

Effect of Different Household Vegetable Processing Practices on the Reduction of Pesticide Residues

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ABSTRACT: In Sri Lanka, different types of pesticides are extensively applied to increase the crop production especially, for vegetables. Pesticide residues present in vegetables are harmful to consumers. In this study, fresh vegetables namely bean, cabbage and tomato samples collected from the Manning Market in the Colombo City were analyzed for pesticide residues. Residues of deltamethrin, fipronil, tebuconazole, chlorothalonil, diazinon, profenofos, chlopyrifos, oxyfluorfen, dimethoate, and phenthoate were determined using Gas Chromatography Mass Spectrometry (GC/MS) with validated QuEChERS method. Bean, cabbage and tomato samples were subjected to household vegetable processing practices such as washing in running tap water, washing in 5% salt solution, cooking with spices and boiling in water. Effectiveness of different household practices were measured as a percentage of pesticide residues removed by each practice. Bean, cabbage and tomato contained residue of diazinon, chlopyrifos, oxyfluorfen and dimethoate above the maximum levels (MRLs) recommended by the EU. Residues of dimethoate in beans, profenofos and dimethoate in cabbages, and diazinon, chlopyrifos and dimethoate in tomatoes were reduced to levels below the MRLs established by the EU after treating with four household processing practices. These household practices could remove 26-81% of chlorothalonil, diazinon, phenthoate, profenofos, chlopyrifos, oxyfluorfen and dimethoate residues present in beans, cabbages and tomatoes. Deltamethrin showed the highest level of resistance as all four methods were able to remove only 10-16% in three types of vegetables. Dipping beans, tomato and cabbage in 5% salt solution showed the highest reduction of pesticide residues compared with other methods used in the study. Monitoring and controlling of pesticide applications on vegetable production is important to avoid adverse health effects.

KEYWORDS: Bean, Tomato, Cabbage, Pesticide residues, Household vegetable processing practices, Gas chromatography mass spectrometry

I. INTRODUCTION

Vegetables are rich in nutritional characteristics and diets rich in vegetables can prevent a number of diseases. In Sri Lanka, rice being the staple food, various kinds of vegetables, prepared as curries and in the fresh form are consumed 2-3 times a day. Annual vegetable production in Sri Lanka is about 1,167,141 Mt [1] and consists more than 80 varieties grown in different agro climatic areas. Yield and quality are central to sustainable vegetable production. For better returns, vegetable farmers apply pesticides to protect their crop from pests and diseases. Dilhani et al. [2] observed that Sri Lankan farmers who cultivate hybrid vegetable varieties using intensive cultivation methods in cold climatic conditions apply pesticides more than the recommendation levels of agricultural authorities. Pandith et al. [3] reported that intensive application of pesticides causes trace contamination of air, water, soil and crop with their residues.

Vegetables that contain excess amounts of pesticide residues can pose a risk to consumers' health varying from allergies to chronic diseases. At the time of purchase, consumers do not know the level of contamination of vegetables with pesticide residues. Therefore, it is advisable to reduce the levels of pesticides in vegetables before consuming. The retention of pesticides depends on the physicochemical properties of the pesticide molecules as well as the type of food. In vegetables, most of the pesticide residues are retained on the surface. As such most of the residues present on the peel can be removed by washing in water, peeling or treatments with chemical solutions such as common salt. Thus, there is an increasing concern about the effects of various processes on the fate of pesticide residues in vegetables both from the regulatory and public perspectives. Therefore, this study was carried out to determine the effect of different

household vegetable processing practices on the reduction of pesticide residues and to suggest suitable methods which can be used to alleviate pesticide residues in the selected vegetables.

II. RELATED WORK

Priyadarshini et al. [4] quantified the residues remained in curry leaves after the application of most commonly used pesticides such as profenofos, triazophos, ethion, carbendazim, chlorpyrifos and cypermethrin at recommended doses. The samples were subjected to various household treatments and analysed for pesticide residues using QuEChERS method to identify the effectiveness of household treatments on the removal percentage of residues. Results revealed that no single treatment was effective in decontamination of all pesticides. However, they observed that washing in tap water and dipping in salt solution were the best household methods for removal of pesticide residues from curry leaves. Both methods were effective in reducing the residues below the Maximum Residue Levels.

