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Monitoring of Pesticide Residues in Summer Fruits and Vegetables From Kanpur, India

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Use of pesticides has become an indispensable input to agriculture, forestry and public health. Pesticides being toxic can become a potential hazard to the manufactures, the user, the public at large and the environment. Extensive deliberate use of pesticides has resulted in contamination of our vital supplies, air, water and food. The risk to humans may be short-term as well as long-term depending on the persistence of the pesticides and the exposure period. Pesticide residues in food has become a consumer safety issue and the consumer has a right to know how much pesticide gets incorporated in the food he eats. The detection and identification of pesticides in the food we eat is a problem of increasing public interest. Not much data is available on the presence of pesticides in vegetables and fruits especially in the Kanpur city (latitude 26.28N, longitude 80.24E) in the northern tropical part of India. With this objective, monitoring studies were undertaken to assess the amount of commonly used pesticides consumed by a common man of Kanpur city, via vegetables and fruits.

In this paper, we present the results of the analysis of residues of twelve commonly used pesticides on twenty three commonly eaten vegetable and twelve fruit samples, by Gas Chromatographya Teflon vessel at 80 wattt power and 2.45 G.Hz (GC) employing multiresidue technique.

MATERIALS AND METHODS

The study included the following parameters: Food sampled, pesticides analysed for, methods used, percent recovery of pesticides and concentrations found for each pesticide.

The standards for the pesticides chosen for study were obtained from RDH Laborchemikalien GmbH & Co. KG D-30918 Seelze via Promochem India pvt. ltd, Bangalore India. β BHC was 99% pure and all the other pesticides were above 99.6% purity level. The pesticides were categorized as:

- organophosphates
    - methyl parathion (O,O-dimethyl O-4-nitrophenyl phosphorothioate)
    - dimethoate (O,O-dimethyl S-methylcarbamoylmethyl phosphorodithiote)
    - malathion (diethyl(dimethoxy thiophosphorylthio succinate)

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ethion O,O,O',O'-tetraethyl S,S'-methylene bis (phosphorodithioate))

- organochlorines

  BHC (1,2,3,4,5,6-hexachloro cyclohexane)
  DDT (1,1'-(2,2,2-trichloro ethylidene)bis [4-chlorobenzene])
  DDE (1,1-dichloro-2,2-bis(p-chlorophenyl) ethene)
  Endosulfan (6,7,8,9,10,10-hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano2,4,3-benzadio-xathiepin 3-oxide)
  Dieldrin (1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a,octahydro-1,4,5,8-dimethanonaphthalene

Selection of vegetable and fruit samples was based on their easy availability and relative importance in the daily diet of a common man of Kanpur city. The most representative vegetables (Table 1) and fruits (Table 2) were included in the study. The samples were purchased in May from the main Kalyanpur vegetable market in Kanpur. Most of the vegetables sold here are supplied from the farms of nearby villages like Bithoor and Billore. Capsicum is not grown in this part of the country but comes from the hilly regions like Shimla. Most of the fruits supplied here, are not grown in this part of the country but are specific to a particular city of India. For e.g. Apples are from Kashmir, Banana from Bhusaval, Litchi, pear, plum and pear from the Nainital belt, mangoes from Lucknow region and papaya, lime, water melon and musk melon are from nearby farms of Kanpur. The vegetable and fruits were analyzed in the form that is offered to the consumer. For e.g. bottle gourd, jackfruit, onions and garlic were taken without peels and leafy vegetables were analyzed after the soil has been removed.
Ribbed gourd, Mint and Brinjal grown organically (Table 3) in the backyard vegetable gardens of houses were also compared with those that are commercially available in the market.

