Chapter 9
Impact of Processing on Pesticide Residues in Vegetables

Shashi Vemuri and Ch.S. Rao

Abstract In the studies conducted on monitoring of pesticide residue levels of organochlorines (OC), synthetic pyrethroids (SP), organophosphates (OP) and carbamates, three vegetables, viz., brinjal, cauliflower and okra, were chosen to evaluate the effect of different household processes (washing and boiling/cooking) by unprocessed and processed means on reduction of residues. Samples were procured from local market at different intervals. Residues were estimated by using multiresidue method using gas liquid chromatograph (GC), with electron capture detector (ECD) and nitrogen-phosphorous detector (NPD) equipped with capillary columns. In all the three vegetables, washing reduced the residues by 25–77 % and boiling by 32–100 %. Maximum reduction of 77 % of insecticides was observed in brinjal, followed by 74 % in cauliflower and 50 % in okra by washing. The same trend was observed by a boiling process where a maximum of 100 % reduction of OP insecticides was observed in brinjal followed by 92 % in cauliflower and 75 % in okra. Boiling was found comparatively more effective than washing in removing the residues.

Keywords Vegetables • Pesticide • Processing • Residues • Washing • Boiling • Cooking

9.1 Introduction

Vegetables are the fresh and edible portion of some of the herbaceous plants. They are important foods and highly beneficial for health. They contain valuable food ingredients, utilised to build up and repair the body. In India, vegetables are major constituents of diet with a per capita consumption of 135 g per day as against the recommended 300 g per day. Their productivity is restricted, mainly due to insect pests and diseases. Among the vegetables, brinjal, cauliflower and okra are very

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common giving better return over investment to the farmers. Brinjal (*Solanum melongena* L.) is an important vegetable crop grown extensively in India but suffers heavily at fruiting stage by the shoot and fruit borer causing 70 % damage to the crop making it totally unfit for human consumption (Duara et al. 2003). Cauliflower (*Brassica oleracea*), an important vegetable crop grown in India with an annual production of 3.39 million tonnes, is heavily attacked by various insects, resulting in severe loss of quality and production (Patel et al. 1999). Okra (*Abelmoschus esculentus* L.) is also an important vegetable crop grown extensively in India, and for the control of insect pests, a number of insecticides have been used (Sinha and Sharma 2007). For better yield and quality, insecticides are repeatedly applied during the entire crop growth including the fruiting stage, accounting for 13–14 % of total pesticides consumption, as against 2.6 % of cropped area (Sardana 2001). Indiscriminate use of pesticides particularly at fruiting stage and non-adoption of safe waiting period lead to accumulation of pesticide residues in consumable vegetables. Contamination of vegetables with pesticide residues has been reported by several researchers (Kumari et al. 2003). The present study was conducted to evaluate the pesticide residues of four different chemical groups, i.e. organochlorines (OC), synthetic pyrethroids (SP), organophosphorus (OP) and carbamates, in brinjal, cauliflower and okra and to assess the effect on residues of some household processes like washing and boiling/cooking.

9.2 Materials and Methods

The composite samples consisting of 1–2 kg of each vegetable, i.e. brinjal, cauliflower and okra, were collected from local market at weekly intervals. Each sample was divided in to three parts and were extracted and analysed within 2 days of collection. Only the edible part was processed and analysed for the analysis of organochlorine (OC), synthetic pyrethroid (SP), organophosphate (OP) and carbamate group of pesticides. In order to assess the effects of household processing like washing and boiling/cooking, one part of the sample of each vegetable was washed for 1 min under tap water and dried on filter paper. To the other part of each unwashed samples of three vegetables, 15 ml water was added and boiled till softness. Washed and boiled samples were processed in a similar manner as of unprocessed samples.

9.2.1 Extraction

All the samples were extracted fresh. Each vegetable was chopped into small pieces and after quartering, a representative sample (25 g) was macerated with 5–10 g anhydrous sodium sulphate in Waring blender to make a fine paste. The macerated sample was extracted with 100 ml acetone on mechanical shaker for 1 h by using the method of Kumari et al. (2001). Extract was filtered, concentrated up to 40 ml and subjected to liquid-liquid partitioning with ethyl acetate (50, 30, 20 ml) after diluting four to five times with 10 % aqueous NaCl solution. Concentrated was the organic phase up to 10 ml on rotary evaporator and divided it into two equal parts. One part was kept for OC and SP and second for OP and carbamates.

