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Residual and health risk assessment of pesticides in commonly consumed vegetables of Panipat, Haryana, India

Sudeep Mishra, Mahesh K Saini, Mukesh K Singh, Samsul Alam*, Lalitesh K Thakur, Jitendra Kumar

Institute of Pesticide Formulation Technology, Sector-20, Udyog Vihar, on NH-8, Gurgaon, Haryana-122016, India.
E-mail id: alam_samsul@rediffmail.com

Abstract : A study was conducted to monitor the presence of 52 pesticides in 168 samples commonly consumed vegetables. Samples of cabbage (24), cauliflower (36), brinjal (17), tomato (20), cucumber (21), chilli (25) and okra (ladyfinger) (25) were received from Directorate of Horticulture, Panipat, Haryana. Quick, Easy, Cheap, Effective, Rugged, and Safe (QuEChERS) method was used for the extraction and processing of samples whereas concentrations and confirmation of pesticide residues were determined by Gas Cromatography and Mass Spectrometry. A total 168 samples were screened for 52 commonly applied pesticides. Chlorpyrifos, pretilachlor, pendimethalin, triazofos, profenofos and atrazine were present in 34% of the samples. Total 56 contaminated samples were recorded, among which 54% of the them were found above maximum residue limit (MRL). Chlorpyrifos and pretilachlor were present in 46% of the total contaminated samples. The assessments of risk on human health were calculated for pesticide residues present in the samples. Health risk assessment of vegetable samples carried out indicated that 3 samples of brinjal, 2 of cabbage, 3 of cauliflower, 3 cucumber, 2 of okra and 1 of tomato were at high Health Risk Index (HRI≥1). All the contaminated chilli samples and rest contaminated samples of above vegetables were free from any health risk (HRI≤1).
Keywords : Vegetables; India; QuEChERS; Pesticide residues; Health Risk Index

Introduction

India is an agriculture based country, which contributes up to 14% to the National GDP [1]. India ranks second in vegetable production in the world [2]. The cultivation of vegetables during 2001-02 was in 3,240 thousand hectares of land which increased to 9,396 thousand hectares in the year 2013-14 [3]. Total vegetable export as per Agricultural and Processed Food Products Export Development Authority (APEDA), for the year 2014-15 was Rs. 4702.78 cores in India. India is the largest producer of ginger and okra whereas potato, onion,

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cauliflower, brinjal and cabbage are the second in the world. WHO recommends that at least 30% vegetables should be included in our daily diet. The meal constitutes about 150-250 g of vegetables per day diet for disease free and good health [4].

Cauliflower, cabbage, brinjal, cucumber, okra (lady finger), chilli, and tomato are commonly consumed vegetable crops which are attacked by insect pests that damage crop at various stages of growth. The percentage of pesticides used on vegetable crops was only 13-14% of the total pesticide use till 1990s [5], while the share has increased to 21% in 2010-11[6].The presence of pesticide residues on an average in vegetables is 50-70% in India [7, 8]. About 51% of the vegetable and fruit commodities record the presence of pesticide residues in India [9]. Charan et al. [7] in his study reported that 35.6 % of total contaminated samples exceeded the maximum residue limit (MRL) values as recommended by the Food and Agriculture Organization (FAO)/ World Health Organization (WHO). Study conducted by Ranga et al. [8] showed the presence of monocrotophos, chlorpyrifos, cypermethrin and endosulfan etc., in the vegetables. According to a report, over 98% of sprayed insecticides, and 95% of herbicides reach the non-target destinations. The exposure of residues is real risk to human health such as headaches, nausea, chronic, cancer, infertility and endocrine disruption. The excessive residues prove to be unsafe for health of the consumers. Farm gate vegetables were contaminated mostly with organo phosphates (OPs) and synthetic pyrethroids (SPs), which clearly shows the changes in the usage pattern from organochlorines (OCs) to other pesticide groups [10-13]. Of the total agricultural area under cultivation in India, about 1.5% of land is under farming in Haryana. Haryana contributes 15% of its agricultural produce to India's total production whereas its growth in agriculture increases 7 times since its inception in 1966. About 96% of its area is cultivated. Haryana played a major role in Green Revolution in 1970s. The present study determines the presence of residue levels of some common and frequently used pesticides in vegetables collected from farmers' farm and market of Panipat district, Haryana. The aim of the study is to determine the concentration levels and risk of pesticides used in the commonly consumed vegetables viz. in cabbage, cauliflower, brinjal, tomato, cucumber, chilli and okra collected from various villages of Panipat district, Haryana. The confirmation and concentrations of pesticides were determined by gas chromatography coupled with mass selective detector (GC-MSD).

