UDC: 634.11-295.028(497.773)
Professional paper

INFLUENCE OF MECHANICAL TRETMENTS AND HEAT TREATMENT ON THE CONTENT OF CYPERMETHRIN RESIDUES IN APPLES AND APPLE JUICE

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Abstract

The use of pesticides to protect apples in conventional production is widely used, and therefore it is important to monitor their residues. This study monitors the concentration of cypermethrin residues in fresh apples, peeled, washed with water, and prepared apple juice with heat treatment. For this purpose, an analysis of cypermethrin in apples was performed using the LC-MS/MS method, previously extracted using the QuEChERS method. From the results obtained, it is observed that by washing the apples with cold water (12°C) for 30 seconds, peeling them and heat treatment (apple juice), the presence of cypermethrin residues decreases in each subsequent processing step. The concentration of cypermethrin residues present in apple juice samples is higher compared to peeled apples, yet lower compared to fresh apples, because apple juice was produced from unpeeled apples (apples with skin). The greatest reduction in pesticide cypermethrin was observed in apples that were peeled, because pesticides are concentrated in the apple peel and removing it reduces the pesticide content. The highest prevalence of residues of the pesticides cypermethrin is found in fresh apples fruits in relation to washed apples, peeled apples and apple juice, while the lowest presence of cypermethrin is in peeled apples fruits. The presence of residues of cypermethrin in all apple samples is within the maximum residue limits (MRLs) of the pesticides and the products are safety for consumption. The main parameter used to estimate pesticide intake through the diet of processed agricultural products is the processing factor (Pf). The values obtained for Pf are less than 1, indicating that mechanical and thermal treatment of apples results in a decrease in the concentration of cypermethrin residues.

Keywords: pesticides, cypermethrin, food safety, reduction of pesticide residues, processing factor

1. Introduction

The production of safe food is of great importance, but on the other hand, the use of pesticides to protect plants from diseases and pests has increased. This means that food contamination is a global problem that is receiving a lot of attention (Rajak et al. 2023). Contaminants ingested through food are responsible for the majority of diseases. Diet is considered to be the dominant route of entry of contaminants into the body. Food contamination can occur at any step of the food chain: raw materials, production, transportation, storage and preparation (Thompson & Darwich, 2019). However, the widespread use of pesticides poses significant threats to ecosystems, human health, and other biotic elements of the environment (Zarębska et al., 2022; Liess & Gröning, 2024).

Pesticides in certain concentrations and quantities are used in apple cultivation to control pests, increase resistance to external influences, and maintain apple quality. When growing apples, it is permitted to use pesticides, but their concentration must be prescribed by law so that there are no negative impacts on human health and the environment (Simon et al., 2011). Pesticides are preparations used in the cultivation of fruits and vegetables to increase yields. The yield of apples not treated with pesticides is significantly lower than the yield of untreated apples. Apples that are not treated with pesticides are organic apples, but when growing them, the

https://doi.org/10.62792/ut.jftn.v8.i15-16.p3183

recommendations of the state authority that prescribes them should be followed and implemented. In untreated apples, the yield of apples is lower than in treated apples, and therefore their price is much higher (Damos et al., 2015). Pesticides used in apple cultivation must be approved by law and the concentration of pesticide residues must not exceed the maximum permitted concentration. The maximum permitted concentrations of pesticide residues in food are precisely prescribed and in order not to exceed them, it is necessary for growers of agricultural and fruit plantations to comply with the recommendations of the authorities, regarding the frequency of use of pesticides, their concentration and the method of application (Official Gazette of the Republic of Macedonia, 91, 2018). According to Siddiqui, 2024, cypermethrin is a synthetic pyrethroid, and a widely used pesticide in commercial agriculture and domestic settings to control pests and boost crop yields. Despite its effectiveness in controlling pests, there are concerns about the potential environmental and human health impacts associated with its use. Cypermethrin has been identified as one of the important constituent pesticides associated with human health risks (Liao et al., 2011). Pesticide residues in fruits and vegetables can be reduced by their processing, such as mechanical processing, i.e. by washing, peeling and thermal processing. The aim of this research is to detect cypermethrin residues in apples and monitor their concentration after mechanical and thermal treatment.

