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Pesticide Residues in Vegetable and Fruits

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Abstract: Vegetable samples of brinjal, okra, green chilli, cabbage, cauliflower, tomato and capsicum from farmers'; field, Fruit samples like Banana, Pomegranate, Sweet Orange, Guava, and Grapes were collected from Market in Indore and were tested for the presence of organochlorine (OC), organophosphorus (OP) and synthetic parathyroid (SP) compounds using a gas chromatograph equipped with electron capture and Thermo sensitive detectors.Of the samples tested, 36.60 % were found to have pesticide residues. Among the OC compounds, α-endosulfan, β-endosulfan, were detected in 3.33 % of the samples with residues. These were taken from Cabbage and Brinjal samples. SP compound residues such deltamethrin were detected in 1.66 % of the samples with residues.OP compound residues such as chlorpyrifos, profenofos, ethion, dimethoate, Malathion, Quinalphos and methyl parathion were found in 22 % of the samples with residues, which were taken from all vegetable and fruit samples.15.3 % were found to contain residues exceeding the prescribed maximum residue limit. The average pesticide residue content across all the vegetable samples was 0.03 ppm, with values ranging from 0.03 to 1.18 ppm. Multiple residues of more than one compound were detected in 13.33 % of samples containing residues.

***Keywords*:** Pesticide residues, vegetables, fruits

INTRODUCTION

Vegetables are an important part of balanced diet providing many essential minerals and vitamins. Besides, higher intakes of vegetables are associated with healthier lives including lower risks of cancer, cardiovascular diseases and obesity. But the yield and quality of vegetables are affected by pests and diseases infestation during production and storage necessitating the use of pesticides. The pesticide use has increased over the years for effective controlling of a pest complex of vegetable crops due to rapid action and less manpower requirement. However, injudicious use of these compounds often leads to the presence of pesticide residues in harvested produce in amounts exceeding prescribed maximum residue limits (MRL), which may pose serious health risks as some of the vegetables are eaten raw or undercooked.

India is one of the largest agricultural pesticide consumers worldwide and is the second largest manufacturer of pesticides in Asia (Mathur 1999). There is a sequential rise in the production and consumption of pesticides in India during last three decades. The consumption pattern of pesticides differs from rest of the world, as in India, 76 % of total pesticide consumption is insecticides as against 44 % worldwide. Of the total pesticide usage 45 % goes to cotton crop followed by paddy and wheat. While only 10–12 % of total pesticides are used for fruits and vegetables (Kumari et al. 2003; Bhattacharyya et al. 2009). Intensive cultivation, coupled with the evailing humid tropical climate, has resulted in increased pest and disease incidence. Nearly 75 to 80 % of total pesticide consumption of 5175.4 MT is used for vegetable crops alone (Andaman and Nicobar Administration 2009) as against the national average of 10–12 %. As the vegetables are grown in 449.2 ha only, the per capita pesticide consumption in the vegetable-growing areas (3,586 g) far exceeds the national average of 450 g (Bhattacharyya et al. 2009).

There are several reports on environmental contamination and long-term health implications resulting from the intensive use of pesticides in agriculture, animal husbandry, and public healthprograms (Igbedioh 1991; Waliszevski et al. 1996; Bhanti and Taneja 2007; Chen et al. 2011).As fruits and vegetables are the most frequently consumed food group, which makes up 30 % of Food consumption on mass basis (WHO 2003), the presence of pesticides in vegetables is a moreserious health concern, since they are consumed raw, without much processing and storage (Kalra and Chawla 1985; Kumari et al. 2003). Because of which, they are expected to contain higher levels of pesticide residues than other food groups of plant origin. Aside from causing acute and chronic toxicity, they can also affect the immune system and cause arthritis, carcinogenicity, reduced fertility, increased cholesterol, high infant mortality, etc.(Singh 2001). Thus, the monitoring of pesticide residues is essential to regulate the application of pesticides to food crops especially vegetables so as to ensure healthy products to the consumers.