Materials and methods

2.1. Apparatus

Gas chromatographs-GC Model 7890A (Agilent Technologies) with mass (5975C inert XL EI MSD) triple axis detector was used for estimation of pesticide residues. The instrument operating conditions were, injector port temperature was set at 280^{o}C. The interface, ion source and quadruple temperatures were set at 280^{o}C and 230^{o}C and 150^{o}C respectively. One microliter of concentrated extract was injected in splitless mode with carrier gas helium (grade-1). The injector was operated in splitless mode at 280^{o}C temperature. The mass spectrometer was operated in electron impact ionization source with energy of 70eV and Scan mode with solvent delay time of 3 min. Chromatography column used in gas chromatograph was DB-5MS fused silica capillary column (Agilent J&W GC column, 5% phenylated methyl siloxane, 30 m length × 0.25 mm i.d. × 0.25 µm film thickness) with He carrier gas having linear flow at 1mL/min. The pesticides were were well resolved and separated under the run time of 40.75 min with oven programming. The initial temperature was set at 50 ^{o}C and hold for 2 min followed by a ramp rate of 8^{o}C /min. up to a temperature of 280°C with a hold time of 6 min.

2.2. Reagents

(a) Solvents-Acetone, n-hexane, and acetonitrile, all solvents of high purity >99.999

(b) Chemicals-$MgSO_4$ (Merck Life Science Private Limited, Mumbai, Maharashtra, India), Primary Secondary Amine (PSA), C18, (Sigma-Aldrich Laborchemikalein GmbH, Seelze, Lower Saxony, Germany) and Graphitized Carbon Black sorbent,(Agilent Technologies Incorporation, Folsom, CA)

(c) Pesticide reference standards- α-HCH, β-HCH, γ-HCH, δ-HCH, alachlor, aldrin, dicofol, pendimethalin, o,p DDE, α-endosulphan, heptachlor, p,p DDE, endosulphansulphate, dieldrin, o,p DDD, β-endosulphan, p,p DDD, o,p DDT, p,p DDT, bifenthrin, fenpropathrin, lambda-cyhalothrin, β cyfluthrin, cypermethrin, fenvalarate, fluvalinate, deltamethrin, anilophos, chlorfenvinfos, chlorpyrifos, butachlor, pretilachlor, chlorpyrifos-methyl,

dichlorvos, ethion, malathion, parathion methyl, monocrotophos, phorate, profenofos, quinolphos, triazophos, fenitrothion , phosalone, paraoxon-methyl, fenamiphos, edifenphos, dimetoate, diazinon, fenthion, parathion and phosphamidon were procured from Sigma Aldrich, Germany which were screened for their presence in brinjal, cabbage, cauliflower, chilli, cucumber, okra and tomato samples of district Panipat of Haryana for the period of five years from 2013-2017. The study includes the application of Quick, Easy, Cheap, Effective, Rugged, and Safe (QuEChERS) methods [14] for the estimation of used/generic pesticides in commonly consumed vegetables of the area. All reference materials were certified standards of Sigma Aldrich (USA) make. The stock solution of different concentration was prepared in n-hexane and acetone.

2.3. Sample collection location

Panipat is located at 29.39°N 76.97°E with average elevation of 219 meters (718 feet). Panipat is situated on ShershahSuriMarg (now known as G.T. road or NH-1), 90 km north of Delhi. It is surrounded by three districts of Haryana i.eKarnal in the north, Jind in the west and Sonipat in the south. Panipat is big commercial and industrial city of Haryana. It is a developed state with industries and educational institutions, and has attracted a large population. The agricultural produce of the area are mostly consumed locally and it makes it important to regulate the pesticide residues in vegetables, to guarantee food quality, so as not cause public health problem and alimentary risk. Vegetables sold in the city of Panipat are mainly grown in villages around the city, are harvested and sold fresh.

2.4. Sample collection

A total of 168 samples of which brinjal (17 nos), cabbage (24 nos), cauliflower (36 nos), chilli (25 nos), cucumber (21 nos), okra (25 nos), and tomato (20 nos) were collected from farms and several local markets of Panipat, during 2012 to 2017 by Directorate of Horticulture, Panipat, Haryana. The sample size was one kg. The collected samples were sealed, labeled and placed in an iced box. All the samples were transported to Institute of Pesticide Formulation Technology,Gurugram, Haryana,a pesticide residue laboratory, accredited by NABL as per ISO IEC 17025/2017. All the samples were refrigerated (@ ±5°C). These samples were then processed and analyzed (within 24h from the time of their collection) for the presence of pesticide residues. Samples were analyzed for the presence of 52 pesticides, belonging to different class like organophosphorus, organochlorine compounds, herbicides and pyrethroids. The standard mixture of 0.5 ppm (mg/kg) was prepared for 52 pesticides (Figure 1). The mixture was used for calculating recovery, linearity, repeatability parameters of the tested method.