2. Material and methods

Fresh apples, washed apples, peeled apples and apple juice were analyzed. The apples are of the Red Delicious variety and were grown in the Resen Region, by private growers, at two different locations, Evla and Kriveni.

2.1 Preparation of fresh apples for analysis: According to the standard method for pesticide residue analysis, the apples were not washed and were used for analysis in their whole form, without any treatment.

2.2. Preparation of washed apples for analysis: The apples were washed with cold tap water (12°C) for 30 seconds, using gentle circular motions. After all the apples were washed, they were placed in a bowl to drain and after wiping each apple, the preparation continued.

2.3 Preparing peeled apples: Apples were prepared by mechanical preparation, i.e. washing and peeling with a knife. The apples were first washed and then peeled. The thickness of the peeled apple skins was about 1 mm ± 0.3 mm. Then the peeled apples were homogenized and placed in plastic airtight containers, frozen at -20 °C, until they were analyzed.

2.4 Preparation of apple juice: The apples were washed according to the method described above, and the stems and seeds were removed. The juice was prepared from apples that were not peeled. The next step in the production of apple juice was to chop the unpeeled apples into smaller pieces, then blend and homogenize them with a blender. The blended and homogenized apples were placed in a cooking pot, 1 L of water was added and cooked at low temperature for 3 minutes. The next step was to strain the juice with a strainer and obtain apple juice, then add 250 g of sugar and boil the squeezed juice together with the sugar for 2 minutes and 30 seconds. After boiling the juice, the juice was cooled. The juice was packaged in glass jars, which were appropriately labeled. Then, as the last step in the production of apple juice, the apple juice was frozen and stored in a freezer at -20°C until analysis for the presence of cypermethrin residues was performed.

2.5 QuEChERS method for extracting pesticide residues: Extraction of pesticide residues was performed using the QuEChERS method, according to the MKS EN 15662:2018 LC-MS/MS standard. The procedure used is according to Anastassiades et al., 2003; Dimoski, et al., 2021a.

2.6 Analysis by liquid chromatography-mass spectrometry (LC-MS/MS): The samples were analyzed by liquid chromatography (Waters, UPLC-MS/ MS), mass spectrometer with triple quadrupole (XEVO TQ-S micro,Waters) (Dimoski, et al., 2021a; Dimoski et al., 2021b)

2.7 Processing factor: The processing factor is calculated from the level of pesticide residues in the processed product divided by the level of residues in the corresponding raw product (unprocessed product) (Scholz et al., 2018; El-Sayedet al., 2021) (formula 2.7.1).

$$Pf = \frac{\text{Pesticide residues in processed foods (mg/kg)}}{\text{Pesticide residues in raw product (mg/kg)}} \quad \text{(Formula 2.7.1)}$$

Where:
Pf > 1: The residues are concentrated in the processed product
Pf < 1: Residues are reduced in the processed product (due to dilution, removal or degradation).
Pf = 1: Processing does not result in a change in residue concentrations.

3. Results and Discussion

3.1 Cypermethrin in apples and apple juice: The concentrations of cypermethrin in fresh (unwashed) apples, washed apples, peeled apples, and apple juice prepared from the variety Red Delicious, from Evla, are presented in Figure 1.