The effects of household processing on removal of profenofos, chlorpyrifos, dimethoate, malathion, phosalone, quinalphos, triazophos and cyhalothrin residues in brinjal were studied by Cherukuri et al. [5]. The samples were subjected to various household treatments (washing in tap water, washing in lemon water, dipping in 2% salt water for 15 min, dipping in 2% tamarind water for 10 min, washing with 0.1% sodium bicarbonate solution, washing with 4% acetic acid solution, biowash and cooking), and analyzed for residues using QuEChERS method followed by Electron Capture Detector (ECD), Flame Photometric Detector (FPD) and GC/MS analysis, so as to estimate the percentage removal and their effectiveness. Out of all treatments, dipping in 2% salt solution for 10 min was very effective in removing 45%, 43%, 52%, 50%, 54%, 48% and 76% of dimethoate, chlorpyrifos, quinalphos, profenofos, phosalone, cyhalothrin and malathion respectively. Cooking removed insecticides in the range of 55-80%. Dipping brinjal in 2% salt solution for 15 min was identified as the best household method for removal of above pesticide residues.

Alamgir et al. [6] studied the effect of different household processes on the residual levels of cypermethrin, chlorpyrifos and diazinon applied with recommended doses for tomato. Tomato samples were subjected to different household processing at zero day and third day of storage. Samples were analyzed by High Performance Liquid Chromatography equipped with Photodiode-Array Detector. Both washing and cooking reduced human risk index value by ~12%-69% for chlorpyrifos, ~9-43% for cypermethrin and ~47-90% for diazinon on the zero day. After 3 days of storage, washing and cooking reduced human risk index value by ~26%-84% for chlorpyrifos, ~11-53% for cypermethrin and ~46-95% for diazinon. Moreover, boiling was more effective than washing in reducing residual levels of three pesticides.

Raw, washed and cooked forms of tomato were subjected to different household processing methods by Thanki et al. [7] and effects were studied. Analysis of tomato for pesticide contamination was carried out on GC-ECD and Thermionic Ionization Detector with capillary columns. Findings showed that washing and cooking process minimized the residues of eleven pesticides in the range of 2-65% and 38-90% respectively. The study found that cooking was more effective than washing and boiling.

Vemuri et al. [8] evaluated several methods for removal of pesticide residues (dimethoate, methylparathion, profenofos and endosulfan) from tomato. Pesticides treated samples were subjected to different decontamination methods namely washing under running tap water, washing with 2% salt solution, direct cooking, and dipping in 2% salt solution and cooking. Remaining residues were determined by using QuEChERS method utilizing ECD, FPD and GC/MS. Cumulative effect of all four household processes caused substantial reduction in residues up to 95%. However, cooking with pressure cooker for 5 minutes reduced pesticide residues from 30-93%.

III. METHODOLOGY

Preparation of stock and working standard solutions

Individual stock standard solutions of selected pesticides (500 µg/mL) were prepared by dissolving reference standards in acetone and methanol according to their solubility and stored in a freezer at -20 °C. Working standard solutions (0.1 - 5 µg/mL) were prepared freshly from each stock standard solution and the calibration curves were developed.

Method verification

By using certified, pesticides free vegetable samples, percentage of recovery, limit of detection (LOD) and limit of quantification (LOQ) were determined.

Sample preparation and analysis

One kilogram of each vegetable type namely bean, cabbage and tomato bought from the Manning Market, Colombo, Sri Lanka was divided into equal five portions. One portion (200g collected randomly) was used as the control sample without any processing. The remaining four portions were subjected to several risk mitigation methods prior to analysis. The decontamination methods used in the study are presented in Table 1.

Table 1. Decontamination methods used in the risk mitigation

Treatment No.	Procedure	Duration
T1	Washing under tap water.	2 min
T2	Dipping in 1 L of 5% salt solution	10 min
T3	Cooking on a gas cooker under a medium flame with spices (0.5g of turmeric powder, 1g of chillie powder, 2.5g of curry powder and 2g of salt) and 300mL of coconut milk. General household cooking procedures were followed.	10 min
T4	Soaking in boiling water.	5 min

Sample extraction and clean-up

The acetate-buffered QuEChERS sample preparation method for pesticides (AOAC Official Method 2007.01) [9] was applied to all the samples and subjected for the analysis on GC/MS under standard operational conditions.