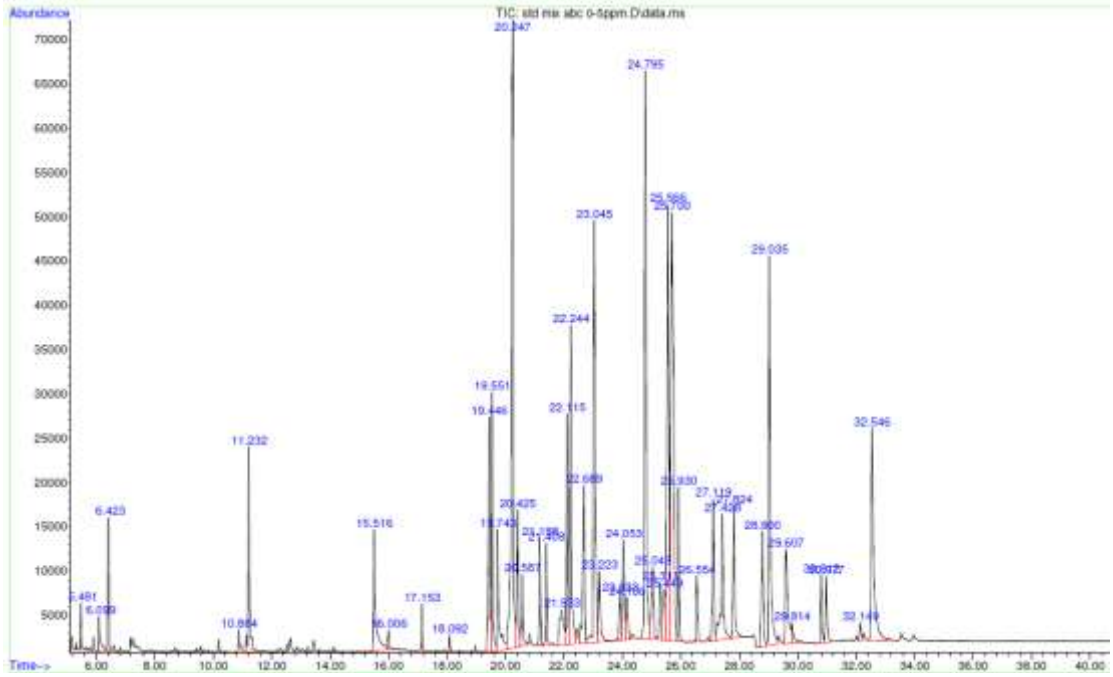

Figure 1. GC-MS chromatogram of standard mixture for 52 pesticides

2.5.Extraction and cleanup

Samples were processed according to the QuEChERS method[15]. Samples were finely chopped and homogenized in a mixer grinder. 10 gram of homogenized sample was weighed into a 50 mL centrifugation tube and 10 mL of acetonitrile was added and shaken for 1 min using vortex shaker. 4g anhydrous $MgSO_4$ was added and shaken vigorously for 1 min by hand. The tubes were centrifuged at 6,000 rpm on the centrifuge machine for about 5 min. Highly pigmented food samples required cleanup before estimation. Cleanup was performed according to Lehotay et al.[16].1.5 mL extract was transferred from the upper layer into a 2 mL centrifuge tube in which 150 mg anhydrous $MgSO_4$, 40mg PSA and 40mg C18 were added and shaken vigorously on a vortex shaker for 1 min. The tubes were centrifuged at 5,000 rpm for 6 min. The supernatant solvent 1 mL was transferred to a 2 mL vial, dried and finally made up to 0.1 mL n-hexane for injection in Gas chromatography and mass spectrometry (GC-MS).

2.6. Quality assurance procedure

Analytical methods and instruments were fully validated. Analytical lab is accredited by NABL as per quality assurance system ISO/IEC 17025 (2017) and Bureau of Indian Standard (BIS) is audited from time to time. All criteria of the Codex Committee, for performance of the multi-residue method for quality assurance were followed. The recoveries of test compounds of 52 pesticides ranged from 70 to 120% and reproducibility were good with the relative standard deviation (RSD), was <20%. The limit of detection in vegetable samples ranged between 0.01 and 0.1 mg/kg. The measurements of uncertainty of random and systematic error at 95% confidence level were less than ±20%.

2.7. Risk assessment

Risk assessment process for the risk assessment of pesticide residues in vegetables follows some steps such as hazardousness, characterization (dose-response assessment), exposure and risk.

2.8. Hazardousness

Hazardous nature of any pesticides involves identification of its adverse effects to an organism population[17].As per Central Insecticide Board (CIB) recent regulations there is a requirement of hazardous nature identification before any pesticide which can be approved for usage in agriculture. The hazardous nature of pesticides disrupts reproductive and endocrine, neuro, immune system, causes cancer and respiratory distress[18].Various studies have to be carried out in test organisms (microbial, cells or animals) at different exposure level. The highest dose at which pesticide does not cause any detectable toxic effects on the test organisms is called the no-observed-adverse-effect-level (NOAEL) which is expressed in milligrams per kilogram of body weight per day[19].NOAEL is used to calculate ADI (Acceptable Daily Intake).

2.9. Hazard characterization

Hazard characterization involves comparing the pesticide exposure concentration with the Acceptable Daily Intake (ADI). Without appreciable health risk for life time, the ADI is the estimated amount of pesticides in food (mg/kg body weight/day) that can be taken daily[19].ADI is calculated by dividing the NOAEL for animal studies with an uncertainty factor of 100 to convert to a safe level for humans[20].

2.10. Exposure assessment

The amount of pesticide that reaches a target organism population in a specific frequency for a certain time[17].The pesticide a residue is divided by the body weight is ADI. Exposure = (Concentration of pesticide residue x Food consumed)/ body weight. The exposure assessment data comes from field residue trials, national pesticide monitoring programs and food consumption surveys.

