PESTICIDES RESIDUES IN VEGETABLES IN AND AROUND DELHI

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Abstract. This article presents the development of a multiresidue method for the estimation of 30 insecticides, 15 organochlorine insecticides and 6 organophosphorus insecticides, 9 synthetic pyrethriods and 2 herbicides and their quantification in vegetables. The monitoring study indicates that though all the vegetable samples were contaminated with pesticides, only 31% of the samples contained pesticides above the prescribed tolerance limit.

Keywords: organochlorine insecticides, organophosphorus insecticides, 9 synthetic pyrethriods and 2 herbicides, vegetables

1. Introduction

Vegetables are a main source of diet in the Indian sub-continent. The average Indian diet constitutes of about 150–250 g of vegetables in the total meal per day. Literature reveals that vegetables (Mukherjee and Gopal, 1996; Dogherni *et al*., 1996; Elliion *et al*., 2000), may contain remnants of insecticides above the prescribed maximum residue levels (MRL), which may pose health hazard to the consumers. Monitoring of pesticides are conducted throughout the world to assess the environment load of the pesticides. Organochlorines have been detected in bovine milk (Mukherjee and Gopal, 1993), baby food (Mukherjee and Gopal, 1996) animal feed (Mukherjee and Gopal, 1995), human milk (Cox *et al*., 1999; Pertsovsky *et al*., 1998) water (Mukherjee and Gopal, 2001; Dua *et al*., 1998) skin (Dua *et al*., 1998a). These pesticides find their way into the human system through food, water and environment. One of the main sources has, however, been identified as the food chain. In view of the above and to assess the environmental load of the pesticides it is imperative to monitor the amounts of insecticides in the farm gate vegetable samples and fruit samples in and around Delhi. This article presents the development of a multiresidue method for the estimation of 32 insecticides, 15 organochlorine insecticides and 6 organophosphorus insecticides, 9 synthetic pyrethriods and 2 herbicides and their quantification in vegetables.

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2. Materials and Methods

2.1. CHEMICALS

The solvents were glass distilled before use. Acetone was refluxed over potassium permanganate for 4 hr and then distilled. Hexane was refluxed over sodium metal and the boiling fraction 60–80 °C was used for extraction and analysis. Sodium sulfate, sodium chloride, silica gel 60–120 mesh were used of branded companies. Appropriate concentrations of the standard solutions were made and used for the analyses.

2.2. APPARATUS

Gas Chromatograph (Hewlett Packard Model 5890 Series II), equipped with ^{63}Ni electron capture detector and SE 30 glass column, 2 m long, 2 mm id coated on chromosorb WHP. The operating conditions were, column 190±5 °C (10 min) to 220±5 °C (5 min), 250 °C (25 min). The injector post and detector were set at 270 and 300 °C, respectively. The carrier gas, nitrogen flow was maintained at 32 mL min^{-1}.

2.3. SAMPLE COLLECTION

Vegetable samples procured from farms in and around Delhi were processed for the determination of residues. A grab sampling method was employed The vegetables surveyed for the present study were cabbage, cauliflower, chilli, eggplant, tomato, mustard, onion and okra.

2.4. SAMPLE EXTRACTION AND CLEANUP

Vegetable sample (50 g) were grinded in a Waring blender. A five-gram representative sample was taken for multiresidue analysis. Five g of the homogenized sample was mixed with 10 g Florisil and blended until free flowability was obtained. Free flowing Florisil mixture was transferred to a glass column (40 cm long, 1.5 cm diam.) packed with a layer of sodium sulfate (3 g). The top of the Florisil was covered with sodium sulfate (3 g). The column was eluted with a mixture of 1:1 hexane:acetone (150 mL). The solvent was concentrated under reduced pressure to about 5 mL. A glass column (50 cm long, 1.5 cm diam.) was packed with a layer of sodium sulfate (2 g) + silica gel (1 g) + sodium sulfate (2 g). The column was prewashed with hexane (20 mL) and the concentrated hexane obtained from the first column eluate was passed through the silica gel column. The column was eluted with a mixture of 9:1 hexane:acetone (30 mL). The eluent was concentrated completely using under rotary vacuum evaporator and the residue was made up in hexane 5 mL for analysis.