Several studies have been reported on the contamination of vegetables in India (Agnihotri 1999;Mukherjee 2003; Kumari et al. 2004; Bhanti and Taneja 2005; Mandal and Singh 2010; Chowdhuryetal. 2011) and world (Adeyeye and Osibanjo 1999; Amoah et al. 2006; Nishina et al. 2010;

Bempahetal. 2012). The intensive cultivation of vegetables has gained momentum in recent years with excessive pesticide usage due to increased market demand. As the presence of pesticide residues in food produce is a serious concern and no data are available on the levels of pesticide residues in vegetables, a Study was conducted to ascertain the presence of pesticide residues in major vegetables.

MATERIALS AND METHODS

Brinjal, okra, cauliflowers, cabbages, tomatoes, chilies, and cucurbits are the major vegetables grown. Of the total pesticides used, approximately 75–80 % is applied for vegetable cultivation alone. The vegetable cultivation is practiced in an open-field condition under conventional management practices. The vegetable growers are only small to medium farmers with average land holding not exceeding 2 ha. The major pesticides used on the islands are cypermethrin, malathion, dimethoate, quinalphos, chlorpyrifos, endosulfan, phorate, and carbofuran (Jeyakumar et al. 2008)

Fruit crops occupy major portion of area . The major crops are mango, citrus, banana, gauva, custard apple, papaya etc.. During the year 2004-2005 increase in production, area and productivity was achieved through technology and management practices. Capacity building through training is also a thrust area.

The multi residue extraction was done following a modified QuEChERS method (Anastassiades et al. 2003), where the samples are cut into pieces and macerated with a mixer grinder. A 15-g macerated sample is then weighed into a 50-mL centrifuge tube along with 30 mL acetonitrile and shaken well for 1 min in a vortex shaker. The supernatant is transferred quantitatively to a second centrifuge tube containing 4 g anhydrous MgSO4 and 1 g NaCl. The tube was then shaken vigorously again for 1 min in a vortexshaker and centrifuged at 3,000 rpm for 5 min. A8-mL extract of this sample is added to a 15-mL centrifugetube that contains 1.2 g anhydrous MgSO4 and0.4g primary secondary amine, shaken vigorously for 1 min in the vortex shaker, and centrifuged at3,000 rpm for 5 min. A 2-mL extract sample is pipettedout into a glass tube and the solvent is evaporated usinga TurboVap evaporator at 30 °C using 10 psi N2 gas over15 min. The residues are reconstituted using n-hexanefor final GC and GC/MS analysis.

The detection and quantification of different pesticide compounds was carried out by injecting
1 μL of the extract into the gas chromatograph (GC-Shimadzu GC-2010) equipped with both an electron capture detector and a flame thermionic detector. The residue levels were estimated by comparing the peak areas of the samples to those of standards run under identical conditions. Any detected residues were confirmed using GC/MS (GC/MS-TQD Brukers) to avoid the misinterpretation of any results. Three vegetable samples with no residues were spiked with 0.01 ppm levels of organochlorines, 0.05ppm for organophosphorus, and0.1ppm for Synthatic pyrethroids compounds and separately analyzed following the same procedure. More than 80 % recovery was obtained for the spiked samples and results were reported as such with no correction for recovery rate. The average pesticide residue contents in the vegetable samples were calculated using the equation given by Poulsen et al. (2007).

RESULTS AND DISCUSSION

Pesticide residues were found in 38.3 % of the total samples analyzed which is lower than the reported contamination levels elsewhere in India (Kumarietal. 2004; Charan et al. 2010) and world (Hjorth et al. 2011; Bempah et al. 2012). In 33.3 % of the samples, residues were found at or below MRL, while in 5.0 % samples, residues are above the MRL (PFA 1954). Among individual vegetables, green chillies, capsicum, Tomato, Okra, Brinjal, and cruciferous vegetables like cabbage and cauliflower showed presence of residues in more than 33.3 % of samples analyzed (fig 1). In fruits, Grapes, Pomegranate samples showed presence of residues in more than 3.3 % of samples (fig 3). This trend is in consonance with the reports of higher levels of contamination of Okra (Ashutosh 2010), Tomato (Crentsil Kofi Bempah 2011) and Green chilli (Z Praveen 2005) samples. In green chillies , 16.6 % samples showed residues more than specified MRL, followed by Tomato (33.3 %). In Grape 3.3% samples showed the residues followed by Pomegranate 1.66% samples (BeenaKumati 2006, Mutwakil M.A 2005-09).(Table 1) Percentages of different commodities contaminates shown in (Fig 2,3).