The vegetables taken were:

- Leafy vegetable — Spinach, Coriander, Mint
- Root and Tuber Vegetable — Carrot
- Brassica vegetable — Cabbage
- Fruiting vegetable — Cucumber, Tomato
- Legume vegetable — Cluster Beans
- Bulb vegetable — Onion, Garlic
- Underground vegetable — Potato, Ginger, Arum
- Other vegetables — Chilli, Brinjal, Bottle, Bitter, Evy and Ribbed gourd, Capsicum, Parwal, Pumpkin

Each sample size taken was 1kg out of which three representative subsamples weighing 20g were randomly taken and the pesticides were extracted for 4 hrs at the rate of 4-5 cycles per hour, in 150 ml n-hexane in a soxhlet extractor (EPA, method 3540C). In general, the EPA protocols with certain modifications were used for the residue analysis. The extract obtained was cooled, filtered and concentrated *in vacuo* in a rotary evaporator. The concentrate contained aqueous as well as organic residue. The organic part was extracted in n-hexane with the help of a separating funnel and a pinch of sodium sulphate was added to it. The solution thus obtained was filtered and concentrated again. To this 5ml of hexane was added and 0.5μl of the sample thus prepared was injected and analysed for the presence of twelve pesticides, by Gas-Chromatograph (Perkin Elmer- Autosystem XL) with the selective electron-capture detector (ECD) coupled with an integerator. This detector allows the detection of contaminants at trace level concentrations in the lower ppb range in the presence of a multitude of compounds extracted from the matrix to which these detectors do not respond. The capillary column used was PE-17, length 30m, ID 0.25mm, film 0.25mm with a 2ml/min flow. The carrier gas and the makeup gas was nitrogen employing the split mode. The oven temperature was kept at 190°C to 280°C with a ramp of 5°C/min. The detector and injector were maintained at 300°C. The samples were calibrated (retention time, area count) against 1 and 10 ppm standard mixed solutions of all twelve pesticides. Each peak is characterised by its retention time and the response factors in ECD. Sample results were quantitated in ppm automatically by the GC software. The detection limit was 0.001mg/kg for organochlorines and 0.01mg/kg for organophosphate pesticides.

One GC injection (0.5μl) of 30 min. was required in order to cover all twelve pesticides included in the analysis. Pesticides were identified according to their retention times. The actual relative retention times for the different pesticides were 11.60 (α BHC), 13.04 (β BHC), 13.09 (γ BHC), 13.78 (dimethoate), 14.50 (δ BHC), 15.41 (methyl parathion), 16.10 (malathion), 19.16 (endosulfan), 19.57 (DDE), 20.35 (dieldrin), 22.14 (ethion), 23.46 (DDT). For accurate results the concentration of the standard and concentration of sample to be estimated was kept the same. The multiresidue method that can detect all twelve pesticides in one analytical run has a broad scope of application, good recoveries and sensitivity and low solvent consumption, coupled with good analytical quality control. It is ideally suited for the large number of samples analysed in the laboratory.

The presence of Malathion (Kid and James, 1991), DDE in the samples were further confirmed by ^{1}H NMR (Jeol, 400MHz) and IR (Bruker) spectral studies. ^{1}H NMR and IR spectra of the standard pesticide was taken separately and compared with that of the sample containing that particular pesticide.

Recovery studies were performed separately for three original organic vegetable sample types (Table 4) by spiking the samples with known quantities of different pesticides and subjecting them to similar analytical procedures. The reproducibility of results for all the pesticides was 96.4% and above for all the samples. However, the mean average reading of a particular type of sample analysed in triplicate, was considered.

RESULTS AND DISCUSSION

The average percentage recovery of the twelve pesticides from spiked vegetables by soxhlet extraction was found to be more than 90%. However, the organochlorines showed (94%) higher recoveries than the organophosphates

(91%). The data presented in Table 1, 2, and 3 have not been corrected for recovery.

It is clear from the data that malathion is the most abundantly used organophosphate pesticide for both fruits and vegetables. Higher concentrations of malathion is found in vegetables compared to that of fruits. The organochlorine pesticides found in some vegetables are in moderate amounts. Although DDT is banned, yet residues of DDT and its metabolite DDE were detected in traces in a few samples. BHC, dimethoate, endosulfan and ethion were also detected in a few samples. Vegetables like jack fruit and garlic which were analysed without peels, showed lesser levels of malathion contamination. Capsicum, which is not grown in this region also has lower concentration of malathion.

