UDC: 634.11-295.028(497.773)
*Original Scientific Paper*

# PESTICIDE RESIDUES IN FOOD: FOOD SAFETY, NUTRITION AND HEALTH EFFECTS

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**Abstract**

Pesticides are chemical substances which used to ensure high crop yields. From year to year the sales of plant protection products (fungicides, herbicides, insecticides) in agriculture are increasing. The use of pesticides during production often leads to the presence of pesticide residues in fruit after and during harvest. Exposure to food pesticide residues through the diet can negatively affect the central nervous system, the cardiovascular system and respiratory system. For these reasons, monitoring the presence of pesticides in food is of great importance. The aim of this study was to evaluate the residues of pesticides in apples from Resen. The UPLC-TQ/MS method was used for determining pesticide residues. The pesticide residue is extracted with QuEChERS. From the total number of samples, it was noted that in the apples from the Evla location, the most abundant pesticide is chlorpyrifos with 20 %, then pyrimethanil and dimethoate with 13.33 %, in comparison with other pesticides etc. In apples from the Kriveni location, the most common pesticides are tebuconazole and omethoate with 13.16% in comparison with other pesticides. The permissible pesticide residue level in foods is an important criterion for food safety. Future longer term studies are required in this area and would help attain a deeper knowledge about the fruit production with respect to the use of pesticides and their presence in samples.

*Keywords:* pesticides, chlorpyrifos, dimethoate, apples

## 1. Introduction

From year to year, the sales of plant protection products (fungicides, herbicides, insecticides) in agriculture are increasing. Reasons for the application of pesticides are numerous, starting from solving agronomic problems that have not been solved so far, to the emergence of new or resistant pests as well as the reduction of economic damages affecting food producers. Food producers are required to meet the requirements of food safety regulations, at a minimum, in order to protect consumers from the dangers of unsafe food (Lawley et al., 2008). In many countries, food safety is regulated by laws, regulations by national authorities or by authorized institutions. In the Republic of North Macedonia, the maximum residue levels (MRLs) for pesticides are regulated in the Regulation on general food safety requirements regarding maximum tolerated levels of pesticide residues in or on food (Official Gazette of the Republic of North Macedonia, No.156, 2013).

Pesticides are usually organic synthetic compounds, rarely inorganic, which are highly soluble in fats, oils and waxes (liposoluble) and poorly or relatively poorly soluble in water (hydrophobic). Their application is in agriculture, forestry, water management, livestock and veterinary healthcare and a small percentage in the food industry (Lazić and Šovljanski, 2007). The classification of pesticides is according to their biological activity, degree of poisoning, genotoxicity and ecotoxicity. The pesticides authorised for treatment of apples belong to different chemical families, such as organophosphates, carbamates, pyrethrins, triazoles, neonicotinoids etc. After their application, they decompose and this depends on the nature of the pesticide, solubility, formulation, atmospheric conditions, method of application and particle size. Passarela et al.,

2009, followed the dissipation of fungicide residues, namely of captan, cyproddinil, fludioxonil in apples, dithianon and tebuconazole in pears, apples and peaches. Pesticide residues in greenhouse tomato dropped by half within 2.8 – 3.5 days (Garau et al., 2002).

The presence of pesticide residues is regarded as a potential hazard, especially for infant and yang children who are biologically more vulnerable to exposure than adults (Hercegova et al., 2007). Fruit have been a given a lot of attention in the monitoring program of each country since most of them are eaten raw, and it is expected that they would contain higher pesticide residue level compared to other food groups of plant origin (Łozowicka et al., 2013) but are also expected to be represented at very low concentrations in accordance with the maximum permissible limits provided by authorized institutions. Pesticide monitoring enables us to check the use of allowed compounds, verification and compliance with the maximum residue levels of pesticides and checking the acceptable value of individual pesticides in the food. According to the EFSA report for 2010-2013 between 0.2-2% baby food contains pesticides above the MRL. Of the fresh products (such as apples) used for the manufacture of baby food, it was noted that they mostly contain pesticides and in 9% of them that they are represented above the maximum residue limits (Štpán et al., 2005; Słowik-Borowiec et al., 2012).