A total of 15 compounds, covering organochlorine (OC), organophosphorus (OP), and synthetic pyrethroid (SP) compounds, were detected in this study. The residues of OP (22 %) and SP (1.66 %) compounds were most frequently found, followed by OC (6.6 %) compounds. The residues of OP compounds were predominant in all vegetable groups indicating their widespread usage. The residues of OC (6.6 %) and OP (45.9 %) compounds were detected most in green chillies followed by Tomato and okra vegetables and in fruits (4.9%) grapes followed by pomegranate. (Table 2).

Among the compounds detected, Dimetoate, Profenophos, Quinalphos and Malathion were most frequently found in 41.97 % of positive samples. Dimethoate is the single largest pesticide found with 13.3% of the samples surveyed reporting its use followed by Malathion. Malathion is found 11.66 % of samples. Profenophos and Quinalphosis found

6.66 % of samples. As Malathion has relatively rapid degradation with less persistence, generally no residues were found as a residue in food. However, in recent times, predominance of Malathion residues in fruits and vegetables was also reported by several workers (Singh and Kiran Singh 2006; Chen et al. 2011; Lozowicka et al. 2012) in their respective study area indicating their excessive use. Though endosulfan was banned for its agricultural use , the presence of its residues in recent samples indicated its illegal use which might be from previous stock. Its continuous monitoring helps in ensuring tight control measures not only on farmers,but also on pesticide dealers. The concentration of pesticide residue ranged from 0.03 to 1.18 ppm with a mean concentration of 0.192 ppm. The mean values of OP (0.184 ppm) and OC (0.071 ppm) residues in positive samples exceeded the overall mean of 0.192 ppm (Table 3). The mean content of SP compounds was found to be low, which might be due to their less persistence. Samples were tested for the presence of OC compounds,viz., α-hexachlorocyclohexane (HCH), β- HCH, lindane, delta HCHdicofol, di-chlorodiphenyltrichloroethane(DDT) and metabolites thereof, such as o,p′-DDE,o,p′-DDDp,p′-DDT, p,p′-DDD, p,p- dichlorodiphenyldichloroethylene (DDE), o,p′-DDE, α-endosulfan, β-endosulfan, and endosulfansulfate. Residues of endosulfan T (α-endosulfan, β-endosulfan, and endosulfan sulfate) were detected in 3.33 % across all samples having residues. At the time of sampling, it was also observed that the crops were heavily infested with diamond back moth and shoot and fruit borers. Because of its relatively low cost and broad spectrum application, it might be widely used by many producers for pest control including thrips and aphids. Its residuelevel in contaminated samples ranged from 0.03 to 1.18 ppm with average content of 0.192 ppm. The highest mean concentration was detected in Tomato (0.358 ppm) followed by Okra (0.331 ppm), Green chilli (0.112 ppm), and Cabbage (0.162 ppm) (Fig. 4).

In majority of the samples (60 %), the concentration was found to be less than 33.3 % of specified MRL. The highest level of0.88 ppm that was found occurred in only one sample of Toamto which exceeded the MRLof 0.2 ppm. Synthetic pyrethroids, such as α-cypermethrin, λ-cyhalothrin, bifenthrin, fenpropathrin, β-cyfluthrin,deltamethrin, fenvalerate I, fenvalerate II, fluvalinate I, and fluvalinate II, were also investigated in thevegetable samples. Residues deltamethrin weredetected in the positive samples.

