Bull. Environ. Contam. Toxicol. (2005) 74:170–176

DOI: 10.1007/s00128-004-0564-0

Bulletin of Environmental Contamination and Toxicology

Monitoring of Pesticide Residues in Vegetables (2000–2003) in Karachi, Pakistan

Z. Parveen, M. I. Khuhro, N. Rafiq

Pesticide Research Institute, Southern-Zone Agricultural Research Center, Pakistan Agricultural Research Council, Karachi University Campus, Old Blocks No. 09 and 10, Karachi 75270, Pakistan

Received: 21 May 2004/Accepted: 1 October 2004

Human diet is largely based on plants and their products. Parts of which comes from fresh or cooked vegetables. Pesticide residue studies are essential to assess and generate a baseline data not only to face the challenges of food safety but to trade in an international environment and to support policy makers in formulating food laws especially in least developed countries (LDCs) where such regulations either don't exist or lack holistic approach. Considering chronic environmental and health implications resulting from residues of pesticides, research on this aspect has been initiated in developed nations until recently. However, convenient transmission of information has brought about a change in research priorities even in LDCs. Several countries have initiated residue research projects to evaluate the extent of danger (if any) and health of their food. Pesticide Research Institute (PRI) of Pakistan Agricultural Research Council (PARC) has a mandate to monitor the pesticide residues in foods. In this regard a study was carried out to evaluate the pesticide residues in fresh vegetables procured from retail markets of Karachi during 2000 to 2003.

MATERIALS AND METHODS

Analytical reagent grade chemicals were used. All solvents were redistilled in a glass system before use.

Two hundred and six samples of different vegetables were procured from different selling points of Karachi during 2000-2002. One kg sample of each commodity was purchased as per standard procedure (FAO/WHO, 1993). All samples were homogenized and sub-samples were subjected to extraction. Extraction was carried out on the same day as the sampling was done.

Samples were analyzed in accordance with the described procedures (Zahida and Zafar 2002). Each sub-sample (30 g) was extracted with 75 ml of extracting mixture (Toulene+n-hexne+Ethylacetate) in the ratio of 3:1:1). The decanted extract was concentrated to approximately 2-3 ml and poured on a mini column of Florisil plus activated charcoal and eluate was collected. The cleaned up extract was evaporated to dryness in a rotary vaccum evaporator and taken up in 2-3 ml acetone for Gas Chromatographic determination. For High Performance Liquid

Correspondence to: Z. Parveen

Chromatographic determination, evaporated dry residues were taken up in 2-5 ml methanol (HPLC grade).

A Shimadzu Model SPD -10 A high performance liquid chromatograph (HPLC) equipped with deuterium lamp with changeable wavelength and a Varian AG Model 3600 gas chromatograph (GC) equipped with Flame ionization detector (FID) data system DS – 650 series Model DS – 651 were used.

Light source: Deuterium Lamp with changeable wavelength, Wavelength: 223 or 254 nm, Pressure: 2000 psi, Column: Stainless steel column packed with C-18 (ODS)-15 cm x 6.0 mm i.d., Injection volume: 20 μl, Mobile Phase: Methanol+water (3:1) and Flow rate of mobile phase: 0.5 μl/min were used as instrumental parameters for HPLC.

Column: Glass column packed with 1.5% OV – 17+1.95 OV-210 WHP (80-100 mesh), Temperature of Column: 230 °C, Temperature of Injector: 250 °C, Temperature of Detector: 300 °C, Attenuation and Range: 12, Flow Rate of nitrogen: 13 ml/min, Flow Rate of Hydrogen: 4.5 ml/min and Flow Rate of Air: 175 ml/min were used as instrumental parameters for GC.

RESULTS AND DISCUSSION

Two hundred and six samples of 27 different vegetables procured from retail markets of Karachi during 2000-2003 were analyzed for residues of 24 different pesticides. The results showed an alarming level of contamination of this part of food with pesticides. On an average 63 % samples were found to be contaminated, while 46 % of contaminated samples violated the Maximum Residue Levels (MRLs) as given by FAO/WHO (Codex Alimentarius, 2000).