The fruits (Mango, Musk melon, Lime, Papapya) that are grown in this tropical part of the country have higher malathion compared to the fruits (Pomegranate, Peach, Plum) grown in colder parts of the country. In spite of being thick skinned the fruits grown around Kanpur region showed relatively high concentrations of malathion. BHC and ethion in low concentrations was detected in some fruits.

Malathion, a non-systemic wide spectrum organophosphate insecticide, one of the earliest organophosphate insecticides developed, is very widely used. The wide use of malathion is based on its low toxicity to mammals, its relatively strong pesticidal qualities and its residual behaviour.

The acceptable daily intake (ADI) (Lu, 1995) values are by international standards and are much below to those prescribed by the Indian government. For BHC it is 0.008, DDT 0.02, methyl parathion 0.02, dimethoate 0.01, malathion 0.02, ethion 0.002, and for endosulfan it is 0.006 mg/kg/day. The difference in recommended Maximum residue limits[4] (MRL) in mg/kg by FAO/WHO (FAO/WHO, 1986) and Ministry of Health (MOH) (WHO, 1989) of the Indian government for some organochlorine pesticides, in fruits and vegetables is quite large.

	FAO/WHO	MOH
DDT	1.0	3.5
γ BHC	0.2	3.0
Dieldrin	0.10	0.10

In fact in one of the surveys of Chinese foodstuffs (Chen and Gav, 1993) HCH was found to be 2.5 mg/kg, DDT 6.9 mg/kg whereas the MRL recommended by the Peoples Republic of China is 0.2 in HCH and 0.1 in DDT. An earlier survey in India, conducted by Agnihotri and coworkers (Agnihotri et al, 1974) have reported 0.01- 60 mg/kg of BHC and .01-35 mg/kg of DDT in Delhi vegetables. Most of the earlier surveys (Kannan et al, 1997) reported the presence of concentrations as great as 20mg/kg for BHC in leafy vegetables and 169 mg/kg for DDT in potato from Karnataka in 1970. Leafy vegetables from Bombay during 1975-1979 had greater incidences of contamination than other vegetable types.

Table 1. Pesticide residues in vegetables (mg/kg)

Sample	1	2	3	4	5	6	7	8	9	10	11	12
Spinach	1.85	ND	ND	ND	ND	ND	ND	ND	0.02	ND	ND	ND
Coriander	2.31	ND	ND	ND	0.03	0.01	0.14	ND	ND	0.02	ND	ND
Mint	1.23	ND	ND	ND	ND	0.02	ND	0.12	ND	ND	ND	ND
Carrot	3.17	ND	ND	ND	ND	ND	ND	ND	0.02	ND	0.10	0.01
Cabbage	1.49	ND	0.03	ND	ND	ND	ND	ND	ND	ND	ND	ND
Cucumber	0.96	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Tomato	1.10	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Cluster Beans	1.86	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Onion	1.13	ND	ND	ND	ND	0.21	ND	0.01	ND	ND	ND	ND
Garlic	1.01	ND	ND	ND	0.04	0.03	ND	0.30	0.02	ND	ND	ND
Potato	1.76	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Ginger	2.68	ND	0.45	ND	ND	ND	ND	ND	ND	ND	ND	ND
Arum	3.03	ND	ND	ND	0.03	ND	ND	ND	ND	ND	ND	ND
Chilli	3.53	ND	0.07	ND	ND	0.02	ND	0.11	0.04	0.01	0.01	ND
Brinjal	2.59	ND	ND	ND	ND	ND	ND	ND	0.01	ND	ND	ND
Bottle gourd	3.18	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Bitter gourd	2.88	ND	ND	ND	ND	ND	ND	0.05	ND	ND	ND	ND
Evy gourd	3.46	ND	ND	ND	ND	ND	ND	0.03	ND	ND	ND	ND
Ribbed gourd	3.74	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Capsicum	0.24	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Parwal	2.23	ND	ND	ND	ND	0.01	ND	0.07	ND	ND	ND	ND
Pumpkin	2.50	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Jack fruit	0.81	ND	ND	ND	ND	ND	ND	ND	0.13	ND	ND	ND

