



Effect of Food Processing on Reduction of Pesticide Residues in Vegetables

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Authors' contributions

This work was carried out in collaboration between both authors. Author MHES designed the study, wrote the protocol, and wrote the first draft of the manuscript. Author MTS managed the literature searches, analyses of the study performed the chromatographic analysis. Authors MHES and MTS managed the experimental process, identified the pesticide residues and the effect of processing. Both authors read and approved the final manuscript.

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ABSTRACT

Pesticides are widely used in food production to increase food security despite the fact that they can have negative health effects on consumers. Pesticide residues have been found in various fruits and vegetables; both raw and processed. In this study, the effects of household processing treatments such as washing, peeling, juicing, freezing, cooking and frying were evaluated for their removal efficiency of pesticide residues from orange, strawberry and sweet pepper. Residues were indicated by using gas chromatography mass spectrum (GCMSD). In all three crops for real market samples were detected pesticide residues from 0.004 – 1.573 ppm., and the most pesticide residues was higher than MRL in orange was (lindane, P,P-DDD and fenvalerate), in strawberry was (aldrin, tetradifon, P,P-DDE, pirimiphos methyl and dimethoate) and in sweet pepper was

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(endosulfan II). Reduction of residue levels was indicated by processing treatments with an average response ratio ranging from 19% to 100%. Recommendations are provided for the conduct of storage or processing studies on pesticide residues in food so that data obtained is relevant, comparable and may be extrapolated to other situations.

Keywords: Food processing; fruits; vegetables; pesticide residues.

1. INTRODUCTION

Fruits and vegetables like other foods pass through culinary and food processing treatments before they are consumed. The effects of these culinary and food processing techniques have been investigated by various researchers and they have been found to reduce the pesticide residue levels except in cases where there is concentration of the product like in juicing, frying and oil production. Some toxic metabolites may be produced during processing treatments, especially thermal processing. One of the extensively studied metabolite is ETU that result from thermal processing of dithiocarbamates. However, the consumers can still be encouraged to employ those processing methods that reduce pesticide residues. Food processing studies often results in transfer factors or food processing factors (PF) of the pesticide residue in the transition from raw agriculture commodity to the processed product. These processing factors are expressed as the concentration of pesticide after processing divided by the concentration before processing. Some processing factors are available in public literature while others are only available from the pesticide registering bodies. Processing studies have become a part of pesticide registration requirements. Effect of processing in fruits and vegetables are said to be influenced by the physico-chemical properties of the pesticide as well as the processing method [1,2,3].

Storage and other post-harvest practices prior the further management of the product, as well as household and industrial food preparation processes may alter pesticide residues as compared with raw crops via chemical and biochemical reactions (hydrolysis, oxidation, microbial degradation etc.) and physicochemical processes (volatilization, absorption etc.). Although these processes usually are leading to reduction of any residues left on crops at harvest [4,3], These considerations suggest that effects of postharvest practices and food processing should be taken into account on the fate of a pesticide residue during dietary exposure assessments so as to ensure consumer safety

from pesticide residues and allow a more realistic calculation of the dietary burden of livestock. Food processing studies and their effects on pesticide residues are also very important for the monitoring of the cases that the final residue concentration is exceeding MRL in Raw Agricultural Commodities RAC. Although the established MRLs for processed and ready to eat food are limited to present and concern mainly the processed commodities where the residue could be found concentrated, regulatory attention has been focused on this issue the last decade and a current confrontation practice is the perspective of the processing factors (Pf's) establishment to be used with already specified MRL's of pesticides in RAC's (Codex Alimentarius Commission, 2007). Pf is defined as the ratio of the residue level in processed commodity to the residue level in RAC or in the commodity to be processed. These considerations suggest that effects of postharvest practices and food processing should be taken into account on the fate of a pesticide residue during dietary exposure assessments so as to ensure consumer safety from pesticide residues and allow a more realistic calculation of the dietary burden of livestock [2,5,6].

