Dissipation of Deltamethrin on Supervised Vegetables and Removal of its Residue by Household Processing

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Summary: The effect of washing, peeling and cooking on residue levels of deltamethrin in some winter (spinach, cauliflower, potato) and summer vegetables (brinjal, tomato, okra) was determined. The samples were collected from trials conducted under controlled conditions (supervised field trials). The highest deltamethrin residue (mg kg^{-1}) was found at raw stage in spinach (0.421) followed by cauliflower (0.306) and okra (0.285). The residue of deltamethrin recorded to be the lowest in potato 0.023 mg kg^{-1}. After washing the highest deltamethrin residue (mg kg^{-1}) was detected in spinach (0.378) followed by okra (0.242) and cauliflower (0.208). The washing reduced deltamethrin residue from 10 to 35 %, peeling reduced 76 to 80 % and cooking further lowered it from 19 to 40 % in all the tested vegetables. Deltamethrin residue in all of the analyzed vegetable samples was below maximum residue limits (MRLs).

Introduction

Among several types of foods, vegetables are essential due to their nutritional value. The vegetables grown in subtropical climatic conditions are threatened by the proliferation of insects and results in massive loss in yield. Pesticides are an inevitable tool in controlling these pests. For better yield and quality, insecticides are repeatedly applied during the entire period of growth and sometimes even at the fruiting stage. As a result of pesticide applications the vegetables absorb the agrochemicals and on consumption by human beings create health hazards to human population. Since the vegetables are often consumed either raw or without much processing or storage, this leads to exert adverse effect on human health in addition to disturbing the ecosystem [1, 2].

Deltamethrin {(*S*)-α-cyano-3-phenoxybenzyl (1*R*, 3*R*)-3-(2, 2-dibromovinyl)-2,2-dimethylcyclopropanecarboxylate} is an odourless white powder with a melting point of 98-101 °C and technical grade contains more than 98 % of the material. It is a synthetic pyrethroid broad spectrum insecticidal active ingredient registered for application of various food commodities including fruits, vegetables and stored products. It is stable to light, heat and air, but unstable in alkaline media [3, 4]. It is non-persistent, practically non-volatile, highly soluble in organic solvents like acetone, cyclohexane, ethanol and ethyl acetate [5] but almost insoluble in water (0.02 mg/L). It kills insects on contact and through digestion by disrupting their nervous system and is effective against both sucking and chewing insects and has been widely used to control pests of various vegetables [6].

A number of scientists and food processors have long been interested in the effect of commercial processing on persistence of pesticide residues in food. Early reports [7, 8] showed that several canning operations, such as peeling, washing, juice extraction and heat processing, can reduce residue levels in several US crops such as tomatoes, broccoli, green beans and spinach. Recently, changes in the concentrations of the pesticide residue in potato during washing, peeling and cooking have been pointed out [9]. However, the effect of commercial processing on some economically important agricultural commodities of Pakistan, such as cauliflower, okra and eggplant is less known. The objective of this study was to determine the residue

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level of deltamethrin in vegetables grown at the supervised field trials. Another important mandate was to study the dissipation behavior of deltamethrin during washing, peeling and cooking of vegetables.

Results and Discussion

The method used was validated first to evaluate the recovery of deltamethrin from the studied vegetables (Table-1). From the recovery study, it is revealed that the method is practicable for the extraction and analysis of deltamethrin residue in vegetables.

Table-1: Recovery of Deltamethrin (%) in Vegetables

Vegetable	*Recovery %	MRL (mg kg^{-1})
Spinach	101 ± 3.5	0.5
Cauliflower	93 ± 2.7	0.5
Potato	99 ± 0.96	0.05
Brinjal	91 ± 5.5	0.2
Tomato	102 ± 2.4	0.3
Okra	103 ± 0.56	0.5

* Data is mean of 5 replicates

The deltamethrin residue (mg kg^{-1}) in vegetables of supervised field trial is given in Table-2. The highest deltamethrin residue in raw vegetable sample was detected in spinach (0.421) followed by cauliflower (0.306) and okra (0.285) mg kg^{-1}. The residue of deltamethrin was observed to be the lowest in potato (0.023 mg kg^{-1}). After washing the highest deltamethrin residue (mg kg^{-1}) was detected in spinach (0.378) followed by okra (0.242) and cauliflower (0.208), while the lowest was found in potato (0.017 mg kg^{-1}). After peeling the residue of deltamethrin in brinjal and potato was 0.027 and 0.004 (mg kg^{-1}), respectively. The retention of deltamethrin residue after cooking in spinach, cauliflower, potato, brinjal, tomato and okra was 0.378, 0.208, 0.017, 0.139, 0.178 and 0.242 (mg kg^{-1}), respectively. The residue of deltamethrin in all the tested vegetable samples was below MRLs established by FAO [10]. It may be due to the non-persistent nature of deltamethrin being a member of synthetic pyrethroid group. The results of the present study are inline with [11], who reported that about ten days after use, no deltamethrin residue was observed in the plants. Similarly on asparagus, deltamethrin residues declined to less than 0.1 mg kg^{-1} two days after application [12].