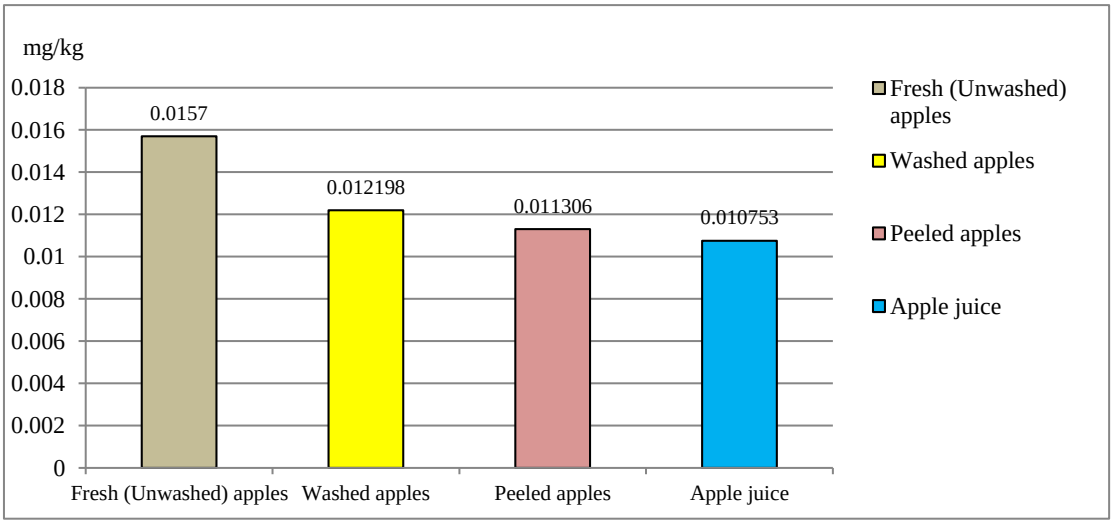

Figure 1. Cypermethrin in mechanically and thermally treated apples of the Red Delicious variety, from Evla location

In Figure 1, we see how the level of residues of the pesticide cypermethrin decreases in all samples of apples of the Red Delicious variety, location Evla. Fresh apples contain residues of the pesticide cypermethrin at a concentration of 0.0157 mg/kg and by washing the apples the concentration of residues of the pesticide cypermethrin is reduced to 0.012198 mg/kg. In peeled apples, the pesticide residues present are at a concentration of 0.011306 mg/kg and there is a difference in the concentration in fresh apples. In apple juice the concentration of residues of the pesticide cypermethrin is 0.010753 mg/kg. According to Keikotlhaile et al., 2009, by

washing, peeling, and processing apples into apple juice, the amount of pesticide residues is reduced.
Figure 2 presents the results obtained from the analysis of cypermethrin in apples and apple products, fresh (unwashed) apples, washed apples, peeled apples and apple juice from the Red Delicious variety, which were grown at the Kriveni location.