The aim of this study is to investigate the main types of processing practices that typically RAC's are being subjected prior their consumption and point out the effects that these processes cause on the fate of pesticide residues that may persist on and in RAC's after harvest. The main chemical, biochemical and physical phenomena in which pesticide residues take part in during these processes and the parameters that may influence these phenomena would further be discussed, through the latest published data on this topic.

2. MATERIALS AND METHODS

2.1 Samples Collection

The composite samples consisted of 2kg of each sample i.e. orange and strawberry were collected from local market. Each sample was divided into

three parts and were refrigerated and analysed within two days of collection.

2.2 Samples Treatments

Only edible part was processed and analysed for the analysis of organochlorine (OC), synthetic pyrethroid (SP), organophosphate (OP) and carbamate group of pesticides. Food processing techniques implies the set of methods and techniques used to transform raw ingredients into food or to transform food into other forms for consumption by humans either in the home or by the food processing industry. This section reviews the most common food processing techniques that would aid in pesticide dissipation. In order to assess the effects of household processing like washing, peeling, juicing, freezing and cooking.

2.2.1 Washing treatment for tested crops

Washing is the most common form of processing which is a preliminary step in both household and commercial preparation. Loosely held residues of several pesticides are removed with reasonable efficiency by washing processes. One part of the sample of each fruits and vegetable was washed for three minute under tap water and dried the samples on filter paper.

2.2.2 Washing with acetic acid on the pesticide residues on pepper

Washing sweet pepper in aqueous washing solution (5% acetic acid) for 3 min, followed by spraying for 15 seconds with tap water with gentle rotation by hand.

2.2.3 Frying treatment technique for the pepper samples

100 g of pepper samples were fried in oil for 5 min and dried.

2.3 Preparation, Extraction, Clean up and Pesticides Determination and Partitioning

The chopped samples (100 g) were placed in a stainless steel jar 1 L and extracted with 200 ml of acetonitrile and 10 g celite, the blender was vigorously homogenized into high speed for 2 min and the mixture was filtrated by using Buchner funnel fitted with shark-skin filter paper into 500 ml suction flask. An aliquot of organic was transferred to 1L separator funnel and

added 100 ml of (PE), the mixture was vigorously shaken for 1-2 min and then was added 100 ml saturated solution of NaCl and 600 water. The mixture was vigorously mixed and the separator funnel was allowed to be held at horizontal position for few minutes. The aqueous layer was discarded and the solvent layer was washed with twice time 100 ml portions of distilled water and the washed layer were transferred into 100 ml beaker and washed with 15 g of anhydrous sodium sulphate. Finally the extract was concentrated to 5 ml volume and transferred directly to florisil column [7].

2.4 Florisil Column Cleanup

Florisil column was prepared according to the AOAC method ([7], chap. 10). The column was contained about 12 cm activated florisil topped with 1 cm anhydrous sodium sulphate, column was washed by 40 ml (PE) and then added extract concentrated to 5 ml and allowed to pass through the column. The walls of the tube were rinsed additional small portions of petroleum ether and elute at 5 ml/min with 200 ml 6% eluting solvent (Diethyl ether in (PE)), and then 200 ml 15% and finally 200 ml 50% eluting solvent (Diethyl ether in (PE)) at 5 ml/min.

2.5 Reagent

All pesticides standard were obtained from (Riedel de Haen and Supelco). We prepared 1 mg/ml stock solution of each by dissolving 20 mg of the pure analytical standard in 20 mg of acetone. A single composite standard solution was prepared by diluting with acetone according to limit of detection (LOD). All standard solutions were stored in glass-Stoppard flasks at 4°C. Mixed compound calibration solutions were prepared in acetone and they were used as spiking solution. Solvents (residue analysis grade) used were acetone, acetonitrile, petroleum ether and other reagents such as sodium chloride and anhydrous sodium sulphate, florisil 60-100 mesh for residue analysis were also from purchased from (Fluka). The florisil and anhydrous sodium sulphate was activated at 100°C over night and stored in 500 ml glass flaska with glass stoppers and stored in oven at 100°C. The equipments used included a high-speed blender with a stainless steel jar (waring, USA), a shaking separation final (GFL, Germany), a rotavapor, R 215 and cooler circulator chiler B-740 (Buchi, Switzerland), Buchner funnel and chromatographic tubes with Teflon stopcocks and course fritted glass

(Agilent, USA) and syringes (Hamilton Bonadus AG, Switzerland). All glassware were rinsed thoroughly using soap and deionization water, then washed with acetone and dried in oven (100-130°C) over night.

