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# Study the Effect of Household Processing on some Pesticide Residues in Olive Fruits

**Lamia M. Ryad and Ali A. Mahmoud**

*Central Laboratory of Analysis of Pesticide Residues and Heavy Metals in Food, ARC, Giza, Egypt.*

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## ABSTRACT

The aim of this work is to quantify the effect of household processing (washing and pickling) on the levels of five pesticide residues (Chlorpyrifos, Cypermethrin, Diazinon, Profenofos and L-cyhalothrin) in contaminated fifty olive samples (black and green).The first step of processing (washing) allowed decreasing the concentration of pesticide residues 26%-67%, while the second process, pickling (after washing), results in a reduction ranging from 10%-82%. Washing and pickling effect to decreasing pesticide residues from olive samples.

***Key words:*** Pesticide residues, processing factor, washing, pickling, olive.

## Introduction

The widespread use of pesticides for improving agricultural productivity has raised public concern about the possible presence of residues in food. Laws have been established in each country and internationally in an attempt to protect the health of humans, wildlife, and the environment from harmful effects of pesticides. Monitoring of pesticide residues is done to help ensure that pesticide applications are made in accordance with national and international guidelines.

Maximum legal admissible levels, known as the maximum residue limits (MRLs) (or tolerances in the USA), are established depending on each registered pesticide and commodity pair. The trend in regulations regarding pesticide residues in food is that they are becoming more stringent, and the number of active substances for crop treatment is increasing.

The presence of pesticide residues is a concern for consumers because pesticides are known to have potential harmful effects to other non-targeted organisms than pests and diseases. The major concerns are their toxic effects such as interfering with the reproductive systems and foetal development as well as their capacity to cause cancer and asthma (Gilden *et al.*, 2010). Some of the pesticides are persistent and therefore remain in the body causing long term exposure. The concern has led to governments setting up monitoring systems in order to assess the safety situation and make informed decisions when passing legislation.

Pesticide residues in fruits and vegetables are a major concern to consumers due to their negative health effects. They have been found in both raw and processed fresh produce. However, food processing techniques have been found to significantly reduce the pesticide residues in fruits and vegetables in several studies (Chavarri *et al*., 2004; Dejonckheere *et al*., 1996; Elkins, 1989; Krol *et al*., 2000; Schattenberg *et al*., 1996). The techniques used in the studies focused on commercial or home processing of fruits and vegetables and they included washing, blanching, peeling, pureeing, cooking, roasting, frying and boiling.

The retention of pesticides depends on the physiochemical properties of the pesticide molecules as well as food. In fruits and vegetables, most of the pesticide residues are retained on peel surface (Awasthi 1993). This is the reason that majority of the residues are removed by washing, peeling or treatments with chemical solutions like vinegar, turmeric, sodium bicarbonate, common salt or alcohol (Gupta 2006).

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 (Holland *et al*., 1994).

**Corresponding Author:** Lamia M. Ryad, Central Laboratory of Analysis of Pesticide Residues and Heavy Metals in Food, ARC, Giza, Egypt.
E-mail: lamia.ryad@gmail.com

The effects of different food processing techniques on pesticide residue levels in fruits washed by anon-toxic solution can decrease the concentration of pesticide residues in the vegetable and fruit samples (Shweta *et al.*, 2010). Washing was shown to be the most studied method of processing. Washing has been found to reduce pesticides that are loosely attached to the surface of the fruits or vegetables (Abou-Arab and Abou-Donia, 1999). The removal extent depended on the physical and chemical properties of the pesticide, method of application, as well as the nature of the cultivated plant. The removal of pesticide residues by washing has also been found to depend on the age of the chemical (Guardia-Rubio *et al.*, 2007). These researchers found that it was easier to wash off the pesticide residue from olives one day after spraying than after one week.

## Materials and Methods

*Chemicals for Analysis:*

Acetonitrile, Methylene chloride, and hexane were HPLC grade from Lab-scan (with certified purity of at least99%).Anhydrous magnesium sulphate fine powder, anhydrous sodium sulphate, Di Sodium citrate, tri Sodium citrate dehydrade and magnesium sulphate grit from Fluka. Sodium Chloride, Primary secondary amine bulk sorbent (PSA) and sodium acetate from Ridel de Haen (99%). Florisil (60-100, Fluka) activated overnight at 300ºC. Silica 60 (Fluka) activated overnight at 300ºC then deactivated by distilled water 1mL for each 100g of silica.