These vegetable samples were also tested for 15organophosphorus compounds, including dichlorvos, phorate, dimethoate, methyl parathion, fenitrothion, malathion,chlorpyrifosmethyl, chlorpyrifos, quinalphos, profenofos, ethion, and Phosalone. Of these residues, profenofos, chlorpyrifos, Dimethoate,malathion, Quinalphos, Methyl parathion,Ethion and Phorate were found in 36.6 % of the positive samples. These residues were found in all the vegetable groups with values ranging from 0.03 to 1.18 ppm. Chlorpyrifos was dominant OP compound in Green chilli have 0.35ppm have the above MRL (0.2ppm) followed by Phorate 0.08pmm is above MRL.The concentration of individual compounds varied with mean values ranging from 0.03 to 1.18 ppm (Sajjad Ahmed Baig 2009). The residues were found in fruits ranging from 0.05 to 0.10 ppm. The mean concentration of Dimethoate, Chlorpyrifos ,Profenophos,Quinalphos, and Malathion was higher than the average value of all OP compounds Table 4).

CONCLUSIONS

The residues of more than one compound were found in 13.33 % across the samples and 38.3 % of samples containing residues. Among different pesticides, Dimethoate was the most frequently found along with Malathion, profenofos, Quinalphos, and endosulfan. Besides, the Methyl parathion and Ethion association was found in few samples of Green chilli. Multiple residues were highest in green chilli (8.33 %), followed by Okra. In this study, a distinct pattern of pesticide use is discernable from the maximum number of samples containing different pesticide residues. Accordingly, Profenophos, Chlorpyrifos and Dimethoate compounds were mainly used for green chilli and okra;Quinalphos for brinjal, Endosulfan and Deltamethrin were used for all vegetables.

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Figure Legends:

1. Fig-1. In total samples percentage of samples vegetables detected.
2. Fig-2. Percent contribution of different vegetables to samples with detected samples.
3. Fig-3. In total samples percentage of samples fruits detected.
4. Fig-4. Percent contribution of different Fruits to samples with detected samples.

Tables:

1. Table 1: Summary of pesticide residue analysis in vegetables and fruits
2. Table 2: Distribution of various pesticide groups among contaminated vegetable groups
3. Table 3: Pesticide residue levels in vegetables and fruit samples
4. Table 4: Concentration of OCs, OPs and SPs in Vegetable samples

Fig-1. In total samples percentage of samples vegetables detected

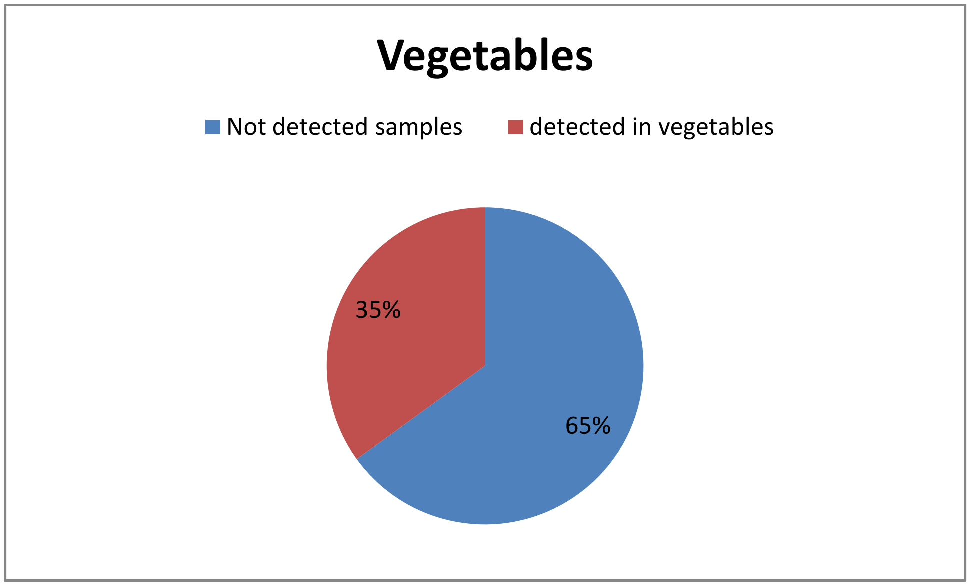

Fig-2. Percent contribution of different vegetables to samples with detected samples

