3. Organochlorine pesticide residues in vegetables belonging to different places

S. No.	Common English name	Botanical name	Source	Date of sampling	Pesticides found	
					Pesticides	Quantity* mg kg^{-1}
1.	Cauliflower	*Brassica oleracea*	Karachi	07.01.83	Alpha-BHC Aldrin	0.008, 0.01, 0.006 0.75, 0.75, Nil
2.	Tomato	*Lycopersicum esculenlum*	Karachi	07.01.83	Nil	Nil
3.	Mustard	*Brassica nigra*	Karachi	07.01.83	Nil	Nil
4.	Carrot	*Daucus carota*	Karachi	07.01.83	Gamma BHC Heptachlor	0.01, 0.01, 0.03 0.009, 0.009, Nil
5.	Potato	*Solanum tuberosum*	Karachi	28.01.83	Nil	Nil
6.	Turnip	*Brassica rapa*	Karachi	28.01.83	Nil	Nil
7.	Beet	*Beta Vulgaris*	Karachi	28.01.83	Nil	Nil
8.	Coriander	*Coriandrum sativum*	Karachi	28.01.83	Beta-BHC	0.10, 0.15, 0.15
9.	Lettuce	*Lactuca sativa*	Karachi	04.02.83	Nil	Nil
10.	Spinach	*Spinacia oleracea*	Karachi	04.02.83	Nil	Nil
11.	Cabbage	*Brassica deracea*	Karachi	04.02.83	Nil	Nil
12.	Onion	*Allium cepa*	Mirpurkhas	18.02.83	Delta BHC	0.45, 0.48, 0.51
13.	Amaranthus	*Amaranthus hennus*	Karachi	18.02.83	Nil	Nil
14.	Radish	*Raphanus sativus*	Karachi	18.02.83	Nil	Nil
15.	Gram (Leaves)	*Cicer arietinum*	Karachi	18.02.83	Nil	Nil
16.	Brinjal	*Solanum melongena*	Karachi	25.02.83	Nil	Nil
17.	Chilli (small variety)	*Capsicum Frutescens*	Karachi	25.02.83	Nil	Nil
18.	Chilli (large variety)	*Capsicum frutescens* L	Karachi	25.02.83	Nil	Nil
19.	Gourd	*Cucurbita pepo*	Karachi	25.02.83	Nil	Nil
20.	Arum	*Arum colocasia*	Karachi	04.03.83	Nil	Nil
21.	Mint	*Mentha piperita* L	Karachi	04.03.83	Nil	Nil
22.	Fenugreek	*Trigonella foenumgraecum*	Karachi	04.03.83	Alpha-BHC	0.26, 0.29, 0.26
23.	Cucumber	*Cucumis sativus*	Karachi	04.03.83	Nil	Nil
24.	Tinda gourd	*Citrulus vulgaris varfistalosus*	Karachi	11.03.83	Nil	Nil
25.	Pumpkin	*Cucurbita maxima*	Karachi	14.03.83	Nil	Nil
26.	Lady's finger	*Hibiscus esculentus*	Karachi	14.03.83	Camma-BHC	0.20, 0.25, Nil
27.	Bitter gourd	*Momordica charantia*	Hyderabad	16.03.83	Nil	Nil
28.	Pea	*Pisum sativum*	Hyderabad	18.03.83	Nil	Nil

* Three samples were drawn from every lot for analysis and each figure in this column is the mean of three replicates.

No unidentified peak was observed on gas chromatograms during GLC analysis. Occasionally, spurious peaks at very low levels were obtained and were assumed to be the results of negligible amounts of some coextractives but did not interfere in our analysis.

CONCLUSION

On the basis of the present study on fruits/vegetables, it is suggested that the farmer should be properly educated with regard to hazards involved in the misuse of toxic/ persistent pesticides and the "Agricultural Pesticides Ordinance" should be rigidly enforced in the country. In this way, risks to human beings and livestock etc. can be minimized considerably. Further, periodical monitoring for pesticide residues in foodstuffs should be continued to assess the level of contamination of these commodities with pesticides.

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REFERENCES

1. H. Egan and R.E. Weston. Pestic Sci. 8, 110 (1977).
2. H.A. Mughal and A. Rehman, Arch. Environ. Health, 27, 396 (1973).
3. R.D. Johnson and D.D. Manak, J. Pestic. Monit. 9, 157 (1976).
4. S.Z. Masud, Pakistan J. Sci. Ind. Res., 27, 94 (1984).
5. A. Shanker and V.S. Kavadia, All India Symp. Modern Concepts of Plant Protec. Udaipur, p. 75 (1976).
6. A.K. Klein and J.O. Watts, J. Assoc. Off. Anal. Chem., 47, 311 (1964).
7. L. Albert, Proc. 5th Int. Cong. Pestic. Chemistry (IUPAC), Koyoto, Japan, August 29-September 4, 1982, Topic VIIe-14.
8. S. Bailey, G.B. Collins, F.B. Fishwick, H.V. Hart, D.F. Horler and K.A. Scudamore, Pestic. Sci., 13, 373 (1982).
9. Codex Committee on Pesticide Residues. Recommended Method of Sampling for the Determination of Pesticide Residues. Codex Alinorm 79/24, Appendix-IV, Annex I (1979).
10. C.E. Johansson, Pestic. Sci., 9, 313 (1978).
11. S.Z. Masud, Pakistan J. Agr. Res., 3, 265 (1982).
12. Pesticide residues in food. Report of join meetings of FAO and WHO expert bodies on pesticide residues (1965-1978). FAO Plant Production and Protection paper No. 11, Rome, 1978.