

THE CONTENT OF CYPERMETHRIN PESTICIDE RESIDUES AFTER DIFFERENT METHODS OF APPLE PREPARATION¹

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ABSTRACT

The apple considered as an important food source due to its nutritive composition as well as biological activities of its compounds. Due to the positive health benefits, apples are present in the daily diet in a fresh and in different processed forms. However, different types of pesticides used during apples cultivation in order to improve the yield, quality, but also to combat the insects and pests. On the other hand, pesticides can affect the human health, like that their monitoring strongly recommended. Food processing is one of the most effective strategies for decontaminating of food items from pesticides and obtaining safe products for consummation. This study summarizes the presence of cypermethrin, as one of the most used pesticide for apple crops, in fresh as well as in processed apple products prepared by various methods including mechanical and thermal. The extraction of pesticide residues of cypermethrin from apple products performed by QuEChERS method while the analysis performed by liquid chromatography-mass spectrometry (LC-MS/MS). The concentration of cypermethrin presented in various products was in the range of 0.01024 mg/kg to 0.0142 mg/kg that concludes that all analyzed samples are

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safe to consume, while the apple peeling method is the most effective in reducing the cypermethrin in the final products.

Keywords: pesticide residue, cypermethrin, food processing, apple juice, food safety

INTRODUCTION

In order to get a higher yield of apples, pesticides may be used in their cultivation, but the concentration of the pesticides should be prescribed by national regulations, so that there will not be any risk to the consumers' health and the environment (Simon et al., 2011; Jallow et al., 2017). Pesticides are chemicals; their metabolites applied to apple orchards to protect them from pests and diseases as well as to maintain fruit quality (Baba et al., 2017; Jacoboa et al., 2017; Velkoska-Markovska et al., 2019; Hassaan & Nemr, 2020). Consuming foods that contain toxic substances such as pesticides and their residues, increases the potential risk to human health, causing cancer, congenital defects, neurological and endocrine disorders as well as changes in reproductive system (Alavanja & Bonner, 2012; Jara & Winter, 2019). The health risk is higher for children than the elderly when apples with high concentration of pesticides are consumed according to Jankuloska et al. (2020). Cypermethrin is a synthetic pyrethroid insecticide; pyrethroids are a family of compounds similar to the natural pyrethrin insecticides (Crowley et al., 2021). They bind to sodium channels of neuron membranes, disrupting electrical signals in the nervous system, thus acting as a neurotoxin (Silver et al., 2014). The main symptom of cypermethrin intoxication is skin irritation and redness, eye irritation, numbness, tingling and itching. Exposing to this substance for a long period of time can lead even to death (Singh et al., 2012). High concentrations of pesticide residues in food, which exceed the maximum residue level (Official Newspaper of the Republic of Macedonia, 2018), can be accumulated in the body and cause a negative impact to human health, therefore it is necessary to monitor their concentration in fruits (Hawari et al., 2019). Pesticide monitoring by public health and food safety institutions is one of the most important procedures that guarantees safe and quality products (Yu et al., 2017; Kailani et al., 2019). Pesticide residues should not exceed the permitted maximum residue levels (MRLs) of pesticide in the products (Mebdoua et al., 2017) if Good Agricultural Practice (GAP) is followed.

Apple and apple juice have a rich nutritional composition and are often present in the human diet (Xu et al., 2018; Ullah et al., 2018). From the most well varieties of apples, Idared is characterized by large and round fruits, with a firm elastic and smooth skin. The pulp of the apple is firm, crunchy and juicy; usually harvested in late September or early November (Mohebi et al., 2017; Dana et al., 2018). Available scientific studies have showed that mechanical and thermal processing of fruit could remove some of the present pesticide residues, depending on the nature of the pesticide and the fruit (Satpathy et al., 2012; Nguyen et al., 2020).

In this study, the pesticide cypermethrin analyzed in fresh apples and their processed products. The influence of the preparation method for apple-based products on pesticide residue concentration was monitored.

MATERIALS AND METHODS

Table 1 presents the examined samples in this work. Eight samples taken from 2 different locations in the Resen region (R. N. Macedonia), villages Evla (location 1) and Kriveni (location 2), after harvesting period in October 2020 were analyzed.