GC/MS analysis

GC/MS analysis was conducted using an Agilent Technologies, USA, 7890 A series gas chromatography equipped with an electron impact ionization detector, 7693 auto sampler and 5975C mass spectrometer. Chromatographic separation was achieved on fused silica capillary column Agilent 19091S-433HP-5MS 5% Phenyl Methyl Silox (30 m x 250 µm x 0.25 µm).

The operating conditions of the GC/MS were as follows: Column pressure: 8.989 psi, average velocity: 41.83 cm/sec, injection mode: split less, inlet temperature: 250 °C, inlet pressure: 6.44 psi, purge flow: 20 mL/min, purge time: 1.00 min, total flow: 1.5 mL/min, gas server: on, gas server flow: 20 mL/min, server time: 2.00 min, liner: split/ split less liner (ID: 4 mm), oven temperature: initial: 80 °C (hold 1 min), ramp 1: 80 °C to 160 °C (10 °C/min hold 1 min), ramp 2: 160 °C to 250 °C (6 °C/min hold 1 min), ramp 3: 250 °C to 300 °C (10 °C/min hold 5 min), total run time: 36.00 min.

In the verification process, all pesticides showed high level of linearity with more than 0.99 correlation. For fortified organic vegetables, the recoveries were more than 70%. With regard to repeatability, all the pesticides produced relative standard deviations (RSD) of <10%. The quantification limits (LOQs) and detection limits (LODs) were calculated based on the standard deviations of the intercept and calibration curve parameters.

IV. EXPERIMENTAL RESULTS AND DISCUSSION

Chromatographs obtained for beans, cabbage and tomato in GC/MS are shown in Figure 1.

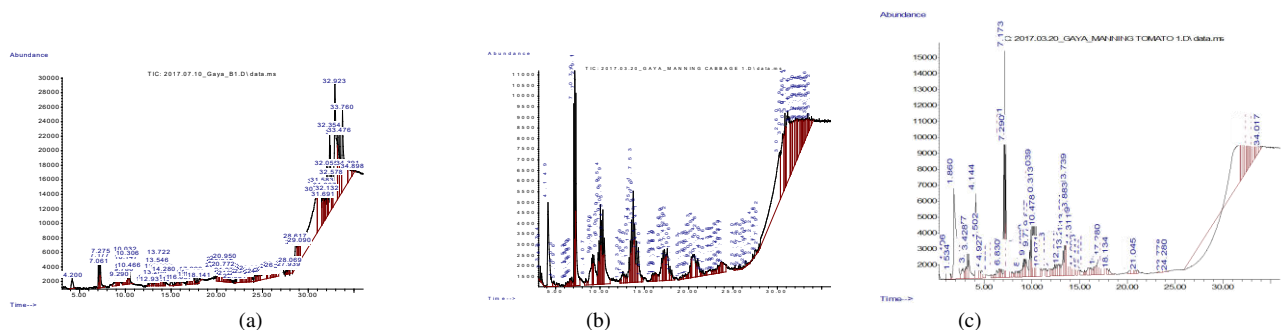


Fig1. GC/MS Chromatographs for (a) Bean (b) Cabbage (c) Tomato samples

Bean, cabbage and tomato samples reported substantial reduction of pesticide residues after subjecting to different household processing practices. The concentration of pesticide residues in selected three fresh vegetables and percentages of reduction of residues by household processing practices are presented in Table 2, 3 and 4. Samples were analyzed in duplicate and the mean values of pesticide residues were expressed as mg/kg.



Results revealed that deltamethrin showed the lowest reduction as an average of 10% by all vegetable processing practices. Bozena et al. [10] explained the less reduction of deltamethrin in vegetables through the analysis of physicochemical properties of the pesticides, including their solubility in water. Non-polar, water-insoluble pesticides are less readily removed compared with high-polarity materials. The less reduction was obtained due to the low water solubility (0.0002 mg/L) of deltamethrin residues.