Presence of pesticide residues in food items up to such an extent though requires lot of attention yet it is not a new phenomenon. These results are in conformity with the finding of an earlier study (Naqvi et al. 1999) in which blood/serum samples from people of Karachi were taken and most of the samples were found to contain pesticides in low or high quantities. In many of LDCs food safety laws either do not exist or are not given required consideration that results in marketing of commodities even after few hours of spraying pesticides. Even in countries populating highly quality conscious people and having tough food safety laws, contamination problem exists such as in Canada 68.5 % samples of fruits and vegetables were found to contain one or more pesticides during a five year study, however residue levels were low and only 3.2 % samples violated MRLs (Ripley et al. 2000). In Denmark 54 % fruits and 13 % vegetables were found contaminated while MRL violation were 4 % and 1 % for fruits and vegetables respectively (Andersen and Poulsen, 2002). In Kanpur, India, most of vegetables were found to be contaminated, however fruits from cooler regions were less contaminated than from tropical regions (Sanghi and Tewari, 2002). Monitoring studies in Italy and Thailand have also shown that residue levels found in many food items are within the legal limits as given by particular countries and their daily intake was far below than the Acceptable Daily Intake (ADI) calculated from food consumption data (Girotti et al. 2002; Amara et al. 2002).

In this study, an annual increasing trend is observed as 49, 68, 72 and 62 % for 2000, 2001, 2002 and 2003 respectively for contaminated samples, while in case of MRL violation a decreasing trend is observed as 62, 56, 37 and 31 % for 2000, 2001, 2002 and 2003 respectively. Intensive cropping, easy access to information, aggravated pest problems and pesticide availability at reduced market prices support the existence of residues at such levels, however the data clearly shows that growers do not care about food safety and exposure of consumers to health risks associated with these toxic chemicals.

Grouping vegetables on the basis of part consumed it is inferred that contamination is root/tuberous vegetables> fruiting vegetables> leafy vegetables; however MRL violation pattern is somewhat different; leafy vegetables> root/tuberous vegetables> fruit vegetables.

Studies in India (Sanghi and Tewari, 2002) show that leafy vegetables are the most affected groups of vegetables, but here this general tendency is not followed and root/tuberous vegetables are found to be the most contaminated category. Market forces such as price and demand also have some role to play with reference to pesticide residue quantity. As the leafy vegetables fetch less price in our market environment the frequency of pesticide application is also less, however high contamination of root/tuberous vegetables might be due to absorption of sufficient residues of pesticides applied on previous crops as the soil conditions in our agro-ecosystem favour accumulation of toxins in root zone rather than removal by biodegradation run off or infiltration. MRL violation of vegetables, showing leafy vegetables the most violative category indicates the lack of follow-up of waiting period.

Pesticide group-wise allocation in five classes (table 2) indicates that in contaminated samples of vegetables organochlorine (4.5 %) and miscellaneous (3.5 %) are very small entities, while organophosphorous (35 %) and synthetic pyrethroids (34.5 %) occupy central part followed by fungicides (11.5 %) and carbamates (9 %). MRL violation pattern indicates that carbamates are at the top (65 %). Carbamates are not easily degraded so their residues mostly violate MRLs followed by organophosphorous, organochlorine, miscellaneous, synthetic pyrethroids and fungicides. In organophosphorous, methamidophos is the most frequently detected pesticide and violating MRL (73 %).

Franco et al. (2002) reported that MRL of methamidophos as suggested by FAO/WHO reaches at around 15 days after application on lettuce: while Miter et al. (2002) found a period of 21 days between application and harvest so as its toxic residues degrade and reach the acceptable level under Argentine Laws. Such persistent pesticides if applied on an agro-ecosystem where farmers don't care, good agricultural practices (GAPs) do more harm than good and Methamidophos is doing this job.

Table 1. Extent of pesticide contamination and MRL violation in vegetables.