2.6 Chromatographic Instrumentation and Quantification

Gas chromatograph-mass spectrometer (Agilent model 6890N) gas chromatograph coupled with (model 5975B) quadrupole mass spectrometer with a GC column HP-5MS 5% phenyl - 95% methyl siloxane, 30 m x 0.25 mm id x 0.25 µm film thickness. GC operating conditions: splitless injection, injector temperature 250°C, helium carrier gas (99.9999 purity) at flow rate 0.9 ml/min with column head pressure 7.4 psi, oven temperature from 70°C (2 min hold), then raised to 130°C at the rate (25°C/min) afterwards raised to 220°C at (2°C/min) and then raised to 280°C at (10°C/min) and eventually (4.6 min hold). The sample (1 µL) was injected in splitless modes. The MS system was routinely set in selective ion monitoring (SIM) mode and each compound was quantitated based on peak area using one target and one or two qualifier ion. Mass spectrometer parameter was set as follows: electron impact ionization mode with 70 eV electron energy, scan mass range 100-400 at 0.62 sec/cycle. Ion source temperature 230°C, MS quad temperature 150°C, EM voltage 1450 and solvent delay 4 in.

2.7 Recovery Data

Sweet pepper with no pesticides detected previously were used for the fortification

experiments. 50 g homogenized sample was spiked prior to determination procedure by addition of a mixture of standard pesticides solution 0.1-0.5 µg/ml of each compound depending of the sensitivity. Spiking samples were left to stand for 3 h to allow pesticide absorption onto the sample. They were then prepared according to the determination procedure described above.

2.8 Determination of Pesticides Residues

An appropriate aliquot (2 µl) of samples was injected in Gas Chromatography Mass spectrum under the mentioned conditions and then pesticides residues had been identified by comparison of retention time values with reference standard. Confirming the result was done by kind of ions are used for identifying the pesticides, one is a target ion and the other is a qualifier ion. The target ion is a second major ion used for confirming the pesticide with the target ion. which showed that the retention time and characteristic masses (m/z) for each pesticides.

3. RESULTS AND DISCUSSION

3.1 Effect of Different Household Processing on Sweet Pepper to Removal Pesticide Residues

Data in Table 1 and Fig. 1 showed that the initial residues in sweet pepper before washing and other treatments were 0.487, 0.007, 0.007, 0.013, 0.020, 0.186 and 0.156 ppm. for methomyl, endosulfan II, dicofol, dimethoate, Pirimiphos methyl, cypermethrin and metalaxyl respectively. After washing (tap water) the

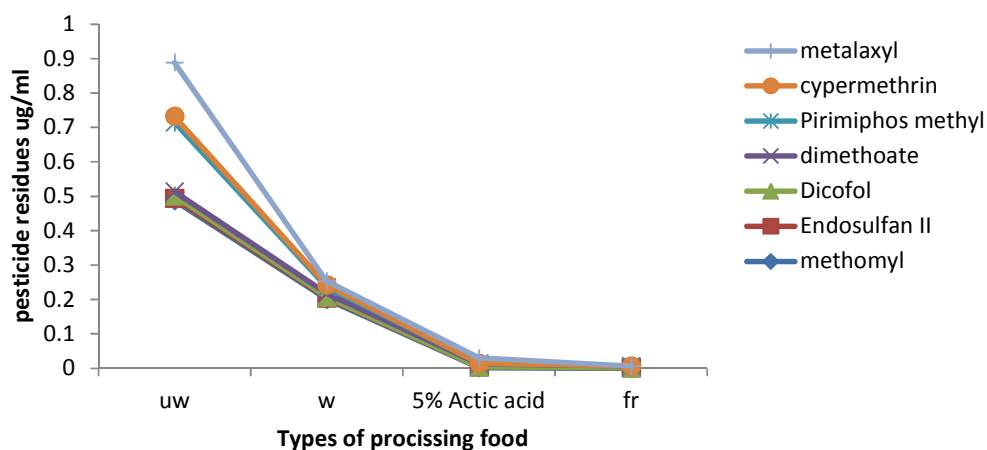


Fig. 1. Effect of different household processing on removal pesticide residues from sweet pepper