9.2.2 Cleanup

For OC and SP insecticides, cleanup was carried out by using column chromatography. Column (60 cm × 22 mm) was packed with Florisil and activated charcoal (5:1 w/w) in between the two layers of anhydrous sodium sulphate. The extract was eluted with 125 ml mixture of ethyl acetate/hexane (3:7 v/v). The eluate was concentrated to 2 ml for residue analysis. Residues of OP and carbamates were also cleaned by adopting column chromatographic technique. The column was packed with silica gel and activated charcoal (5:1 w/w) in between the layers of anhydrous sodium sulphate. The extract was eluted with 125 ml mixture of acetone/hexane (3:7 v/v). After concentrating the eluate on rotary evaporator, the final volume was made to 2 ml for analysis by gas liquid chromatography (GC).

9.2.3 Estimation

The cleaned extracts were analysed on Shimadzu 2310 GC equipped with capillary columns using electron capture detector (ECD) and nitrogen-phosphorous detector (NPD). Operating conditions were as per details: for OC and SP insecticides, detector: ECD, column: SPB-5 of 5 % diphenyl/95 % dimethyl fused silica capillary column (30 m × 0.32 mm ID, 0.25 μm film thickness) with split system.

Temperatures (°C):150 (5 min) → 8 min^{-1}→ 190 (2 min) → 15 min^{-1} 280° (10 min); injector port: 280; detector: 300; and carrier gas: (N_2), flow rate 60 ml min^{-1}, 2 ml through column and split ratio 1:10. For OP and carbamates: detector: NPD, megabore column: HP-1 of methyl silicone (10 m × 0.53 mm ID, 2.65 μm film thickness). Temperatures (°C): Oven: 100 (1 min) → 10 min^{-1} → 200 (0 min) → 20 min^{-1} → 260 (3 min); injector port, 250, detector, 275, carrier gas N_2 18 ml min^{-1}, H_2, 1.5 ml min^{-1} and zero air 130 ml min^{-1}.

9.3 Results and Discussions

The average percent recoveries at the spiking levels of 0.5 $\mu g g^{-1}$ of each pesticide were in the range of 80–111, 73–95, 83–125 and 82–104 for OC, SP, OP and carbamate insecticides, respectively. The data collected during this study is presented in Tables 9.1 and 9.2. In the analysed samples, the detected pesticides comprised of

OC (HCH isomers [α, β, γ, δ-HCH], DDT analogues, [o,p-DDT, p, p′-DDT, p, p′-DDE and p, p′-DDD], α-endosulphan, β-endosulphan, endosulphan sulphate), SP (cypermethrin, permethrin, fenvalerate, λ-cyhalothrin and β-cyfluthrin), OP (monocrotophos, dimethoate, malathion, chlorpyriphos and quinalphos) and among carbamates (carbophuran) only. The study revealed contamination of all the three vegetables with HCH, DDT and endosulphan among the OC group. Σ-HCH was detected in the range of 0.010–0.044 μgg^{-1} in brinjal, 0.034–0.52 μgg^{-1} in cauliflower and 0.027–0.268 μgg^{-1} in okra. The level of contamination was maximum in okra and minimum in brinjal, whereas Σ-DDT concentration was maximum (0.056–0.178 μgg^{-1}) in brinjal and minimum (0.018–0.025 μgg^{-1}) in cauliflower. Residues of endosulphan were detected in the range of 0.042–0.057 μgg^{-1} in brinjal,

Table 9.1 Pesticide residues* (μgg^{-1}) in brinjal, cauliflower and okra

Insecticides detected	Brinjal			Cauliflower			Okra		
	1	2	3	1	2	3	1	2	3
α-HCH	0.007	0.003	0.009	0.002	0.005	0.007	0.003	0.025	0.005
β-HCH	0.003	0.001	0.003	ND	ND	ND	0.004	0.024	0.003
γ-HCH	0.010	0.005	0.025	0.008	0.006	0.031	0.018	0.213	0.024
δ-HCH	0.008	0.001	0.007	0.042	0.019	0.007	0.002	0.006	0.006
Σ-HCH	0.028	0.010	0.044	0.052	0.030	0.045	0.027	0.268	0.038
o,p′-DDT	0.012	ND	0.001	ND	ND	ND	ND	ND	ND
p,p′-DDT	0.029	0.160	0.038	0.018	0.019	0.025	ND	ND	ND
o,p′-DDE	ND	ND	ND	ND	ND	ND	ND	ND	ND
p,p′-DDE	0.008	0.018	0.012	ND	ND	ND	0.041	0.042	0.053
p,p′-DDD	0.009	ND	0.005	ND	ND	ND	0.018	ND	ND
Σ-DDT	0.058	0.178	0.056	0.018	0.019	0.025	0.059	0.042	0.053
α-Endosulphan	ND	ND	0.007	0.006	0.010	0.017	0.013	0.011	0.009
β-Endosulphan	0.017	0.048	0.027	0.001	0.005	0.008	0.084	0.077	0.078
Endosulphate	0.025	0.009	0.013	0.022	0.029	0.035	0.312	0.055	0.176
Σ-Endosulphan	0.042	0.057	0.047	0.029	0.044	0.060	0.409	0.143	0.263
Cypermethrin	0.012	0.003	0.008	ND	ND	ND	0.034	0.010	0.014
Permethrin	0.022	ND	0.024	0.673	0.725	0.633	ND	ND	ND
Fenvalerate	ND	ND	ND	0.007	0.011	0.017	ND	ND	ND
λ-Cyhalothrin	0.004	ND	0.002	ND	ND	ND	ND	ND	ND
β-Cyfluthrin	0.087	0.047	0.075	ND	ND	ND	ND	ND	ND
Monocrotophos	ND	ND	ND	ND	ND	ND	0.002	0.005	0.008
Dimethoate	0.001	ND	0.002	ND	ND	ND	0.002	0.002	0.006
Malathion	ND	0.008	0.004	ND	ND	ND	ND	ND	ND
Chlorpyriphos	0.022	0.021	0.018	0.024	0.027	0.031	ND	ND	ND
Quinalphos	0.007	0.002	0.009	ND	ND	ND	0.006	0.002	0.007
Carbophuran	0.020	0.009	ND	ND	ND	ND	ND	ND	ND