S. No.	Vegetable	No. of samples analyzed				(n)	No. of samples contaminated				Total no. of contaminated Samples	No. of samples exceeding MRLs
		2000	2001	2002	2003		2000	2001	2002	2003		
1	Carrot	2	1	1	3	7	1	1	1	2	5	4
2	Garlic	1	2	1	2	6	1	2	1	ND	4	4
3	Ginger	2	1	Nil	4	7	2	ND	ND	3	5	2
4	Onion	2	2	2	2	8	1	2	2	2	7	3
5	Potato	3	1	2	1	7	1	ND	2	1	4	1
6	Radish	3	Nil	4	3	10	2	ND	3	2	7	5
7	Sugarbeet	Nil	Nil	2	1	3	ND	ND	2	1	3	1
8	Turnip	2	1	1	2	6	1	ND	1	2	4	2
9	Brassica leaves	Nil	Nil	2	1	3	ND	ND	2	ND	2	1
10	Corriander	1	Nil	Nil	5	6	ND	ND	ND	2	2	2
11	Methi	1	Nil	2	1	4	ND	ND	ND	1	1	0
12	Mint	2	1	Nil	4	7	1	1	ND	1	3	2
13	Salad	Nil	1	Nil	4	5	ND	1	ND	3	4	2
14	Spinach	3	1	4	2	10	1	1	3	2	7	5
15	Brinjal	3	3	3	3	12	ND	2	2	1	5	1
16	Bitterguord	2	3	1	Nil	6	ND	2	1	ND	3	1
17	Chillies	3	3	1	1	8	1	3	1	1	6	2
18	French beans	1	1	4	1	7	ND	1	2	1	4	1
19	Indian squash	3	2	Nil	Nil	5	3	1	ND	ND	4	3
20	Cucumber	2	4	2	3	11	1	3	2	1	7	4
21	Lady's finger	Nil	3	2	3	8	ND	3	1	2	6	2
22	Luffa	2	2	Nil	Nil	4	2	2	ND	ND	4	1
23	Pumpkin	1	5	3	2	11	1	3	1	1	6	3
24	Peas	2	Nil	2	3	7	ND	ND	2	3	5	1
25	Tomato	6	14	4	3	27	3	6	3	2	14	4
26	Cabbage	1	2	1	1	5	1	2	ND	1	4	1
27	Cauliflower	1	1	Nil	4	6	1	1	ND	2	4	2
	Total	49	54	44	59	206	24	37	32	37	130	60

ND= Not detected

Table 2. Pesticide distribution and MRL violation pattern.

Sample No.	Pesticide	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	Total	>MRL
1	Endosulfan	0	0	0	0	0	0	1	2	0	0	0	1	0	0	0	1	0	1	1	1	1	1	2	0	1	1	0	14	7
2	Clorpyriphos	0	2	1	1	1	0	0	0	0	0	0	0	0	0	2	0	1	0	0	1	0	0	0	0	0	0	0	9	6
3	Dimethoate	0	1	1	1	0	1	0	0	0	0	0	0	0	0	1	1	1	0	1	2	0	1	1	0	2	1	1	16	3
4	Ethion	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	1	0	1	1	2	0	6	0
5	Fenitrothion	0	0	0	0	0	0	0	0	1	0	0	0	0	1	0	1	0	1	0	0	0	0	0	0	0	0	1	5	2
6	Methamidophos	1	1	0	4	1	3	1	2	2	2	0	0	2	6	0	0	0	1	3	3	1	1	2	1	5	1	0	45	33
7	Methyl Parathion	0	0	0	0	0	0	0	0	0	0	0	1	0	1	0	0	0	0	0	1	0	1	1	0	0	0	0	5	5
8	Monocrotophos	1	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	2	0	2	1	1	3	0	0	1	0	0	12	6
9	Profenofos	0	0	2	0	0	1	0	0	0	0	0	0	1	0	1	0	2	0	2	1	1	0	1	0	2	0	0	14	5
10	Bifenthrin	0	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	1	2	1	2	0	1	0	1	11	5
11	Cyfluthrin	0	0	0	1	0	0	0	0	0	0	0	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	3	1
12	Cyhalothrin	0	3	0	0	2	0	0	2	0	0	0	2	0	1	0	0	1	0	0	0	4	1	0	1	4	2	1	24	8
13	Cypermethrin	0	2	0	2	0	1	1	2	0	0	0	1	3	2	1	0	3	0	0	1	2	2	1	1	1	3	1	32	5
14	Deltamethrin	1	0	1	0	1	2	0	1	2	0	0	0	0	3	0	0	0	0	0	0	0	0	1	1	1	0	0	14	1
15	Fenpropathrin	0	1	0	0	0	2	0	0	0	0	0	1	0	1	1	1	0	0	0	0	2	0	0	1	1	1	0	12	1
16	Fenvalerate	0	0	0	2	0	0	0	0	0	0	0	2	1	2	1	0	2	1	0	1	0	0	0	0	3	1	1	15	4
17	Carbofuron	2	3	1	0	0	2	0	0	0	0	0	1	0	1	0	1	0	0	1	1	0	0	1	1	0	0	1	19	13
18	Carbosulfan	0	1	0	1	0	1	0	0	0	0	0	1	0	0	0	0	1	0	0	0	3	0	0	0	1	0	2	10	6
19	Abamectin	1	0	0	0	0	1	0	0	0	0	1	0	1	1	0	0	0	1	0	0	1	0	0	0	3	0	2	10	4
20	Acetamiprid	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	2	0	0	0	0	1	1	1	0	0	8	0
21	Benomyl	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	1	0	0	0	0	1	1	0	0	0	5	2
22	Carbendazim	1	1	0	2	1	0	0	0	0	0	0	0	0	1	0	0	1	1	0	0	1	0	1	0	0	0	0	10	0
23	Metalaxyl	2	0	0	2	1	1	0	0	0	0	0	0	0	1	0	0	2	1	0	2	0	1	0	0	0	1	0	14	4
24	TBZ	1	0	0	0	1	0	0	0	0	0	0	0	0	0	1	0	0	1	0	1	0	0	0	0	2	0	0	7	0
	Total	10	16	7	16	8	16	3	9	5	2	1	13	9	21	8	6	19	11	10	17	19	13	15	9	33	13	11	320	121