Table 1. Effect of different household processing on removal pesticide residues from sweet pepper

Detected pesticides	uw	w	5% actic acid	fr	MRL
Methomyl	0.446-0.563 (0.487)	0.191-0.213 (0.201) [59]	0.01-0.02 (0.016) [99.7]	Nd [100]	1.0
Endosulfan II	0.06-0.08 (0.07)	0.03-0.04 (0.036) [49]	0.02-0.03 (0.023) [67]	0.01-0.03 (0.0016)[77]	-
Dicofol	0.06-0.08 (0.07)	0.02-0.03 (0.023) [67]	Nd [100]	Nd [100]	1.0
Dimethoate	0.012-0.015 (0.013)	0.09-0.012 (0.011) [15]	0.08-0.09 (0.086) [34]	0.05-0.06 (0.005) [62]	1.0
Pirimiphos methyl	0.018-0.022 (0.020)	0.016-0.020 (0.018) [10]	0.02-0.03 (0.023) [89]	Nd [100]	1.0
Cypermethrin	0.018-0.019 (0.0186)	0.06-0.07 (0.066) [65]	Nd [100]	Nd [100]	0.5
Metalaxyl	0.100-0.189 (0.156)	0.09-0.015 (0.011) [30]	0.04-0.06 (0.015) [90]	Nd [100]	1.0

Uw: Unwashed; W: Washing (tap water); fr: Frying.

() : the mean of detected pesticides

[] : is % reduction of residues

percentage of redaction were 59, 49, 67, 15, 10, 65 and 30 % for methomyl, endosulfan II, dicofol, dimethoate, pirimiphos methyl, cypermethrin and metalayl respectively. On the other hand, the washing and treatment with 5% actic acid showed high reduction percentage reached 99.7, 67, 100, 34, 89, 100 and 90 % for methomyl, endosulfan II, dicofol, dimethoate, pirimiphos methyl, cypermethrin and metalayl respectively. The obtained results are in harmony with several investigators [8,9,2,10,11]. They found that washing with water and/or other solutions processes resulted in a great reduction of pesticide residues from treated vegetable fruits and lead to the residue level lower than the Maximum Residue Limits (MRLs). On the other hand, the effect of thermal processing by frying on residues in sweet pepper, completely removed for residues of methomyl, dicofol, pirimiphos methyl, cypermethrin and metalayl, which have initially residues of 0.487, 0.007, 0.020, 0.0186 and 0.156 ppm respectively. The heat can increase volatilization, hydrolysis or other chemical degradation and thus reduce residue levels [1,3,5,12].

4. CONCLUSION

The above mentioned results obtained from Table 1 emphasizes the fact that the advantages associated with the application of pesticides in enhancing the agricultural productivity must be weighed against the possible health hazard arising from the toxic pesticide residues in food. First and foremost the application of pesticides

should be in compliance with good agricultural practices GAP, using only the required amounts. Further the current shift in world opinion from 'chemical farming' towards 'organic farming' is a sustainable approach to minimize the damage posed by widespread contamination of environment by pesticides. Pesticide residues in food are influenced by storage; handling and processing which is post-harvest of raw agricultural commodities but prior to consumption of prepared foodstuffs. Extensive literature review demonstrates that in most cases processing leads to large reductions in residue levels in the prepared food, particularly through washing, peeling and cooking operations. Washing with water and various chemical solutions for domestic and commercial use are necessary to decrease the intake of pesticide residues [6]. Freezing as well as juicing and peeling are necessary to remove the pesticide residues in the skins. Cooking of food products helps to eliminate most of the pesticide residues.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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