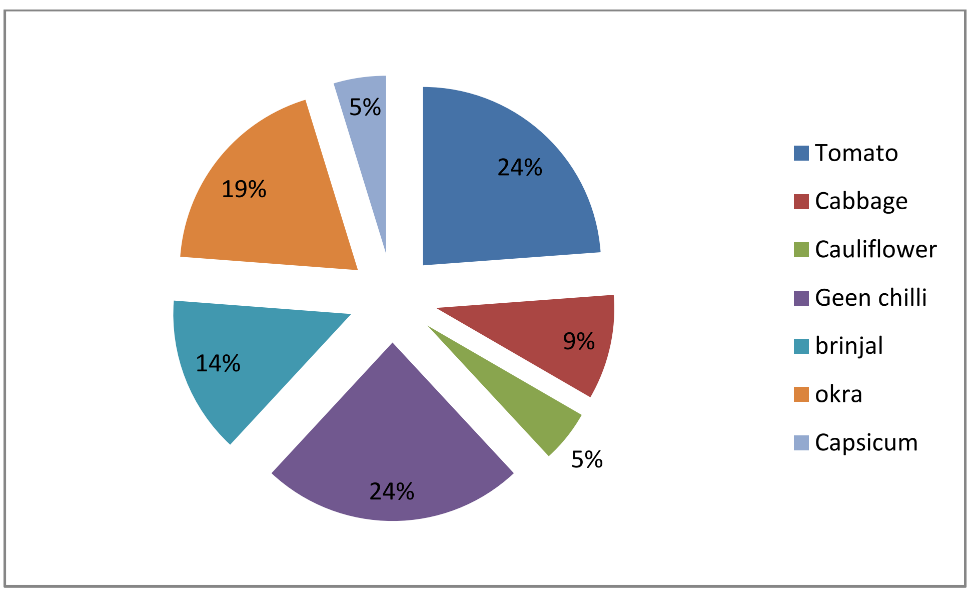

Fig-3. In total samples percentage of samples fruits detected

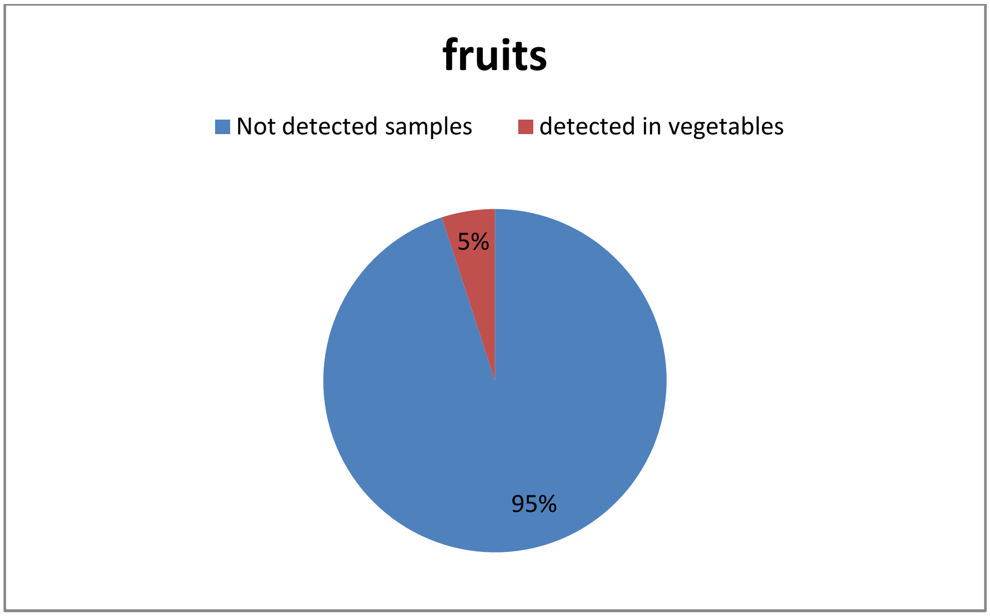

Fig-4. Percent contribution of different Fruits to samples with detected samples

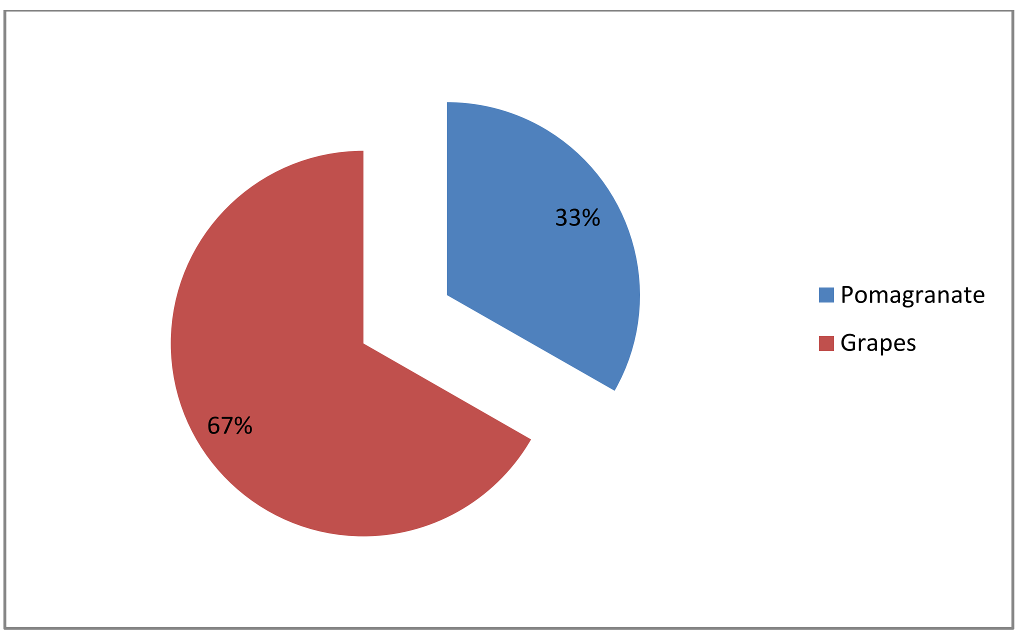

Table 1: Summary of pesticide residue analysis in vegetables and fruits

Commodity	No of samples analyzed	Samples With detected residues	% total samples	Samples With out detected residues	% total samples	Samples With detected residues Below MRL or without MRL	% total samples	Samples With detected residues above MRL	% total samples
Vegetables	30	20	66.6	10	33.3	17	56.6	3	10
fruits	30	3	10	27	90	3	10	0	0

Table 2: Distribution of various pesticide groups among contaminated vegetable groups

Pesticide group	% Contribution	% contribution of vegetables and fruits to each group											
		Brin jal	Cabb age	Okra	Tom ato	Green chilli	Capsi cum	Caluli flower	Gra pes	Poma garante	Ban ana	Sweet orange	guava