3. Results and Discussion

The retention times and the limit of detection of the insecticides are presented in Table I. The insecticide analysed were atrazine, phorate, α-HCH, β-HCH, γ-HCH, δ-HCH, α-endosulfan, β-endosulfan, endosulfan sulfate, heptachlor, chlorpyrifos methyl, o,p-DDE, p,p-DDE, o,p-DDT, p,p-DDD, p,p-DDT, malathion, methyl parathion, quinalphos, fenvalerate, cypermethrin, permethrin, lambda-cyhalothrin, cyfluthrin, chlorpyrifos, dicofol, fenproparthrin, butachlor, fenvalerate, fluvalinate, alphamethrin and chlorthalonil. The pesticides recorded below the detection limits were considered as non detectable. The MRLs of the pesticide was given in Table II.

The analytical method used in the present study was GLC using electron capture detector. The method of extraction, cleanup and analysis for the organochlorine insecticides has been documented (Mukherjee and Gopal, 1996a). Various other groups have also developed newer methods to detect residues in much lower amounts (Cook *et al*., 1999; Gelsomini *et al*., 1997). However, in the present study quantification by GLC has been used.

Six farm gate eggplant samples, analyzed in duplicate (Table III) for the presence of insecticide residues, revealed that all the six samples were contaminated with endosulfan, four were contaminated with cypermethrin, three each were contaminated with fenvalerate, two each with chlorpyrifos and malathion and one with quinalphos (Table II). The insecticides were, however, below the prescribed MRL.

All the farm gate cabbage samples were contaminated with insecticides (Table III). The insecticides detected were endosulfan, methyl parathion, cypermethrin, malathion, chlorpyrifos, quinalphos and fenvalerate. Endosulfan was detected in all the seven samples of cabbage, cypermethrin was detected in four samples, three samples each were contaminated with both chlorpyrifos and malathion, two samples each were contaminated with fenvalerate and methyl parathion, one sample was contaminated with quinalphos.

Endosulfan, methyl parathion, cypermethrin, malathion, chlorpyrifos, fenvalerate, chlorthalonil and quinalphos were the insecticides detected in all the seven farm gate samples of cauliflower (Table III). The residues exceeded the MRL in one sample each contaminated with chlorpyrifos, quinalphos and cypermethrin.

All the five chilli samples analysed were contaminated with endosulfan, three each were contaminated with malathion, fenvalerate and cypermethrin, one was contaminated with chlorpyrifos. The residues were below the tolerance limit in all the samples (Table III), except in one sample of chlorpyrifos.

All the five farm gate samples of mustard (Table III) were contaminated with endosulfan, three with cypermethrin, two with malathion and one each with chlorpyrifos, fenvalerate, quinalphos and methyl parathion, respectively. The insecticides were below the tolerance limit in all, except one sample each of chlorpyrifos and quinalphos.

TABLE I
Pesticides, their retention times and limit of detection

Serial No.	Name of compound	Retention time (min)	Limit of detection (μg g^{-1})
1.	Atrazine	1.90	0.001
2.	Phorate	3.83	0.01
3.	Alpha-HCH	4.20	0.001
4.	Beta-HCH	4.26	0.001
5.	Gamma-HCH	4.84	0.001
6.	Delta-HCH	4.94	0.001
7.	Chlorthalonil	6.28	0.001
8.	Cypermethrin	6.35, 14.07	0.01
9.	Permethrin	6.56	0.01
10.	Methyl parathion	6.90	0.01
11.	Chlorpyrifos methyl	7.05	0.01
12.	Heptachlor	7.91	0.01
13.	Cyfluthrin	7.55	0.01
14.	Malathion	8.85	0.01
15.	Chlorpyrifos	9.61	0.001
16.	Quinalphos	12.27	0.002
17.	o,p-DDE	13.34	0.01
18.	Endosulfan-A	14.26	0.001
19.	Deltamethrin	14.32	0.01
20.	p,p-DDE	15.38	0.01
21.	o,p-DDT	16.85	0.01
22.	Endosulfan-B	16.53	0.001
23.	p,p-DDD	17.61	0.01
24.	p,p-DDT	17.76	0.001
25.	Endosulfan sulfate	18.32	0.01
26.	Butachlor	16.37	0.01
27.	Dicofol	17.70	0.01
28.	Fenproparthrin	26.05	0.01
29.	Lambda-cyhalothrin	29.80, 30.66	0.001
30.	Fenvalerate	37.76, 42.75	0.01
31.	Alphamethrin	38.97	0.01
32.	Fluvalinate	45.16	0.01

TABLE II
Maximum residue limit (MRL) of pesticides on vegetables

Serial No.	Pesticide	MRL (mg kg^{-1})	Reference
1	Endosulfan	2	Agnihotri (1999)
2	Cypermethrin	0.2	Agnihotri (1999)
3	Fenvalerate	2	Agnihotri (1999)
4	Malathion	3	Agnihotri (1999)
5	Quinalphos	0.01	Agnihotri (1999)
6	Methyl parathion	1	FAO/WHO (1986)
7	Chlorpyrifos	0.2	Agnihotri (1999)
8	Chlorthalonil	1	Agnihotri (1999)
9	Cyhalothrin	0.2	Agnihotri (1999)
10	Parathion	0.5	Agnihotri (1999)

All the farm gate okra samples were contaminated with endosulfan, three each with malathion, fenvalerate and cypermethrin, two with chlorpyrifos and one with imidacloprid (Table III). The insecticides were below the tolerance limit in all the samples, except two samples of chlorpyrifos.