2.11. Hazard Risk Index (HRI)

It is important to compare exposure of pesticides for the establishing toxicological criteria such as Estimated Daily Intake (EDI) which estimates pesticides residues exposure as per international guidelines [21, 22]. EDI is calculated by multiplying pesticide residue concentration (mg/kg) and food consumed per day (kg/day) and dividing by a body weight of 60 kg for an adult people. The average daily vegetable intake for

adult was considered to be 0.345 kg/person/day [23]. Hazard Risk Index (HRI) of the residues was calculated by Equation:

HRI = EDI/ADI …… equation-(1)

Where EDI is estimated daily intake, ADI is acceptable daily intake. If the value of HRI is more than 1, then it is considered as not safe for human health [24].

Results and discussion

A total of 168 samples of vegetables i.e cabbage, brinjal, chilli, tomato, okra, cucumber and cauliflower were monitored for presence of pesticide residues for study for a period of five years. The samples were collected as per the protocol of Directorate of Horticulture, Haryana. All the samples were collected from farmer's farm and market of district Panipat. The samples were screened for the presence of 52 pesticides which are commonly applied in the area. The vegetables selected for the study are consumed and transported to the nearby cities and neighboring states.

Seventeen brinjal samples (5 of farm & 12 of market) were analysed for the presence of pesticide residues in which 12 samples showed the presence of pesticides (Table 1& 2). Chlorpyrifos, lambda-cyhalothrin, pretilachlor, atrazine, pendimethalin, butachlor and DDT isomers were detected in 9, 1, 10, 1, 1, 1 and 2 samples each with concentration range of 0.41-2.23, 0-3.79, 0.34-6.71, 0.81, 7.0, 0.52 and 0.18-0.22 mg/kg, respectively (Table-4). All the samples detected with chlorpyrifos and lambda cyhalothrin were found above their Maximum Residue Limit (MRL) of 0.2 mg/kg (Codex or FSSAI) values whereas MRL of pretilachor, atrazine, pendimethalin, butachlor and DDT isomers is not documented by regulatory body in brinjal. From the 12 brinjal samples from farm and market in which 9 among them recorded pesticides above MRL which were also showed the presence of multi –pesticide residues. Three of the brinjal samples were found contaminated with single pesticide, seven samples with two pesticides, one sample with three pesticides and one sample with five different pesticides (Table-3). Total 24 cabbage samples (16 from farm and 8 from market) were screened for the residual contamination in which chlorpyrifos was detected in 7 samples from farm in the range 0.075 to 3.21mg/kg (Table 1, 2 & 4), 4 samples from farmers field were above MRL (1mg/kg). 36 samples of cauliflower were screened (18 samples from farmers field and 18 from the market) for residual contamination in which 13 samples recorded the presence of pesticides namely, chlorpyrifos, pretilachlor , lambda-cyhalothrin, triazofos and pendimethalin in 10, 10, 1, 1, and 1 sample each at concentration range of 2.56-0.23, 2.50-0.30, 4.56, 0.53 and 0.70 mg/kg, respectively (Table-1, 2 & 4), in which 4 samples were contaminated and above MRL (1mg/kg for chlorpyrifos), whereas 10 samples showed the presence of with multi-pesticide residue. Among 13 cauliflower samples analyzed, 1, 9, 3 samples were detected with 1, 2, and 3 pesticides (Table 3). All the 24 chilli samples (18 from market and 7 from farmers field) were analyzed for residual contamination in which only 3 samples showed the presence of pesticides viz.,chlorpyrifos at concentration range 0.05-1.15 mg/kg, and with one sample above MRL limit (0.2 mg/kg) (Table 1, 2 & 4). From a total 20 cucumber samples (13 samples from farmgate and 8 from market), were analyzed in which 8 samples were detected with pesticide residues. The residual presence of chlorpyrifos, pretilachlor, DDT isomers, lambda-cyhalothrin were observed in 6, 5, 3, and 1sample each in the range 0.19-3.15, 0.3-8.36, 0.11-0.09, 4.50 mg/kg, respectively (Table 1, 2 & 4). 50% of the total cucumber samples analyzed were above MRL (mg/kg). Among the total 8 samples detected with pesticides, 5 samples were showed the presence of more than one pesticide. In samples of cucumber, a single pesticide was present in 3 samples, 2 pesticides in 3 samples and 3 pesticides in two samples (Table 3). Twenty five samples of okra (19 from farmers' field and 6 from the market) were screened for 52 pesticides. Chlorpyrifos, pretilachlor, atrazine, pendimethalin and butachlor was detected in 3, 2, 1, 1, and 1 sample each in the concentration range of 0.34-0.56, 0.49-8.36, 3.35, 2.70 and 1.84 mg/kg, respectively (Table 1, 2 & 4). Three of the samples were above MRL (0.2mg/kg for chlorpyrifos), hence contaminated. Out of the total samples detected with pesticides, 1 sample recorded the presence of multi pesticide residues. Out of the total Okra samples showing the presence of pesticides, single pesticide was detected in 3 samples, whereas 1 sample recorded 5 different pesticides (Table 3). Among the 20 tomato samples (3 from farmers field and 17 from market) screened for the pesticides, 8 samples of tomato detected the presence of chlorpyrifos, pretilachor and profenofos in 6, 7 and 1sample each at the concentration range of 1.67-0.93; 2.51-0.34; 0-1.07 mg/kg, respectively (Table 1, 2 & 4). Out of the 8 samples 6 samples were contaminated with chlorpyrifos as residues were above MRL (0.2 mg/kg for chlorpyrifos). Out of samples which detected the presence of pesticides 6 samples of tomato recorded the

presence of multiple pesticide residues. Among the 8 tomato samples, 2 of them showed the presence of single pesticide, 5 samples with 2 pesticides and 1 sample with 3 pesticides (Table 3).