In this study, among all four treatments, dipping in 5% salt solution showed the highest reduction of pesticide residues in three types of vegetables. Table 2 presents the results obtained for beans. Initial concentrations of diazinon, chlorpyrifos, oxyfluorfen, profenofos and dimethoate residues in bean samples were higher than the MRLs set by EU [11]. Even though the four processing methods showed some amount of reduction in residue levels, diazinon, chlorpyrifos, oxyfluorfen and profenofos were remained above the MRLs. However, all four processing methods reduced the levels of dimethoate residues below the MRLs. Moreover, these four vegetable processing practices removed tebuconazole residues completely from beans. The residue levels of chlorothalonil and dimethoate in beans were reduced by 55-81% by all four processing methods. Diazinon, penthoate and oxyfluorfen showed a higher level of resistance to washing, cooking and soaking treatments compared with dipping in 5% salt solution.

In fresh cabbage samples, residues of diazinon, chlorpyrifos, oxyfluorfen, profenofos and dimethoate were higher than the MRLs (Table 3). Profenofos and dimethoate showed the reduction below the MRLs. However, these four processing practices could not reduce residue levels of diazinon, chlorpyrifos and oxyfluorfen below the respective MRLs. All four household processes were able to reduce residues of diazinon, chlorpyrifos, oxyfluorfen, chlorothalonil, profenofos and dimethoate by more than 50% in cabbage. Cherukuri et al. [5] found that washing brinjal under running tap water and cooking reduced profenofos residues by 42% and 52% respectively. Although fipronil was totally removed from cabbage samples by all four treatments, the content of deltamethrin was reduced only by 12%. However, tebuconazole showed a substantial reduction of more than 75% in cabbage samples. Compared with other pesticides, Penthoate showed a higher level of resistance for cabbage processing practices tested.

In tomato samples, initial concentrations of diazinon, chlorpyrifos, oxyfluorfen, deltamethrin and dimethoate residues were higher than the MRLs (Table 4). Processing of tomatoes by all four practices reduced the pesticide residue levels of diazinon, chlorpyrifos and dimethoate for levels lower than MRLs.

Four household processing practices removed fipronil and phenthoate completely in tomatoes. Tebuconazole content was reduced by 40% by washing tomatoes in tap water and it was a higher amount than the other three processing methods. More than 50% of reduction was observed in chlorpyrifos, oxyfluorfen and chlorothalonil in tomato samples. All the processing methods showed 42%-67% reduction of diazinon, profenofos and dimethoate in tomatoes. According to the Priyadarshini et al. [4], the best household method for removal of profenofos residues was dipping in salt solution which was proven by this study as well.

Table 2. Results of different vegetable processing methods on reduction of pesticide residues in beans (mg/Kg)

Pesticide	MRL	Original conc.	Conc. in T1	Reduc. % in T1	Conc. in T2	Reduc. % in T2	Conc. in T3	Reduc. % in T3	Conc. in T4	Reduc. % in T4
Diazinon	0.01	1.0125	0.625	38	0.5	51	0.75	26	0.75	26
Chlorpyrifos	0.01	0.25	0.1	60	0.075	70	0.15	40	0.125	50
Oxyfluorfen	0.05	0.2125	0.125	41	0.075	65	0.125	41	0.125	41
Phenthoate	NA	0.0225	0.015	33	0.01	56	0.015	33	0.0125	44
Deltamethrin	0.2	0.025	0.022	12	0.0225	10	0.0225	10	0.0225	10
Tebuconazole	2	0.0225	ND	100	ND	100	ND	100	ND	100
Chlorothalonil	5	0.025	0.0075	70	0.005	80	0.01125	55	0.01	60
Profenofos	0.01	0.1875	0.075	60	0.075	60	0.1	47	0.1	47
Dimethoate	0.01	0.02	0.005	75	0.00375	81	0.006	70	0.005	75

T1-Washing under tap water; T2-Dipping in 5% salt solution; T3-Cooking with spices; T4-Soaking in boiling water; ND- Not detected; NA- Not available