*The comparison between the treatments in terms of significance was not worked out as the impact of processing only was studied

MRL (mg kg^{-1}) from PFA: HCH (γ-HCH): 3.0, DDT: 3.5, endosulphan: 2.0, chlorpyriphos: 0.01, malathion: 0.5, fenvalerate: 2.0 and cypermethrin: 0.2 and 2.0 in cabbage MRL (mg kg^{-1}) from FAO/WHO: DDT: 1.0, endosulphan: 2.0, cypermethrin: 0.5, fenvalerate: 0.2, monocrotophos: 0.2 and carbophuran: 0.1

Table 9.2 Effect of processing on pesticide residues (μg g^{-1}) in brinjal, cauliflower and okra

Insecticides detected	Range of residues (mean) Brinjal [% reduction]			Range of residues (mean) Cauliflower [% reduction]			Range of residues (mean) Okra [% reduction]		
	UW	W	B	UW	W	B	UW	W	B
Σ-HCH	0.010–0.044	0.007–0.028	0.005–0.023	0.034–0.052	0.022–0.030	0.005–0.019	0.027–0. 268	0.023–0.158	0.021–0.131
	(0.027)*	(0.015)	(0.013)	(0.042)	(0.027)	(0.017)	(0.111)	(0.069)	(0.059)
		[44]	[52]		[36]	[59]		[38]	[47]
Σ-DDT	0.056–0.178	0.035–0.107	0.015–0.079	0.018–0.025	0.005–0.021	0.003–0.013	0.042–0.059	0.034–0.051	0.020–0.047
	(0.097)	(0.061)	(0.044)	(0.021)	(0.014)	(0.008)	(0.051)	(0.041)	(0.033)
		[37]	[55]		[34]	[61]		[20]	[35]
Σ-Endosulphan	0.042–0.057	0.029–0.042	0.022–0.034	0.029–0.060	0.017–0.042	0.012–0.029	0.143–0.409	0.139–0.263	0.123–0.224
	(0.048)	(0.035)	(0.029)	(0.044)	(0.029)	(0.019)	(0.280)	(0.178)	(0.172)
		[27]	[39]		[34]	[57]		[36]	[38]
SP	0.002–0.013	0.016–0.026	0.015–0.022	0.650–0.736	0.451–0.648	0.394–0.434	0.010–0.034	0.009–0.020	0.006–0.020
	(0.027)	(0.020)	(0.017)	(0.688)	(0.490)	(0.412)	(0.019)	(0.013)	(0.011)
		[26]	[37]		[29]	[40]		[31]	[42]
OP	0.008–0.010	0.001–0.004	0.005–0.012	0.024–0.031	0.005–0.008	0.002–0.003	0.003–0.007	0.001–0.003	0.001
	(0.009)	(0.002)	(0.009)	(0.027)	(0.007)	(0.002)	(0.004)	(0.002)	(0.001)
		[77]	[100]		[74]	[92]		[50]	[75]
Carbamates	0.009–0.020	0.004–0.018	0.001–0.014	–	–	–	–	–	
	(0.014)	(0.011)	(0.007)						
		[21]	[50]						

*The comparison between the treatments in terms of significance was not worked out as the impact of processing only was studied