Effect of Household Processing on Deltamethrin Residue in Vegetables

The reduction of deltamethrin residue after washing, peeling and cooking is presented in Fig. 1. The effect of washing was found to be the most pronounced on tomato sample followed by cauliflower and potato but least effect was found on spinach samples. The process of washing decreased deltamethrin residue up to 35 % in tomato, 32 % in cauliflower, 26 % in potato and 10 % in spinach. In general, it is clear that washing with water is advisable to remove most of the surface residue from vegetables. A significant reduction (10 to 35 %) in deltamethrin residue was observed during washing of the vegetables. Deltamethrin residue was partially removed by washing operation. Although water solubility of pesticide is an important factor during washing operation, but in the present study, water solubility was not found to be the important factor during washing operation and the results from the current study are consistent with earlier findings which showed that residues of six pesticides on olives decreased after washing with no correlation to water solubility of the pesticides [13]. The results are in line with some previous findings where washing removed 50 % of the cypermethrin residues from eggplants [14] and 35 % in asparagus [15].

Peeling decreased deltamethrin residue by 76 and 80 % in potato and brinjal, respectively. The data clearly indicate that peeling process had a significant effect on the removal of deltamethrin residue and it confirms the presence of deltamethrin residue in the skin of potato and brinjal. This could be due to the non-systemic nature of the deltamethrin on food

Table-2: Deltamrethrin Residue (mg kg^{-1}) in Vegetables of Supervised Field Trial

Vegetables	Raw		Washed		Peeled		Cooked	
	Mean*	CV	Mean*	CV	Mean*	CV	Mean*	CV
Spinach	0.421 ± 0.029	6.80	0.378 ± 0.019	5.07	NA	NA	0.302 ± 0.011	3.76
Cauliflower	0.306 ± 0.014	4.49	0.208 ± 0.019	9.13	NA	NA	0.124 ± 0.011	8.72
Potato	0.023 ± 0.003	11.50	0.017 ± 0.001	5.88	0.004 ± 0.000	5.00	0.003 ± 0.000	8.82
Brinjal	0.174 ± 0.018	10.36	0.139 ± 0.010	7.19	0.027 ± 0.002	6.42	0.022 ± 0.002	9.09
Tomato	0.275 ± 0.015	5.43	0.178 ± 0.013	7.56	NA	NA	0.124 ± 0.01	10.55
Okra	0.285 ± 0.027	9.42	0.242 ± 0.015	6.09	NA	NA	0.174 ± 0.019	10.77

*Mean are replicate of five observations
NA means Peeling was not done

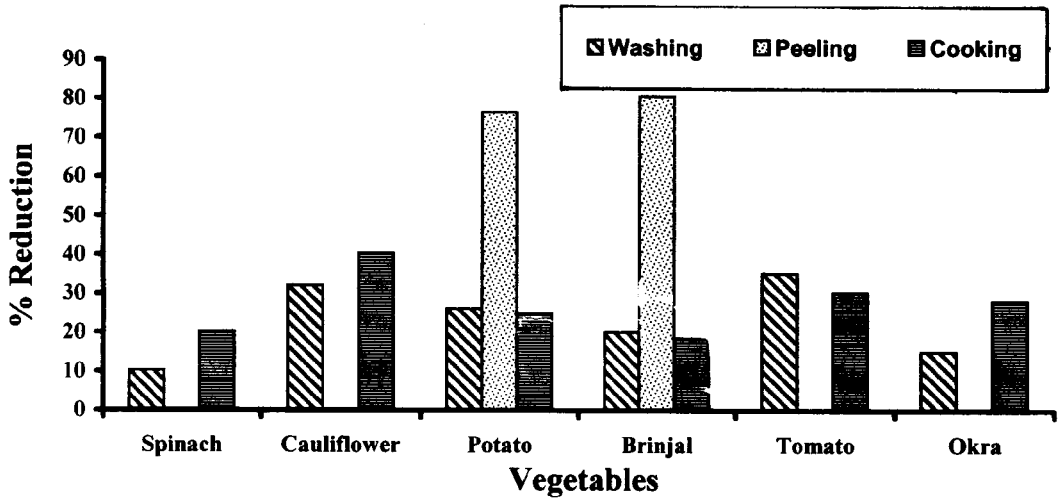

Figure-1. Percent Reduction of Deltamethrin Residue in Vegetables of Supervised Field

crops, lower penetration power of the compound, incorporation into the cuticle layer of the plant surface and resulting in deposits removable by peeling [16]. So, when peel was removed, greater amount of pesticide residue was removed. Similarly, 75 % reduction in cypermethrin residue was observed after peeling of asparagus [15].

The results also showed that the heat treatment during cooking had a significant effect on decomposition of the pesticides in all the tested vegetable samples. The decrease ranged from 19 to 40 %. The effect was more pronounced in cauliflower and tomato while least effect was observed in case of spinach and brinjal (Fig. 1). The present results agree fairly with previous studies [17], who reported the changes in deltamethrin residues in edible crops resulting from processing and cooking and found that, depending on the commodity, pre- or post-harvest residues were reduced by 20-98 % by processing and especially by cooking. Similarly, deltamethrin residue in spinach was reduced by 20 % on cooking [14].