Table 3. Results of different vegetable processing methods on reduction of pesticide residues in cabbage (mg/ Kg)

Pesticide	MRL (EU)	Original conc.	Conc. in T1	Reduc. % in T1	Conc. in T2	Reduc. % in T2	Conc. in T3	Reduc. % in T3	Conc. in T4	Reduc. % in T4
Diazinon	0.01	0.2125	0.075	65	0.05	76	0.0625	71	0.0625	71
Chlorpyrifos	0.01	0.175	0.075	57	0.0625	64	0.0875	50	0.075	57
Oxyfluorfen	0.05	0.2125	0.1	53	0.05	76	0.05	76	0.075	65
Phenthoate	NA	0.125	0.0875	30	0.0875	30	0.0725	42	0.075	40
Deltamethrin	0.1	0.0088	0.0076	14	0.0076	14	0.0078	11	0.0078	11
Fipronil	0.005	0.0025	ND	100	ND	100	ND	100	ND	100
Tebuconazole	0.7	0.2	0.05	75	0.0375	81	0.05	75	0.05	75
Chlorothalonil	0.6	0.25	0.1	60	0.0875	65	0.075	70	0.075	70
Profenofos	0.01	0.0213	0.0088	59	0.01	53	0.0075	65	0.0075	65
Dimethoate	0.01	0.015	0.005	67	0.005	67	0.0075	50	0.0075	50

T1-Washing under tap water; T2-Dipping in 5% salt solution; T3-Cooking with spices; T4-Soaking in boiling water;ND- Not detected; NA- Not available

Table 4. Results of different vegetable processing methods on reduction of pesticide residues in tomato (mg/ Kg)

Pesticide	MRL (EU)	Original conc.	Conc. in T1	Reduc. % in T1	Conc. in T2	Reduc. % in T2	Conc. in T3	Reduc. % in T3	Conc. in T4	Reduc. % in T4
Diazinon	0.01	0.01875	0.01	47	0.0075	60	0.0075	60	0.0075	60
Chlorpyrifos	0.01	0.02	0.0075	62	0.005	75	0.00875	56	0.00875	56
Oxyfluorfen	0.05	0.1875	0.075	60	0.05	73	0.05	73	0.05	73
Phenthoate	NA	0.005	ND	100	ND	100	ND	100	ND	100
Deltamethrin	0.07	0.1125	0.1001	11	0.1001	11	0.0979	13	0.0945	16
Fipronil	0.005	0.0025	ND	100	ND	100	ND	100	ND	100
Tebuconazole	0.9	0.625	0.375	40	0.125	80	0.25	60	0.25	60
Chlorothalonil	6	1	0.5	50	0.25	75	0.375	62	0.375	62
Profenofos	10	2.25	0.75	67	0.75	67	1	56	1	56
Dimethoate	0.01	0.015	0.00625	58	0.005	67	0.00875	42	0.0075	50

T1-Washing under tap water; T2-Dipping in 5% salt solution; T3-Cooking with spices; T4-Soaking in boiling water;ND- Not detected; NA- Not available

V. CONCLUSION

Bean, cabbage and tomato contained residue levels of diazinon, chlopyrifos, oxyfluorfen and dimethoate above the maximum levels set by the EU. In tomato, phenthoate and fipronil were completely removed by washing under tap water, dipping in 5% salt solution, cooking with spices and soaking in boil water. Tebuconazole in beans, fipronil in cabbage and tomato, and penthoate in tomato were completely removed by four household vegetable processing practices. Residues of chlorothalonil, diazinon, phenthoate, profenofos, chlopyrifos, oxyfluorfen and dimethoate present in bean, cabbage and tomato were removed by 26-81% by all four practices. Deltamethrin showed a high level of resistance to all four practices. Under household conditions, dipping beans, cabbage and tomato in 5% salt solution

showed the highest reduction of pesticide residues. Residues of dimethoate in beans, profenofos and dimethoate in cabbages and diazinon, chlopyrifos and dimethoate in tomatoes were reduced to levels below the MRLs recommended by the EU after treating with four household processing practices. Results emphasized the need of monitoring and controlling of pesticides applications in vegetable production with a view to avoid possible health issues to consumers.

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