0.017–0.042 μgg^{-1} in cauliflower and 0.143–0.409 μgg^{-1} in okra showing thereby maximum concentration in okra. Thus, in all the three vegetables, Σ-HCH was detected in the range of 0.010–0.268, Σ-DDT, 0.019–0.178 and Σ-endosulphan, 0.029–0.263 μgg^{-1}. Although all the samples were found contaminated with OC insecticides, none of the samples contained residues of any of these insecticides above maximum residue limits (MRL) fixed by the Prevention of Food Adulteration Act (PFA) 1954 and FAO/WHO (1996). Presence of endosulphan in the present study is due to use of endosulphan in almost every crop in AP India among the OC pesticides. Residues of cypermethrin (0.003–0.012 μgg^{-1}), permethrin (ND-0.024 μgg^{-1}), λ-cyhalothrin (ND-0.004 μgg^{-1}) and β-cyfluthrin (0.047–0.087 μgg^{-1}) in brinjal, permethrin (0.633–0.725 μgg^{-1}) and fenvalerate (0.007–0.017 μgg^{-1}) in cauliflower and only cypermethrin (0.010–0.034 μgg^{-1}) in okra were detected among the SP insecticides. Among OP, chlorpyriphos (0.018–0.031 μgg^{-1}) was detected in all the samples of brinjal and cauliflower. This major contaminant was detected in the range of 0.018–0.022 μgg^{-1} in brinjal and 0.024–0.031 μgg^{-1} in cauliflower, whereas no sample of okra showed presence of chlorpyriphos residues in detectable amounts. Some other insecticides like monocrotophos, dimethoate, quinalphos and malathion were also detected in detectable amounts in few samples. Only carbophuran, among carbamate insecticides, was detected in the range of 0.009–0.020 μgg^{-1} in brinjal. Residues of none of the pesticide exceeded the MRL value. The results obtained from the present study are consistent with an earlier study that show residues of these pesticides are present in different vegetables (Kumari et al. 2003; Deka et al. 2005).

9.3.1 Effects of Washing and Boiling

Among the household processes, washing process reduced the OC residues by 27–44 % in brinjal, 34–36 % in cauliflower and 20–38 % in okra, whereas the residues of SP insecticides in brinjal, cauliflower and okra were reduced to 26, 29 and 31 %, respectively. Maximum reduction of residues was observed in case of OP where the residues decreased to the extent of 77, 74 and 50 %, in brinjal, cauliflower and okra, respectively. Among the carbamate insecticides, carbophuran residues, which was detected in brinjal only, reduced by 21 % by washing. In the present study, washing was found effective in dislodging the residues as it depends on a number of factors like location of residues, age of residues, water solubility and temperature and type of washing. In earlier studies also, effects of these factors were observed in different vegetables by various researchers (Dikshit et al. 1986). Sarode and Lal (1982) reported 20–89 % reduction of DDT in potatoes and tomatoes, fenitrothion in okra, parathion in cauliflower and malathion in okra by washing. In present study, washing was found comparatively less effective in reducing the residues of SP insecticides than that of OC and OP insecticides. Current results are in consistent with some earlier reports where reduction (10–30 %) of alphamethrin residues in tomato and brinjal and cauliflower by Gill et al. (2001) and Malik et al. (1999)

was found. Reduction of fenvalerate residues on tomatoes to the level of 62 % was reported by Jain et al. (1979). Rinsing of various vegetables was found very effective (Krol et al. 2000). Boiling/cooking was observed to be more effective in reducing the residues. By this process, reduction of residues of OC insecticides was observed in the range of 39–55 % in brinjal, 57–61 % in cauliflower and 32–47 % in okra. Reduction to an extent of 37, 40 and 42 % of SP insecticides was observed in brinjal, cauliflower and okra, respectively. Among OP insecticides, reduction was 100 % in brinjal, 92 % in cauliflower and 75 % in okra. Carbophuran residues, detected in brinjal only, reduced to the level of 50 % by boiling. Thus, great variation in reduction of residues by boiling was observed which may be attributed to the rates of degradation and volatilization of residues as the concentration of residues increases by heat involved in boiling. Reduction of fenvalerate residues to an extent of 27–56 % in brinjal was reported by Sharma and Kumar (1993). Reduction of alphamethrin in the range of 25–32 % in brinjal and tomatoes and 12–17 % in cauliflower was reported by Gill et al. (2001) and Malik et al. (1999). Holland et al. (1994) reported appreciably reduction in pesticide residues in different commodities by using different processing methods. Hence, the present results are in consistent with the earlier results.

9.4 Conclusions

It can be concluded that the residues of none of the pesticides tested exceeded MRLs. Processing lowers the residues in vegetables. The pesticide residue reduction is important for evaluating the risk mitigation in vegetables. The overall results indicate boiling to be more effective in reducing the pesticide residues.

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