*Overview of Processing and Sampling Steps:*

Olive samples were collected randomly from different places at Egyptian local markets, the samples were collected in plastic bags and stored in a freezer at (-20°) until analysis (Rubio *et al.,* 2007). The total number of samples collected were fourteen with two major type black and green and subtypes (Picual, Manzanilla, Kalamata, Gaeta and Amphissa) as shown in table (1), each sample was coded with a number before carrying out the analysis.

**Table 1:** Type of olive samples which have been collected

| No | Color | Olive type |
|---|---|---|
| 1 | Black | Gaeta, Kalamata and Amphissa |
| 2 | Green | Picholine and Manzanilla |

**Table 2:** Three portions used in processing

| Portion 1 | Portion 2 | Portion 3 |
|---|---|---|
| Direct grinding and analysis. | Washing with water and grinding analysis of olive. | Washing with water, pickling, wait for one month, grinding, then analysis. |

*Notice that: Pickling was done by water (1liter), salt (100g) and vinegar (100m) for each kilogram (close carefully using glass jar).*

*Sample preparation:*

The olive samples (10 kg) were cleaned with hand brush to remove soil and then cut into small pieces then frozen until analysis. This samples is the positive control sample, which did not undergo any processing (reference sample) to calculate processing factor.

*Sample analysis:*

Olive sample (8.1 g) was weighed into a 50 ml Pete tube and 10ml acetonitrile was added and shaked for one minute then 4.0 g anhydrous magnesium sulphate grit was added; 1g sodium chloride, 0.5g di sodium citrate and 1g tri sodium citrate were added and shaked vigorously for one minute. The samples were centrifuged at 3000 rcf for 5 min. The upper clear solution was taken (extracts) and transferred into another tube and stored in refrigerator for 2 hours at -20°C, then was taken into centrifuge for 2minute at 3000 rcf then 7 ml was transferred to another tube containing 0.2 g primary secondary amine (PSA) sorbent and 1g anhydrous magnesium sulphate fine powder. The tubes were caped, then the extract with the sorbent/desiccant mixed vigorously for one minute and centrifuged at 3000 rcf for 5 min. Three milliliter of the clear solution was transferred into 50 ml glass flask and was evaporated using rotary evaporator at 40°C and dissolved in 3 ml of injection standard and then was injected into GC-NPD and took another two milliliter of the clear solution to 50ml glass flask and evaporated using rotary evaporator at 40°C,then added 2ml of n-hexane and transferred to column (florisil & silica) then added to flask 10ml of mixture (hexane with ethyl acetate 80:20), transferred to column with medium rate and collected all into flask 50ml then evaporated using rotary evaporator at 40°C then dissolved in 2 ml of injection standard and injected into GC-ECD.

*Processing Factors:*

Processing factors (PFs) were calculated for all processing steps by a ratio between the pesticide residue concentration (mg/kg) in the processed sample and the pesticide residue concentration (mg/kg) in the raw (non-processed sample) is calculated as follows:

*Pf* = residue level in processed commodity/ residue level in the RAC or commodity to be processed

If a PF is lower than 1, it indicates the processing step is effective, while if higher than 1, it indicates a processing step is not effective. To obtain a PF for each individual processing step:

1. Washing step: by calculating the ratio between the residue level in processed olive sample to residue level without processing (raw sample).
2. Pickling step: by calculating with the concentration of pickling olives and the concentration of washed olives.

## Results and Discussion

The study of the degradation of pesticides during processing of olives allows calculating the PFs for selected pesticides.

### Unprocessed olive

Raw sample to know the pesticide concentration to calculate a PF. All the concentrations of the pesticides measured for the two types of olives are showed in Table 3. The three highest concentrations were obtained for Cypermethrin, Profenofos and L-cyhalothrin. The Chlorpyrifos and Diazinon were measured but were not detected. The concentrations were below the minimal concentration (0.1 mg/kg or 10 x LOQ) to calculate a PF (OECD, 2008).