Experimental

Field Trials for Deltamethrin

The field trials for the determination of deltamethrin residue in winter vegetables; spinach (*Spinacia oleracea* L.), cauliflower (*Brassica oleracea* L.), potato (*Solanum tubersum* L.) and summer vegetables; brinjal (*Solanum melongena* L.), tomato (*Lycopersicon esculentum* L.), okra (*Abelmoschus esculentus* L.) were conducted in the field area of The Institute of Horticultural Sciences, University of Agriculture, Faisalabad, Pakistan in separate plots measuring 150 x 30 feet each in 3 replicates. The supervised field plots, received all the routine agronomic practices and the vegetables were sprayed with commercial deltamethrin-based product (Decis Super 10 EC) at a dose of 1 mL L^{-1} of water. Keeping in view the pest population, the winter vegetables were sprayed 2 times, while the summer vegetables were sprayed 3 times during their growing period and harvested after 7 days of the last spray. The spray was carried out with a Knap-sack hand sprayer in the absence of precipitation and wind. Meteorological data were continuously recorded by an automatic weather station at the University of Agriculture, Faisalabad. The monthly averages of the climatic data during the whole experiment are given in Table-3.

Processing of Vegetables

The potato and brinjal samples were hand peeled with stainless steel peeling knife after washing and reduced into slices of suitable size and cooked. Rest of the vegetables (spinach, cauliflower, tomato and okra) was washed and sliced into suitable size and cooked. All vegetable samples collected from the supervised fields were analyzed at following stages *i.e.* raw, after washing, post-peeling and after cooking to determine the deltamethrin residue.

Table-3: Metrological Data for Winter and Summer Seasons

Month	Temperature (°C)			Relative Humidity (%)	Rain Fall (mm)
	Maximum	Minimum	Average	Average	
October (2004)	35.2	19.0	27.1	44.2	10.0
November (2004)	29.6	13.7	21.7	60.1	9.00
December (2004)	23.8	9.50	16.7	61.0	2.00
March (2005)	27.8	15.3	21.6	56.4	48.6
April (2005)	35.1	18.2	26.6	35.0	10.8
May (2005)	38.1	23.4	30.8	31.6	18.4

Raw

The vegetable samples were dry cleaned to remove soil contamination with a disposable paper towel and blended in a Warring Blender to make a homogenous sample for subsequent analysis.

Washing

The vegetables were washed by placing in a plastic colander and rinsed under normal tap water for 30 seconds [18], with gentle rotation by hand and blotted dry with a paper towel and divided into two parts. One portion was analyzed as such after blending in a Warring Blender and the rest was further treated.

Cooking

The vegetables were cooked by using the method [19] with following modifications: the sliced vegetables were cooked by placing ¾ cup of water in the sauce pan and adding ½ teaspoon of salt. The water was brought to boil and 50 g vegetable was added immediately. The vegetable was covered and cooked for 10-12 minutes and contents were analyzed for deltamethrin residue.

Extraction of Deltamethrin Residue

The residues were extracted from all the samples using the validated method [20] with following modifications: 50 g vegetable was extracted with 50 mL ethyl acetate in the presence of 20 g anhydrous sodium sulphate and 10 g sodium chloride in a Warring Blender at high speed for 3 minutes. The extract was filtered, transferred directly to a column of activated charcoal, leaving it to pass through at a rate of 1 mL min^{-1}. The extract was concentrated on a rotary evaporator at 45 °C just to dryness and redissolved in 10 mL ethyl acetate and cyclohexane (1: 1) and filtered through a 0.45 μm filter membrane. Then the sample was subjected to clean up by gel permeation chromatography using a column with Bio-Beads SX-3 (mesh size 200-400) and ethyl acetate-cyclohexane as eluting solvent. The collected elute was reduced to a small volume under a gentle stream of nitrogen gas and analyzed by HPLC.

HPLC-UV Determination of Deltamethrin

The residues (deltamethrin) were redissolved in acetonitrile and analyzed by HPLC, Perkin Elmer Series 200, following the method [21]. The analyses were performed in isocratic system using reverse phase C_{18} column (25 cm x 4.6 mm i.d.). For separation of deltamethrin, a 75:25 mixture of acetonitrile and water at a flow rate of 1.0 mL min^{-1} was used. The wavelength was 206 nm according to its UV spectrum. The column temperature was ambient and injection was made with a 50 μL SGE syringe and a manual loop injector. Sample filtration was carried out with solvent compatible Gelman acrodisc syringe filter of 0.20 μm GHP membrane. The eluent was degassed by purging with helium.

Statistical Analysis

Three parameters were used to report residue levels: mean value, standard deviation (S.D.) and coefficient of variation (C.V.) derived from five replicate samples at each sampling point, expressed as mg kg^{-1}. Mean values and standard deviations were calculated and analyzed by Minitab Software Package Version 14.0 (Minitab Inc. State College, PA, USA).

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