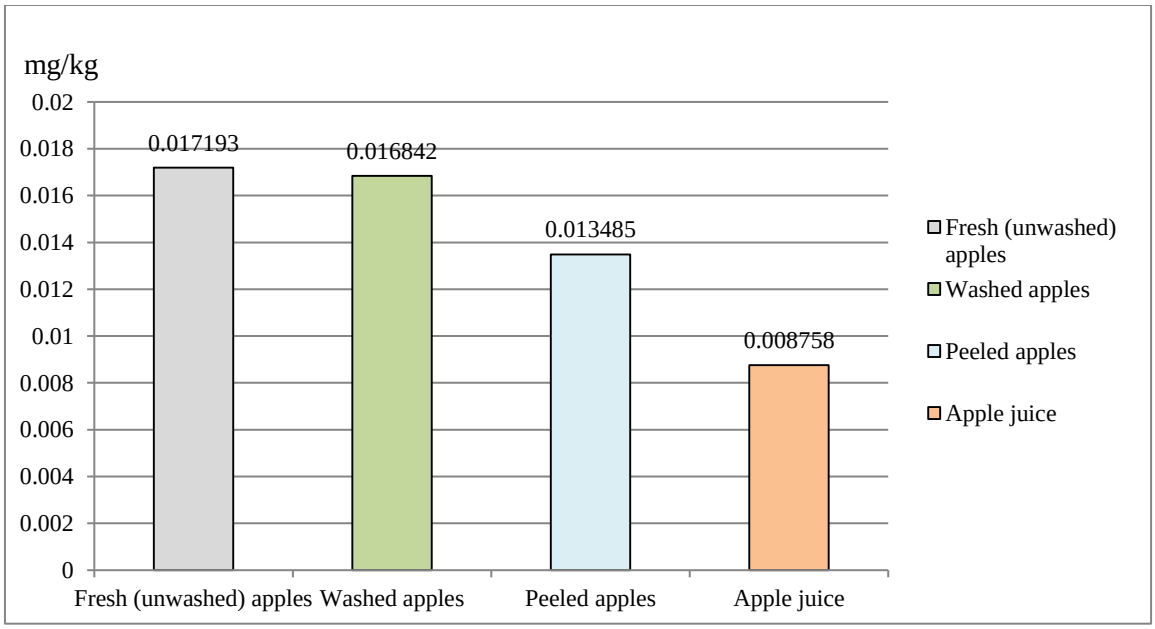

Figure 2. Cypermethrin in mechanically and thermally treated apples of the Red Delicious variety, from Kriveni location

In Figure 2 we see how the level of residues of the pesticide cypermethrin decreases in all samples of apples of the Red Delicious variety, location Kriveni. So, fresh apples contain residues of the pesticide cypermethrin at a concentration of 0.017193 mg/kg, and by washing the apples, the concentration of pesticide residues is reduced to 0.016842 mg/kg. In peeled apples, cypermethrin is present at a concentration of 0.013485 mg/kg. In apple juice the residues of the pesticide cypermethrin are present at a concentration of 0.008758 mg/kg.
The lower presence of residues of the pesticide cypermethrin in the treated samples compared to other samples of the same apple variety is due to the mechanical and thermal processing of the apples, where these procedures remove some of the present residues of the pesticide cypermethrin. The effect of processing apples at home, i.e. washing and peeling apples, has also been analyzed by Kong et al. (2012). According to Pirsaheb et al., 2016, washing apples reduced the amount of pesticide residues, but peeling apples showed the greatest effect on reducing pesticide residues

3.2 Maximum permitted concentrations: According to the Regulation on general and specific food safety requirements regarding maximum permitted levels of pesticide residues in or/on food and feed of plant and animal origin, published in the Official Gazette, No. 91, 2018, the maximum permitted concentration of cypermethrin in apples is 1.0 mg/kg. From the results obtained, we note that the concentration of cypermethrin is approximately 60-114 times lower than its regulated and prescribed maximum permitted concentration. We can conclude that the products are safe for use and that consuming these products in human nutrition will not cause any health problems.

3.3Processing factor : Agricultural products are often not consumed raw, but are first processed. This can change the amount of pesticide residues that the primary products in itially contain. The ratio of pesticide residues in a processed product to that in the corresponding unprocessed product is known as the processing factor. This factor indicates whether the levels of pesticide residues during food processing processes are increased (concentrated) or decreased (Bonnechere et al. 2012; Scholz, 2018). Table 1 shows the values of the processing factor for cypermethrin during mechanical and thermal treatment of apples from both locations.

Table 1. Processing factor in treated Red Delicious apples from different location

Samples	Evla location **Processing factor**	Kriveni location **Processing factor**
Unwashed apple	0,78	0,98
Washed apple	0,72	0,78
Apple jouce	0,68	0,51

The values obtained for Pf are less than 1, indicating that mechanical and thermal treatment of apples results in a decrease in the concentration of cypermethrin residues.

4. Conclusions

The pesticide cypermethrin was detected in all samples, i.e. it was present in fresh (unwashed) apples, washed apples, peeled apples, and in thermally prepared homemade apple juice. The concentration of cypermethrin residues present is highest in fresh (unwashed) apples, lower in washed apples, and lowest in peeled apples due to the removal of the peel, which contains most of the pesticides. The presence of residues of the pesticide cypermethrin in all apple samples is within the maximum permitted concentration, making the apples safe for consumption and will not cause health problems in humans. The processing factor indicates a decrease in cypermethrin concentration during mechanical and thermal processing of apples. Continuous education of fruit crop growers on the use of permitted active substances, good agricultural practice, and compliance with new regulations is recommended, which would contribute to the protection of human health and the production of a quality and safe product. In order to reduce the concentration of pesticides, mechanical and thermal treatment of apples before consumption is recommended. Future research in this field may provide an answer to the impact of pesticide structure on the reduction of pesticide concentration in different treatments.

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