High concentrations of pesticide residues can adversely affect human health. In assessing health hazards, it is important to take into account: the path of entry into the body (respiratory system, digestive tract or skin), exposure time, the toxicity of the compounds and the mechanism of toxic action, of acute and chronic poisoning. In recent years, attention to pesticides has been increasing, knowing that they may be triggers of sterility, neurological and renal diseases, tumours, teratogenic effects, behavioural disorders (Maroni and Fait, 1993). Consuming food with pesticide residue can have negative health effects on the central nervous system, the cardiovascular system and respiratory system. Consumption of apples and their health effects against cancer, cardiovascular disease, asthma and diabetes has been investigated by the authors Boyer and Liu, 2004. A diet rich in fruits and vegetables in adults and children helps maintain and reduce weight (United States Department of Agriculture, 2017). The apple is delicious fruit, easy to process, and contains low calories. It is a source of vitamins and minerals: vitamin A and C, calcium, phosphorus, iron, potassium, soluble and insoluble dietary fibre (Chen et al., 2014). From the soluble fibre in apples is pectin present, which has a major role in reducing cholesterol and preventing atherosclerosis and heart disease. Insoluble fibres in apples protect the body from retaining toxic substances and diseases. Nutritionists recommend and encourage consumers to eat at least five portions of fruit and vegetables daily. Given these recommendations, consumers are directly put at risk if they consume unsafe food. Considering the potential health risk of pesticide residues in food and the high consumption rate of fruit and vegetables in many countries, attention has been focused on the possible presence of residues in food. The purpose of this study was to determinate the presence of pesticide residues in apples from Resen.

## 2. Material and methods

Determining pesticide residues in apple samples is a difficult and laborious analytical risk, therefore, it is important to make good preparation of samples for analysis, and extract purification is necessary in order to obtain reliable results. In this study, 16 samples of apples (Idared varieties) from various areas of Resen (Evla and Kriveni) have been investigated. Representative 1 kg apples (for sampling) were collected and all samples transported to the laboratory and stored at 4$^{o}$C until being homogenized and analyzed. Fresh apples without treatment were analyzed (Jankuloska et al., 2017; Jankuloska et al., 2018). Analyses were performed by ultra-performance liquid chromatography-triple quadruple mass spectrometry (UPLC-TQ/MS) (Agilent UPLC 1290; T=35oC; flow 0,4 ml/min; v=0,7µl, DAD; TQ) after a previous extraction of residue by applying the QuEChERS method MKS following the EN 15662:2011 method (Anastassiades et al., 2013).

## 3. Results and Discussion

Summary results of analysis of pesticide residues in apples from Resen from two different locations are given in figure 1 and figure 2. In table 1 the determined active substances of plant protection products are presented, including insecticides and fungicides.

**Table 1.** Determined active substances of plant protection products in apples

| **Species of pesticides** | | **Active substances** |
|---|---|---|
| **Group (by biological activity)** | **Chemical class** | |
| **Fungicides** | Carbamate | Cabendazim (azole), Pyraclostrobin |
| | Triazole | Difenoconazole, Tebuconazole, Myclobutanil |
| | Ureas | Cymoxanil (curzate) |
| | Aminopyrimidine | Pyrimethanil |
| **Insecticides** | Pyrethroide | Alpha-cypermethrin |
| | Organophosphate | Chlorpyrifos, Dimethoate, Omethoate |
| | Neonicotinoide | Acetamiprid, Imidacloprid, Flonicamid |
| | Organothiophosphate | Phosmet (Imidan) |
| | Carboxamide | Hexythiazox |
| | Pyridines | Pyriproxyfen |

From Figure 1 we can see that in apples from the Evla location many pesticides from different groups of fungicides and insecticides are detected. From the total number of samples, it was noted that the most abundant pesticide is chlorpyrifos with 20%, pyrimethanil and dimethoate with 13.33 %, in comparison with other pesticides. The fungicide pyrimethanil is one of the most frequently encountered fungicides in apples (Łozowicka *et al*., 2011; Słowik-Borowiec *et al*., 2012). Difenoconazole, myclobutanil and omethoate are represented with the same percentage (6.67) in the apple samples from this location. While pesticides dimethoate, acetamiprid and alpha cypermethrin are represented by 10% of the total number of samples. Cymoxanil (curzate) is represented in the smallest number of samples (3.33%).