**Table 3:** Concentrations (mg/kg) of pesticides for the two olive types before and after processing steps:

**Type 1:** Black olive

| Pesticides name | LOQ (mg/kg) | Raw mean values (± SD) | Washing mean values (± SD) | Pickling mean values (± SD) |
|---|---|---|---|---|
| Chlorpyrifos | 0.01 | 0.076(± 0.012) | 0.056 (±0.005) | <LOQ |
| Cypermethrin | 0.1 | 0.21 (±0.02) | 0.11 (±0.009) | <LOQ |
| Diazinon | 0.01 | 0.03 (±0.003) | 0.012 (0.001) | <LOQ |
| Profenofos | 0.01 | 0.27 (±0.03) | 0.09 (0.007) | 0.02 |
| L-cyhalothrin | 0.01 | 0.19 (±0.02) | 0.14(±0.013) | 0.03 |

**Type 2:** Green olive

| Pesticides name | LOQ (mg/kg) | Raw mean values (± SD) | Washing mean values (± SD) | Pickling mean values (± SD) |
|---|---|---|---|---|
| Chlorpyrifos | 0.01 | 0.056(± 0.01) | 0.037 (±0.005) | <LOQ |
| Cypermethrin | 0.1 | 0.31 (±0.017) | 0.16 (±0.007) | <LOQ |
| Diazinon | 0.01 | 0.027 (±0.003) | 0.013 (0.001) | <LOQ |
| Profenofos | 0.01 | 0.29 (±0.03) | 0.1(0.007) | 0.027 |
| L-cyhalothrin | 0.01 | 0.23 (±0.02) | 0.14(±0.013) | 0.035 |

### Washing

Washing is the most common and effective step of processing. It is generally the first step in various types of treatments. Figure 1, 2 presents all processing factors for the each processing steps for the five detected pesticides. Results for both olive types are represented separately. These results can also be seen in Table4, which collects all processing factors for the each processing steps.

Unwashed samples of olives contained an average of Chlorpyrifos 0.076 mg/kg, Cypermthrin 0.21 mg/kg, Diazinon 0.03 mg/kg, Profenofos 0.27 mg/kg and L-cyhalothrin 0.19mg/kg. Washing of olives in cold water for 5 min removed 26%-36% of Chlorpyrifos, 48% of Cypermethrin, 66% of Profenfos, 67% of Diazinon and 26%-39% of L-cyhalothrin.

Washing is generally the first step in various types of treatments which are given to food commodities in combination like washing followed by pickling to allow for effective decontamination from pesticides.

On the other hand Cengiz *et al*., 2006 was found that the initial Diazinon residue level (0.822 ppm) on cucumbers was decreased 22.3% by washing for 15 s by rubbing under running water.

Lentza-Rizos *et al*., 2006, found that the residues of Azoxystrobin on grapes were 0.49–1.84 ppm and washing removed 75% of the residues, on the other hand Cengiz *et al*., 2007, found that the initial procymidone residue level (0.86 ppm) on tomatoes was decreased 68% by washing for 15 s by rubbing under running water.