A total of 168 samples of cabbage, brinjal, cauliflower, chilli, okra, tomato and cucumber which were analysed for the presence of 52 pesticides. Pesticide residues were detected in 55 samples (Table-4). Chlorpyrifos was present in 44 samples in the range of 0.05-3.21 mg/kg. Chlorpyrifos residues were detected in almost all the vegetables samples. Lambda-cyhalothrin was detected in 4 samples in the concentration range of 3.79-4.56 mg/kg in brinjal, cucumber and cauliflower. Pretilachlor was present in 33 samples in the range of 0.30-8.36 mg/kg in brinjal, cauliflower, cucumber, tomato and okra. DDT isomers were recorded in 7 samples in the range of 0.09-0.20 mg/kg in brinjal and cucumber. Atrazine residues were detected in samples of brinjal and okra in the range of 0.81-3.35 mg/kg. Pendimethalin residues were present in brinjal, cauliflower and okra in the range of 0.70-7.0 mg/kg. Butachlor was detected in brinjal and okra in the range of 0.52-1.84 mg/kg. Triazofos and profenofos were observed in cauliflower and tomato, respectively.

Table 1.Results of analysis of samples of vegetables collected from Panipat for a period from 2013-2017.

S.No.	Items	Total Analysed Samples	Pesticides Detected	Contaminated samples with each pesticide	Concentration Range mg/kg	Pesticide Detected in each Commodity		Maximum Residue Limit (MRL) mg/kg	Number of Samples above MRL (mg/kg)		Total Number of Samples above MRL (mg/kg)		Number of Samples with Multi-pesticide residue	
						Numbers	%		Numbers	%	Numbers	%	Numbers	%
1.	Brinjal (Solanum melongena)	17	Chlorpyrifos	9	0.41-2.23	12	70.6	0.2	9	100	10	75	9	75
			L-Cyhalothrin	1	0-3.79			0.2	1	100				
			Pretilachlor	9	0.34-6.71	-	-	-	-	-				
			Atrazine	1	0.81	-	-	-	-	-				
			Pendimethalin	1	7.0	-	-	-	-	-				
			Butachlor	1	0.52	-	-	-	-	-				
			DDT Isomers	2	0.18-0.22	-	-	-	-	-				
2.	Cabbage (Brassica oleracea)	24	Chlorpyrifos	7	3.21-0.075	7	29.16	1.0	4	57.14	4	57.4	-	-
3.	Cauli flower (Brassica oleracea var. botrytis)	36	Chlorpyrifos	10	2.56-0.23	14	39.0	1.0	4	30.76	4	30.76	10	76.92
			Pretilachlor	10	2.50-0.30	-	-	-	-	-				
			L-Cyhalothrin	1	4.56	-	-	-	-	-				
			Triazofos	1	0.53	-	-	-	-	-				
			Pendimethalin	1	0.70	-	-	-	-	-				
4.	Chilli (Capsicum frutescens)	25	Chlorpyrifos	3	1.15-0.05	3	12.50	0.2	1	33	1	33	-	-
5.	Cucumber (Cucumis Sativus)	21	Chlorpyrifos	6	3.15-0.19	8	38.09	0.2	4	50	4	50	5	62.5
			Pretilachlor	5	8.36-0.39			-						
			DDT Isomer	3	0.11-0.09			-						
			L-Cyhalothrin	1	4.50			-						

6.	Okra (Hibiscus esculentus)	25	Chlorpyrifos	3	0.34-0.56	4	16	0.2	3	75	3	75	1	20
			Pretilachlor	2	8.36-0.49			-						
			Atrazine	1	3.35			-						
			Pendimethalin	1	2.70			-						
			Butachlor	1	1.84			-						
7.	Tomato (Lycopersicon Esculentus)	20	Chlorpyrifos	6	1.67-0.93	8	40	0.2	6	75	6	75	6	75
			Pretilachlor	7	2.51-0.34			-						
			Profenofos	1	0-1.07									
Total		168				56	34				32	54	31	100

Table 2. Frequency of commodities with detectable pesticide residues in vegetables collected from farm and market of district Panipat.

Commodity	**Samples collected from farm**		**Samples collected from market**		**Total Samples Analysed**	**Total Contaminated Samples (%)**
	Number of samples analysed	**Number of samples with detectable residues (%)**	**Number of samples analysed**	**Number of samples with detectable residues (%)**		
Brinjal	5	5 (80)	12	7 (58.3)	17	12
Cabbage	16	7 (43.7)	8	0	24	7
Cauliflower	18	7 (38.8)	18	7 (38.8)	36	14
Chilli	7	0	18	3 (16.66)	25	3
Cucumber	13	5 (38.46)	8	3 (37.5)	21	8
Ladyfinger	19	3 (15.8)	6	1 (16.6)	25	4
Tomato	3	3 (100)	17	5 (29.41)	20	8
Total	81	30(38)	87	26(30.0)	168	56

Table 3. Number of samples with multiple pesticide residues for each commodity.