Table 1 Designation of samples

Number of samples	Samples	Location
1	Unwashed apples	Evla
2	Unwashed apples	Kriveni
3	Washed apples	Evla
4	Washed apples	Kriveni
5	Peeled apples	Evla
6	Peeled apples	Kriveni
7	Apple juice	Evla
8	Apple juice	Kriveni

Fresh (unwashed) apples were analyzed from both locations 1 and 2 (samples 1 and 2), then washed apples with tap water (12°C, 30 seconds) are also considered in this study (samples 3 and 4). Furthermore, samples 5 and 6 were

apples that were washed, peeled with a knife (peel thickness was $1 \text{ mm} \pm 0.3 \text{ mm}$), and then homogenized before analysis. Apple juice samples (7 and 8) were prepared in home conditions (Dimoski et al., 2021). Extraction of cypermethrin pesticide residues was performed using QuEChERS (Quick, Easy, Cheap, Effective, Rugged, Safe) method according to standard MKS EN 15662:2018 LC-MS/MS (Anastassiades et al., 2003; Standardization Institute of the Republic of Macedonia, 2011; Dimoski et al., 2021). The processing factor (PF) calculated in order to observe which treatment has the greatest effect on reducing the cypermethrin concentration in the samples. According to Scholz (2018); El-Sayed et al. (2021); processing factors (PFs) are calculated by the equation (1):

$$PFs = \frac{\text{Residue in processed fraction (mg/kg)}}{\text{Residue in raw agricultural commodities (mg/kg)}} \quad (1)$$

RESULTS AND DISCUSSION

Eight analyzes for the presence of cypermethrin in all apple samples performed. Mainly fresh, washed, peeled apples and apple juice samples considered in this study. The obtained results presented in Table 2.

Table 2 Concentration of cypermethrin in analyzed samples and processing factors (PFs)

Number of samples	Cypermethrin / (mg/kg)	Processing factor / (PFs)
1	0.01420	-
2	0.01351	-
3	0.01178	0.83
4	0.01153	0.85
5	0.01100	0.77
6	0.01024	0.76
7	0.01245	0.87
8	0.01237	0.92

When PFs is lower than 1, it indicates the reduction of a pesticide, while if higher than 1, it indicates a concentration in regulatory practice, regardless of

changes in volume or weight for the processed food (due to dilution, removal or degradation) (Bonnechère et al., 2012; Scholz, 2018). Our calculations showed that the PF is less than 1 and they were in the range of 0.76-0.92; this shows that all treatments have a positive effect on reducing the cypermethrin concentration, where peeling treatment has shown the greatest impact; PFs are 0.77 and 0.76 for samples 5 and 6, respectively (Table 2).

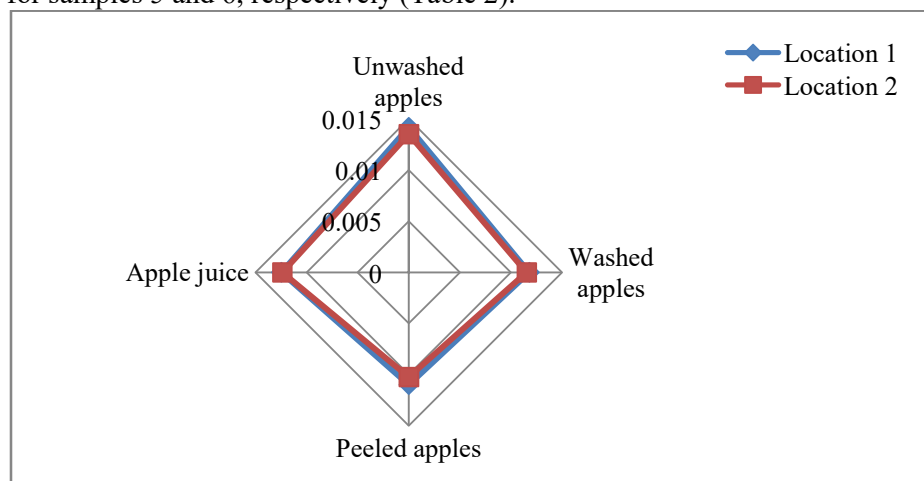


Figure 1 Comparison of the cypermethrin presence in samples taken from both locations in R. N. Macedonia.