1: Carrot, 2: Garlic, 3: Ginger, 4: Onion, 5: Potato, 6: Radish, 7: Sugarbeet, 8: Turnip, 9: Brassica leaves, 10: Corriander, 11: Methi, 12: Mint, 13: Salad, 14: Spinach, 15: Brinjal, 16: Bitterguord, 17: Chillies, 18: French bean, 19: Indian Squash, 20: Cucumber, 21: Lady's finger, 22: Lufa, 23: Pumpkin, 24: Peas, 25: Tomato, 26: Cabbage, 27: Cauliflower

The differences in mean values and medians of pesticide residue values (table 3) show that in most of contaminated samples, few samples on upper side of values are so high that the mean value is sufficiently influenced. Standard deviations for each pesticide also confirm that the residues in each sample are highly scattered and away from the mean values.

Variability in residue studies is most complex problem, variation within species of plants, within different cultivars of same species, even lot of variation is reported even when single fruits/vegetables are analyzed from same lot individually as compared to homogenized sample.

In monitoring studies especially when samples are drawn from markets of cosmopolitan cities where samples come from different agro-ecological zones such deviations are a common phenomenon.

REFERENCES

Amara V, Kanakporn A, Gobthong T, Boonpai S, Yuwadee L, Jitpaka S, Ladda K (2002) Dietary exposure of Thais to pesticides during 1989-1996. J AOAC Int 85: 134-140

Andersen JH, Poulsen ME (2002) Results from the monitoring of pesticide residues in fruits and vegetables on the Danish Market 1998-1999. Food Additives and Contaminants 18: 906-931

Codex Alimentarius (2000) Joint FAO/WHO Food Standard Program Volume. 2B. Publishing and Multimedia Service, Information Division, FAO, Rome, Italy. p. 36-373

Codex Alimentarius Commission, Codex Alimentarius Pesticide Residues in Food, Recommended Methods of Sampling (1993). Joint FAO/WHO Food Standards Program Volume. 2 Section 3 p. 369

Franco AA, Rigitano RLO, Anderson VG (2001) Dissipation of methamidophos insecticide in lettuce (Lactuca satva) plants. Ciencae Agrotechnologia 25: 1307-1313

Girotti S, Errani E, Scurti P (2001) Exposure of Bologona Province consumers to pesticide residues most frequently present in the diet in 1996-1999. Bollettino dei Chimici Igienisti, Parte Scientifica 52: 43-49

Mitre MGB, De Pasenale AA, Ruggeri MA, Wierna NR (2002) Methamidophos insecticide degradation curve in lycopersicon esenlentum Miller Fruits in Jujny-Argentina. Informacion Technologica 13: 87-90

Naqvi SN, Jahan M. (1999) Pesticide residues in serum and blood samples of the people of Karachi. J Environ Biol 20: 241-244

Ripley BD, Lissemore LI, Leishman PD, Denomme MA, Ritter L (2000) Pesticide residues on fruits and vegetables from Ottawa, Canada, 1991-1995 J AOAC Int 83: 196-213

Saeed T, Ali S, Shaikh MA, Yasmin T (1998) Incidence of malathion residues in radish and its effects on the biological system of rats. Pak J of Sci 50; 120-122

Sanghi R, Tewari V (2001) Monitoring of pesticide residues in summer fruits and

vegetables from Kanpur, India. Bull Environ Contam Toxicol 67: 587-593
Zahida Parveen, Masud SZ (2002) Fungicide residues in apple and citrus fruits after post harvest treatment. Pakistan J Sci Indus Res 45: 246