Commodity	**Number of pesticide residue in one sample**				
	1	2	3	4	5
Brinjal	3	7	1	-	1
Cabbage	1	-	-	-	-
Cauliflower	2	9	3	-	-
Chilli	4	-	-	-	-
Cucumber	3	3	2	-	-
Ladyfinger	2	-	-	-	5
Tomato	2	5	1	-	-
Total	17	24	7		6

Table 4. Pesticides detected, Concentration range, Detection percent and tested vegetables samples.

S.No.	Pesticides Detected in range mg/kg	Number of contaminated samples	Detection % (Total= 168)	Range mg/kg	Tested Vegetables						
					Cabbage	Cauliflower	Brinjal	Chilli	Cucumber	Ladyfinger	Tomato
1	Chlorpyrifos	44	26	0.05-3.21	7	10	9	3	6	3	6
2	L-cyhalothrin	3	2	3.79-4.56	-	1	1	-	1	-	-
3	Pretilachlor	33	20	0.30-8.36	-	10	9	-	5	2	7
4	DDT Isomers	5	3	0.09-0.20	-	-	2	-	3	-	-
5	Atrazine	2	1	0.81-3.35	-	-	1	-	-	1	-
6	Pendimethalin	3	2	0.70-7.0	-	1	1	-	-	1	-
7	Butachlor	2	1	0.52-1.84	-	-	1	-	-	1	-
8	Triazofos	1	0.60	0-0.53	-	1	-	-	-	-	-
9	Pofenofos	1	0.69	0.52-1.84	-	-	-	-	-	-	1

Table 5. Estimated Daily Intake (EDI), Acceptable Daily Intake (ADI), Health Risk Index (HRI) and Health Risk estimation of pesticide contaminated samples.

S.No.	Analysed Samples	Pesticides Contaminated Samples	Concentration mg/kg	Estimated Daily Intake (EDI) [Pesticide Conc. (mg/kg) x vegetable consumed/day (kg/day)] / avg body weight (60 kg). Avg. vegetable intake 0.345 kg/person/day	Acceptable Daily Intake (ADI) (mg/kg x body weight/day)	Health Risk Index (HRI)= EDI/ADI	Health Risk in Samples HRI ≥1 Yes HRI ≤1 No
1.	Brinjal (17)	Chlorpyrifos (9)	0.41, 1.04, 1.18, 1.06, 1.19, 1.12, 1.07, 1.15, 2.23	0.0023, 0.005, 0.007, 0.006, 0.007, 0.006, 0.0062, 0.0066, 0.013	0.01*	0.2, 0.6, 0.7, 0.7, 0.6, 0.7, 0.6, 0.6, 1.3	≥1=1 (Nos.)
		L-Cyhalothrin (1)	3.79	0.022	0.001	22	≥1=1 (Nos.)
		Pretilachlor (9)	0.34, 0.76, 1.5, 0.42, 0.89, 0.83, 0.36, 0.37, 6.71	0.002, 0.004, 0.009, 0.005, 0.005, 0.002, 0.002, 0.039	0.018#	0.1, 0.2, 0.5, 0.28, 0.028, 0.1, 0.1, 2.16	≥1=1 (Nos.)
		Atrazine (1)	0.81	0.005	0.018	0.27	-
		Pendimethalin (1)	7.0	0.040	0.1	0.40	-
		Butachlor (1)	0.52	0.003	0.037	0.081	-
		DDT Isomers (2)	0.18, 0.22	0.001	0.01*	0.1, 0.1	-
2.	Cabbage(24)	Chlorpyrifos (7)	0.075, 0.46, 0.65, 1.01, 1.58, 1.81, 3.21	0.00, 0.003, 0.004, 0.006, 0.010, 0.009, 0.018	0.01*	0, 0.3, 0.4, 0.6, 1.0, 0.9, 1.8	≥1=2 (Nos.)
3.	Cauliflower (36)	Chlorpyrifos (10)	2.56, 0.99, 0.93, 0.66, 1.18, 0.92, 1.02, 0.26, 0.32, 0.23	0.015, 0.006, 0.005, 0.004, 0.007, 0.005, 0.006, 0.001, 0.002, 0.001	0.01*	1.5, 0.6, 0.5, 0.4, 0.7, 0.5, 0.6, 0.1, 0.2, 0.1	≥1=1 (Nos.)
		Pretilachlor (10)	0.40, 0.33, 0.31, 0.35, 0.42, 0.10, 0.35, 0.30, 0.60, 2.58,	0.002, 0.002, 0.002, 0.002, 0.002, 0.001, 0.002, 0.002, 0.003, 0.015	0.018	0.1, 0.1, 0.1, 0.1, 0.1, 0.05, 0.1, 0.1, 0.16, 0.83	-
		L-Cyhalothrin (1)	4.56	0.026	0.001	26	≥1=1 (Nos.)
		Triazofos (1)	0.53	0.003	0.001*	3.0	≥1=1 (Nos.)
		Pendimethalin (1)	0.70	0.004	0.1	0.04	-
4.	Chilli (25)	Chlorpyrifos (3)	1.15, 0.21, 0.05	0.007, 0.001, 0.000	0.01*	0.7, 0.1, 0.0	-
5.	Cucumber	Chlorpyrifos (6)	0.19, 1.04, 2.79, 3.15, 1.42,	0.001, 0.006, 0.016, 0.018,	0.01*	0.1, 0.6, 1.6, 1.8,	≥1=2 (Nos.)