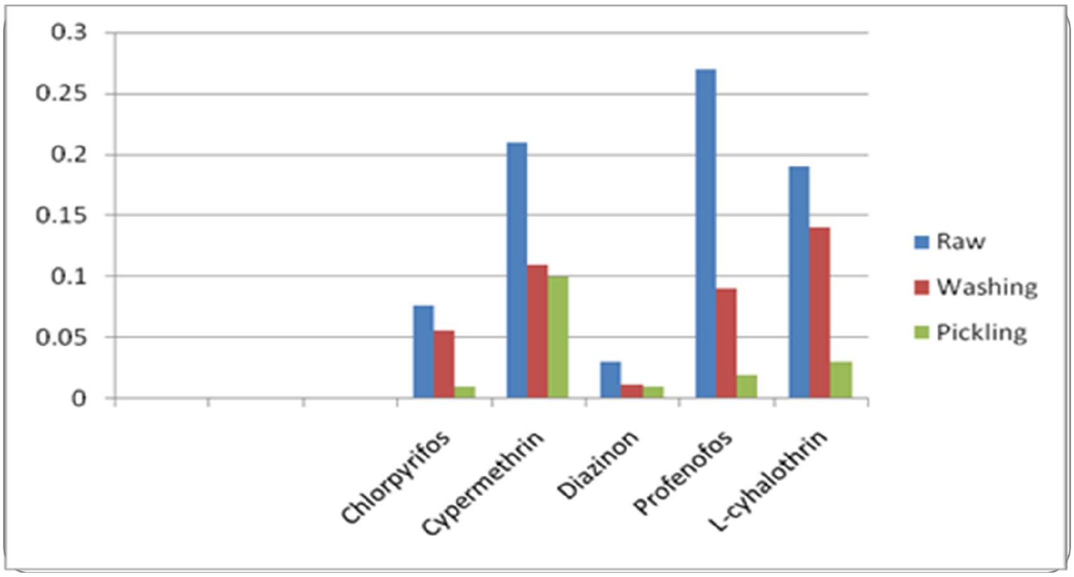


**Fig. 1:** Effect of processing (washing and pickling) for five pesticides in black olive:

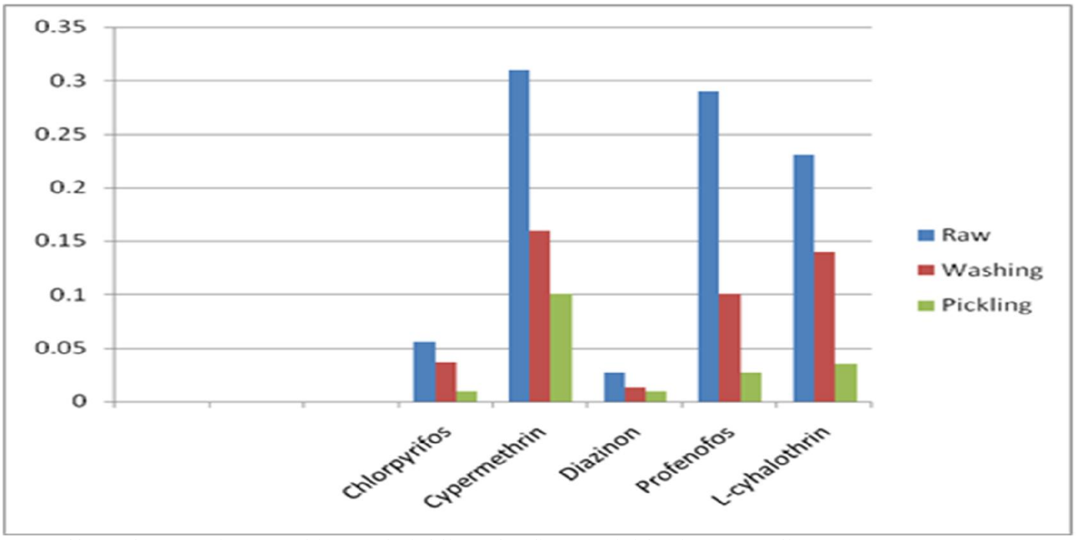


**Fig. 2:** Effect of processing (washing and pickling) for five pesticides in green olive

## Pickling

Pickling is the second step in the processing of olives. In this study, pickling using salt was carried out. As shown in Table 4, the elimination of residues after pickling was important the same to the washing step. Pickling removed 82% of Chlorpyrifos, 10%-37% of Cypermethrin, 73%-78% of Profenofos, 17%-23% of Diazinon and 75%-79% of L-cyhalothrin.

**Table 4:** Mean values of processing factors (PF) for each processing steps for five pesticides in two types of olives.

| Pesticides | PF washing Black green | | PF pickling Black green | |
|---|---|---|---|---|
| Chlorpyrifos | 0.74 | 0.64 | 0.18 | 0.18 |
| Cypermethrin | 0.52 | 0.52 | 0.9 | 0.63 |
| Diazinon | 0.33 | 0.37 | 0.83 | 0.77 |
| Profenofos | 0.33 | 0.34 | 0.22 | 0.27 |
| L-cyhalothrin | 0.74 | 0.61 | 0.21 | 0.25 |

## Conclusion

Various processing factors (washing and pickling) on olives were determined for Chlorpyrifos, Cypermethrin, Diazinon, Profenofos and L-cyhalothrin.

Different processing steps decrease the concentration of pesticide residues, in this work the washing step allowed decreasing the concentration of residues for all pesticides 26%-67%. The second process, pickling, results in a reduction ranging from 10%-82%.In conclusion, washing and pickling are the important steps to reduce pesticide residue in olives.

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