OC	3.33	1.66	1.66	0	0	0	0	0	0	0	0	0	0
OP	35.0	3.33	3.33	6.66	8.33	8.33	1.66	1.66	3.33	1.66	0	0	0
SP	1.66	0	0	0	1.33	0	0	0	0	0	0	0	0

Table 3:Pesticide residue levels in vegetables and fruit samples

Pesticide group	Variations in residue level (ppm)	Mean[a] residues in positive samples	Standard deviation of residues in positive samples (ppm)
All pesticides	0.03-1.18	0.192	0.121
OC	0.087-0.10	0.071	0
OP	0.03-1.18	0.184	0.134
SP	0.88	0.88	0

Table 4: Concentration of OCs, OPs and SPs in Vegetable samples

Name of the pesticides	% samples	Variations in residue level (ppm)	mean[a] (ppm)	SD[b] (ppm)
Organochlorines				
α - Endosulfan	1.66	0.10	0.1	0
β- Endosulfan	1.66	0.087	0.087	0
Organo Phosphates				
Dimethoate	13.3	0.05-1.18	0.309	0.371
Profenophos	6.66	0.08-0.59	0.212	0.217
Malathion	11.66	0.05-0.53	0.191	0.156
Chlorpyrifos	3.33	0.08-0.35	0.219	0.139
Quinalphos	6.66	0.03-0.09	0.075	0.026
Methyl parathion	1.66	0.04	0.04	0
Ethion	1.66	0.05	0.05	0