	(21)		1.65	0.008, 0.009		0.8, 0.9	
		Pretilachlor (5)	8.36, 0.5, 0.39, 0.80, 1.12	0.048, 0.003, 0.002, 0.005, 0.006	0.018[#]	2.6, 0.16, 0.1, 0.28, 0.33	≥1=1 (Nos.)
		DDT Isomer (3)	0.11, 0.095, 0.099	0.001, 0.001, 0.001	0.01[*]	0.1, 0.1, 0.1	-
		L-Cyhalothrin (1)	4.50	0.026	0.001	26	≥1=1 (Nos.)
6.	Okra (25)	Chlorpyrifos (3)	0.34, 0.56, 0.34	0.002, 0.003, 0.002	0.01[*]	0.2, 0.3, 0.2	
		Pretilachlor (2)	8.36-0.49	0.048, 0.003	0.018[#]	2.66, 0.16	≥1=1 (Nos.)
		Atrazine (1)	3.35	0.019	0.018	1.05	≥1=1 (Nos.)
		Pendimethalin (1)	2.70	0.016	0.1	0.16	-
		Butachlor (1)	1.84	0.011	0.037	0.30	-
7.	Tomato (20)	Chlorpyrifos (6)	1.67, 1.58, 1.18, 1.09, 0.93, 1.65	0.010, 0.009, 0.007, 0.006, 0.005, 0.009	0.01[*]	1.0, 0.9, 0.7, 0.6, 0.5, 0.9	≥1=1 (Nos.)
		Pretilachlor (7)	2.51, 0.56, 0.52, 0.41, 0.34, 0.40, 0.37, 2.52	0.010, 0.009, 0.007, 0.006, 0.005, 0.009	0.018[#]	0.50, 0.5, 0.38, 0.6, 0.27, 0.5	-
		Profenofos (1)	1.07	0.006	0.01[*]	0.6	-

Japan Analytical Chemistry Consultant under discussion in food safety commission.
[*] K K Sharma, Pesticide Residue Analysis Manual, Second Edition, February 2013, 230-233.
US EPA

3.1. Human health risk assessment of pesticides

Table 5.shows that Estimated Daily Intake (EDI) was calculated by multiplying the pesticide concentration to the amount of average vegetables taken i.e. 0.345 kg/day/person which is divided by average weight of person (60 kg). Acceptable daily intake (ADI) for chlorpyrifos (0.01 mg/kg), lambda cyhalothrin (0.001 mg/kg), pretilachlor (0.018 mg/kg), atrazine (0.018 mg/kg), pendimethalin (0.1mg/kg), butachlor (0.037 mg/kg), DDT and isomers (0.01mg/kg), triazofos (0.001mg/kg) and profenofos (0.01mg/kg)[25, 26]. Health Risk index (HRI) was calculated by dividing EDI by ADI. The Health risk assessment depends on the value of HRI, if ≥1 indicates health risk, whereas ≤1 indicates of no health risk.

Calculation of EDI, ADI and HRI for estimation of risk in brinjal samples. It was calculated that brinjal sample contaminated with chlorpyrifos (1 sample), lambda-cyhalothrin (1sample) and pretilachlor (1sample) were at high health risk with Health Risk Index ≥1 rest samples detected with chlorpyrifos, pretilachlor , atrazine, pendimethalin, butachlor and DDT and isomers, respectively, were free from any risk (HRI ≤1). Similarly in 2 samples of cabbage detected with chlorpyrifos were at higher health risk and other samples were at no health risk. In cauliflower samples, chlorpyrifos was detected in 1sample, lambda-cyhalothrin in 1sample,triazofos in 1 sample were at higher health risk whereas remaining samples recording the presence of chlorpyrifos, pretilachlor and pendimethalin were free from any risk. All the samples of chilli recording the presence of pesticides were of no health risk. Among samples of cucumber detected with pesticide residues samples in which 4 samples contaminated with chlorpyrifos, lambda-cyhalothrin and pretilachlor exceeded HRI ≥1 whereas rest samples recording the presence of chlorpyrifos, pretilachlor and DDT isomers showed no health risk. Two sample of okra detectected with pretilachlor and atrazine were at high health risk whereas rest recorded with chlorpyrifos, pretilachlor, pendimethalin and butachlor were at no health risk. Only 1 sample of tomato recording chlorpyrifos residues was at health risk, rest samples showing presence of pesticides, namely chlorpyrifospretilachlor and profenofos were free from any risk.