1) Malathion 2) Methyl parathion 3) Ethion 4) Dimethoate 5) α BHC 6) β BHC 7) γ BHC 8) δ BHC 9) Endosulfan 10) DDT 11) DDE 12) Dieldrin

Table 2. Pesticide residues in Fruits (mg/kg)

Sample	1	2	3	4	5	6	7	8	9	10	11	12
Papaya	1.32	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Banana	1.37	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Litchi	1.80	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Apple	1.38	ND	0.02	ND	ND	ND	ND	ND	ND	ND	ND	ND
Pomegranate	0.70	ND	ND	ND	ND	ND	0.66	ND	ND	ND	ND	ND
Mango	1.84	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Pear	1.89	0.10	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Peach	0.73	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Plum	0.43	ND	0.03	0.08	ND	ND	ND	ND	ND	ND	ND	ND
Lime	2.02	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Water melon	0.50	ND	ND	ND	ND	ND	0.62	ND	ND	ND	ND	ND
Musk melon	2.32	ND	0.05	ND	ND	ND	ND	0.06	ND	ND	ND	ND

Table 3. Pesticide residues in organic vegetables (mg/kg)

Sample	1	2	3	4	5	6	7	8	9	10	11	12
Ribbed gourd	0.01	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Brinjal	ND	ND	ND	ND	ND	ND	0.02	ND	ND	ND	ND	ND
Mint	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.01	ND	ND

Table 4. % recovery of pesticide residues in spiked organic vegetables

Sample	1	2	3	4	5	6	7	8	9	10	11	12
Ribbed gourd	90.6	89.9	91.2	91.3	96.1	94.0	94.5	95.2	93.9	92.8	96.0	95.1
Brinjal	89.1	91.9	90.1	90.8	94.1	93.4	92.9	94.9	95.1	94.0	93.1	93.8
Mint	91.0	92.1	91.5	91.8	96.0	94.6	95.0	95.0	95.0	94.2	94.9	95.9

No doubt the concentrations of these pesticides have been on a decline of more than two orders of magnitude in farm products in the last two decades. Residues of most of the pesticides (except malathion) when found on the tested sample were generally well below the level of established tolerances. This is to be expected because of the dissipation of residues between the farm and marketplace and the standard preparation techniques applied prior to the testing. This is assuming the presence of one pesticide residue at a time on the sample whereas many different pesticides may be found on the single serving of the vegetable. These multiple residues may be derived from various sources such as applications of more than one pesticide on a crop during a growing season, possible spray drift or persistent environmental residues.

From the data it is clear, that most of the vegetables were contaminated mainly with high levels of malathion. Leafy vegetables like Spinach, Coriander, Mint were the most affected vegetables. Carrot also showed high levels of contamination. Malathion is one of the more popular pesticides currently in use, by the farmers of Bithoor and Billore region in Kanpur. Most of the fruits that are supplied from the cooler parts of the country have lesser concentrations of malathion compared to those produced in this tropical region. Although there has been no considerable reduction in the consumption of DDT and BHC in India, there is a 100-fold reduction in their concentration in farm products during the last decade. This could be resulting from the increased awareness among farmers of the deleterious effects of pesticide application close to harvest and from the adoption of "good agricultural practice". Already the undetectable DDT residue in samples analyzed shows that the farmers are conscious of the ill-effects of DDT which have been no doubt been widely popularized. Exposure to other pesticides should also be further reduced by spreading awareness amongst farmers.

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