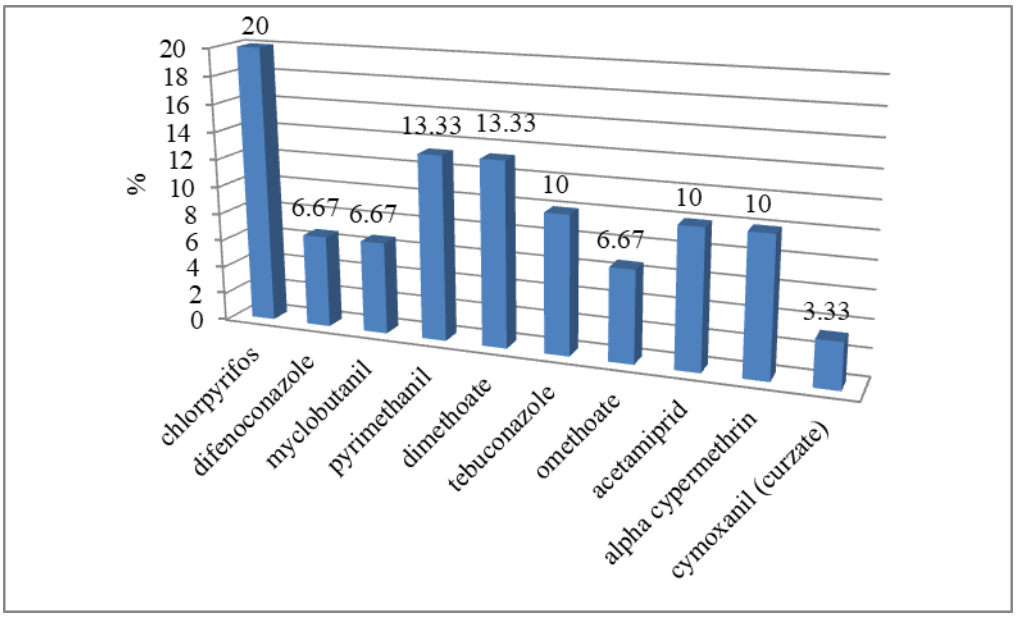


**Figure 1.** Pesticide residues in apples from Evla

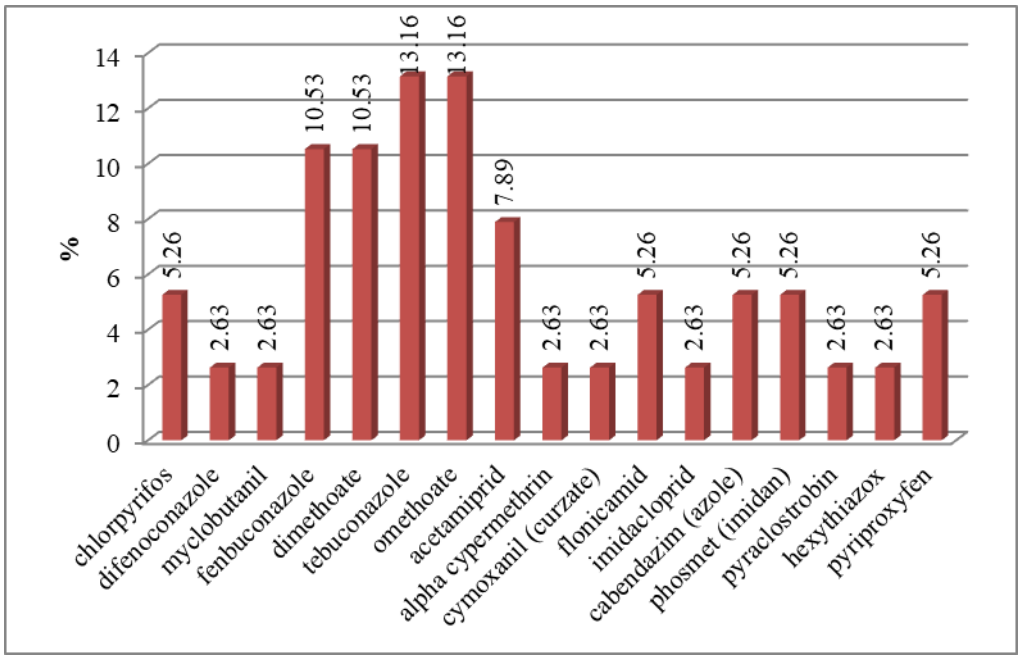


**Figure 2.** Pesticide residues in apples from Kriveni

In apples from the other location (Kriveni), it is noticeable that a large number of different pesticides are detected in comparison with the Evla apples. In apples from the Kriveni location, the most common pesticides are tebuconazole and omethoate with 13.16%, in comparison with other pesticides, while fenbuconazole and dimethoate are represented with 10.53%. Of the total number of samples, acetamiprid is represented in 7.89% and the remaining pesticides difenoconazole, myclobutanil, alpha cypermethrin, cymoxanil, imidacloprid, pyraclostrobin and hexythiazox are represented in a smaller percentage (2.63). Chlorpyrifos and other pesticides (flonicamid, carbendazim, phosmet and pyriproxyfen) are represented only in 5.26% of apples from this location. The detected pesticide residues in the samples range from 0.01 to 0.09

mg/kg (Jankuloska *et al*., 2017; Jankuloska *et al*., 2018) and the permissible pesticide residue levels in foods is an important criterion for food safety. The presence of different pesticides in the same variety of apples from different locations points us to the importance of the geographical location where the apples are grown (Jankuloska *et al.*, 2017).

## 4. Conclusions

This study found that the analysed apples contain pesticide residues from different chemical groups, fungicides and insecticides. The most frequent insecticides are chlorpyrifos from apples at the Evla location and tebuconazole and omethoate from apples at the Kriveni location. Future longer term studies are required in this area and would help attain a deeper knowledge about fruit production with respect to the use of pesticides and their presence in samples. The results can be used when designing future control programs and taking preventive action to minimize human health risks.

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