Figure 2 shows, 12 samples of brinjal recorded the presence of pesticides in which 9 of them were above MRL and recorded with multiresidue whereas 3 samples of the samples were not safe for consumption (HRI≥1). Similar is the case with cabbage in which 7 of the pesticides detected samples in which 4 were above MRL and 2 samples at high health risk. Also 14 samples recorded with pesticides in cauliflower in which 4 samples were above MRL, 10 with multi-residue and 4 samples were not safe for consumers. Three chilli samples recorded for pesticide residue in which only one sample was above MRL. Pesticide recorded 8 samples of cucumber in which 4 of them were above MRL and 5 were detected with multiresidue and three of them were at high health risk. Four samples of were recorded for pesticide residue in okra in which 3 samples were above MRL,1sample with multiresidue and 2 samples were not safe for consumers.

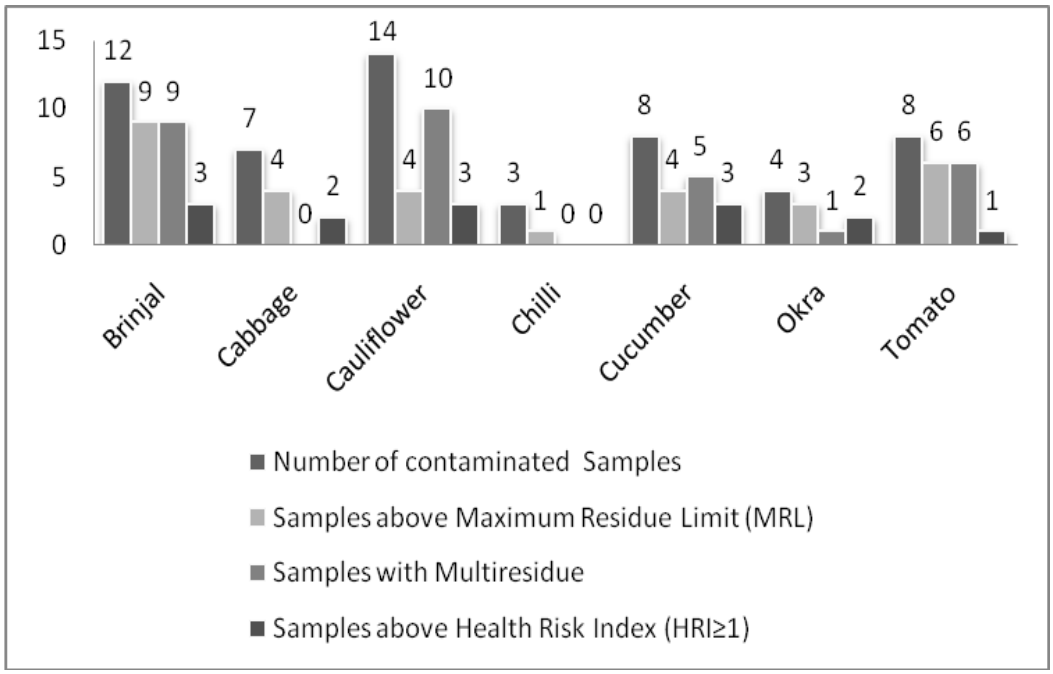

Figure 2. Representing the number of samples with recorded pesticides, above MRL, multiresidue and above Health Risk Index.

Conclusion

A total 168 samples of vegetables were screened , 81 samples from farmers field and 87 from market for 52 commonly applied pesticides in the district Panipat , Haryana (Table-1).Out of the total samples analyzed, 34% of the samples were detected with pesticides, namely, chlorpyrifos, pretilachlor, pendimethalin, triazofos, profenofos and atrazine. Among the 56 samples showing the presence of pesticides, 54% of them were found above maximum residue limit (MRL). All the samples which were above MRL are contaminated with multi-pesticide-residue. From Table 2 & 3, 38% of farmers' field and 30% of market samples were found record pesticides. A total 17 samples were found contain single pesticide, 24 samples with 2 different pesticides, 7 with 3 different pesticides and 6 samples with 5 different pesticides. Table 4.showschlorpyrifos and pretilachlor were found in 46% of the total 56 samples detected with pesticides. Almost all contaminated samples were detected with chlorpyrifos whereas triazofos and profenofos were detected in cauliflower and tomato samples, respectively.

Health risk assessment of brinjal, cabbage, cauliflower, chilli, tomato and okra were calculated. 3, 2, 3, 4, 2, 1 samples of brinjal, cabbage, cauliflower, cucumber, okra and tomato samples respectively whose HRI≥1. Brinjal samples were detected with chlorpyrifos (HRI=1.3), lambda-cyhalothrin (HRI=2.16) and pretilachlor (HRI=2.16) and cabbage with chlorpyrifos (HRI= 1.0, 1.8), cauliflower with chlorpyrifos (HRI=1.5), lambda-cyhalothrin (HR=26) and triazofos (HRI=3) and cucumber samples with chlorpyrifos (HRI=1.6, 1.8),lambda-cyhalothrin (HRI=26) and pretilachlor HRI=2.6), okra with (pretilachlor HRI=2.66, atrazine 1.05) and tomato with (chlorpyrifos HRI=1). All samples of chilli and other vegetable samples though showed the presence of pesticides were free from any health risk HRI≤1. Some sample cucumber and cauliflower shows exceptionally high HRI value. Out of the total 168 samples analyzed, only 15 samples were at high health risk, rest all samples were free from any risk.

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