Seven samples of tomato were analysed for the presence of insecticide residues (Table III). Endosulfan was detected in all samples, chlorthalonil was detected in two out of the seven samples, cypermethrin was detected in four samples, malathion was recorded in two samples, three samples were contaminated with chlorpyrifos and one sample each was contaminated with lambda-cyhalothrin, quinalphos and methyl parathion. Chlorpyrifos in two samples and quinalphos in one sample each exceeded the prescribed limit.

4. Conclusion

The monitoring studies indicate that though all the vegetable samples were contaminated with pesticides, only 31% of the samples contained pesticides above the prescribed tolerance limit. Use of pesticides in the appropriate dose and restricting the spray of pesticides just before harvesting the crop or during transportation will reduce the level remnants on the edible commodity also the environmental contamination. Awareness among the consumers and proper culinary processes will also enable pesticide free edible commodities.

TABLE III
Monitoring of pesticide residues in vegetables

Vegetable	Insecticide detected	Number of samples		>MRL (mg kg^{-1})	Median residues range (mg kg^{-1})
		Analyzed	Contaminated		
Eggplant	Endosulfan	6	6	0	0.035 (0.015–0.21)
	Cypermethrin	6	4	0	0.015 (ND–0.18)
	Fenvalerate	6	3	0	0.005 (ND–0.53)
	Malathion	6	2	0	ND (ND-0.02)
Cabbage	Endosulfan	7	7	0	0.21 (0.15–0.59)
	Methyl parathion	7	2	0	ND (ND-0.41)
	Malathion	7	3	0	ND (ND–0.12)
	Chlorpyrifos	7	3	0	ND (ND–0.12)
	Fenvalerate	7	2	0	ND (ND–0.45)
	Quinalphos	7	1	0	ND (ND–0.09)
Tomato	Endosulfan	7	7	0	0.21 (0.10–0.51)
	Methyl parathion	7	1	0	ND (ND–0.02)
	Malathion	7	3	2	ND (ND–0.07)
	Chlorpyrifos	7	3	2	ND (ND–0.20)
	Cyhalothrin	7	1	0	ND (ND–0.01)
	Quinalphos	7	1	1	ND (ND–0.10)
	Fenvalerate	7	2	0	ND (ND–0.32)
Cauliflower	Endosulfan	7	7	0	0.43 (0.18–0.91)
	Methyl parathion	7	2	0	ND (ND–0.34)
	Cypermethrin	7	4	1	0.08 (ND–0.31)
	Malathion	7	2	0	ND (ND–0.31)
	Chlorpyrifos	7	2	1	ND (ND–0.06)
	Fenvalerate	7	3	0	ND (ND–0.32)
	Chlorthalonil	7	2	0	ND (ND–0.15)
	Quinalphos	7	1	1	ND (ND–0.07)
Chilli	Endosulfan	5	5	0	0.26 (0.11–0.43)
	Malathion	5	3	0	0.015 (ND–0.13)
	Cypermethrin	5	3	0	0.025 (ND–0.16)
	Chlorpyrifos	5	1	1	ND (ND–0.11)
	Fenvalerate	5	3	0	0.075 (ND–0.33)
Okra	Endosulfan	7	7	0	0.19 (0.11–0.49)
	Methyl parathion	7	1	0	ND (ND–0.21)
	Cypermethrin	7	3	0	ND (ND–0.12)
	Malathion	7	3	0	0.11 (ND–0.12)
	Chlorpyrifos	7	2	2	ND (ND–0.02)
	Fenvalerate	7	3	0	ND (ND–0.31)
Mustard	Endosulfan	5	5	0	0.32 (0.29–0.57)
	Methyl parathion	5	1	0	ND (ND–0.21)
	Cypermethrin	5	3	0	ND (ND–0.12)
	Malathion	5	2	0	ND (ND–0.20)
	Chlorpyrifos	5	1	1	ND (ND–0.02)
	Quinalphos	5	1	1	ND (ND–0.19)
	Fenvalerate	5	1	0	ND (ND–0.22)

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