In general, the amount of cypermethrin presented in all samples from both locations is similar (Figure 1); the highest concentration of cypermethrin found in fresh unwashed apples from both locations. The lowest concentration of pesticide is in samples 5 and 6 - the peeled apples from both locations. In washed apples from location 1 (Evla) (sample 3), the concentration of cypermethrin decreased by 17.04% compared to unwashed apples from the same location (sample 1), while in sample 4 the concentration of pesticide decreased by 14.65% compared to sample 2. In peeled apples from location 1 (sample 5), the concentration of cypermethrin decreased by 22.53% compared to fresh apples from the same location (sample 1), while in peeled apples from location 2 (sample 6), cypermethrin decreased by 24.20% compared to unwashed apples from the same location (sample 2). In the case of apple juice from both locations there is a decrease in the concentration of cypermethrin compared to unwashed

apples (samples 1 and 2) by 12.32% (sample 7) and by 8.43% (sample 8), respectively.

The obtained results from analyzes in this research are from 0.01024 mg/kg up to 0.01420 mg/kg and they are lower than the MRL by 98.58 – 98.97%, which indicates that they are safe for consumption. The maximum residue level (MRL) for cypermethrin in apples is 1 mg/kg (Official Journal of the European Union, 2005; Official Newspaper of the Republic of Macedonia, 2018).

The reduction of cypermethrin concentration by mechanical and heat treatment presented in Figure 2.

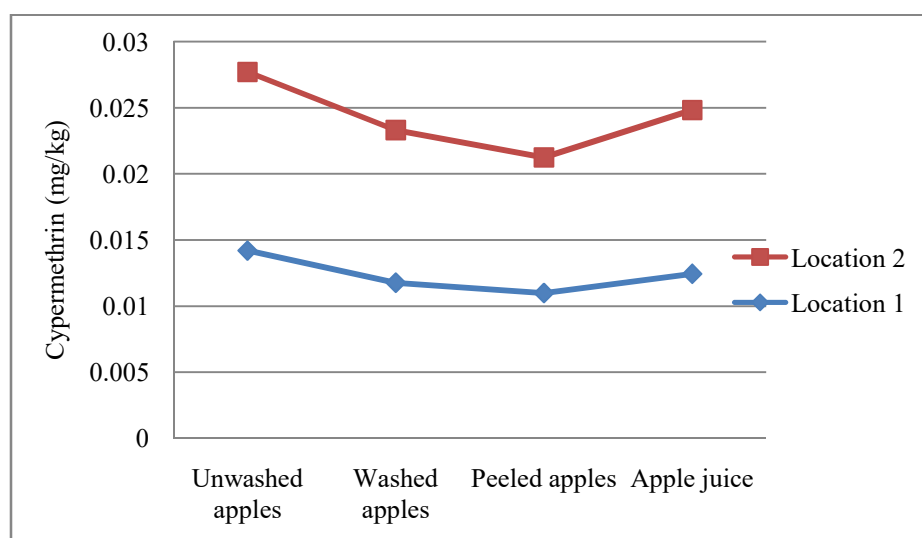


Figure 2 Influence of mechanical and heat treatment on the concentration of cypermethrin in all tested samples.

CONCLUSIONS

The presence of the pesticide cypermethrin in fresh apples and processed apples from two different locations analyzed. Cypermethrin detected in all samples; the highest concentration was found in unwashed apples from both locations, while the lowest concentration was found in peeled samples. During mechanical processing, the pesticide cypermethrin

decreased by 0.0032 mg/kg or by 22.53% in peeled apples from location 1 compared to fresh apples from the same location. In the peeled apples from location 2 the present amount of cypermethrin decreased by 0.00327 mg/kg or by 24.20% in relation to the fresh apples from the same location. During the thermal treatment, a decrease in the concentration of cypermethrin was observed, but in a less percentage unlike the mechanical treatment. Additional analyzes of other pesticides are needed in order to find a suitable treatment for fruit cultivation as well as suitable food processing technique to find the best way for safe and consumable product with good quality.

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