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PESTICIDE RESIDUES IN APPLE SAMPLES ON THE MARKET OF THE REPUBLIC OF SERBIA 2004–2007

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Abstract: *Our study comprised the determination of the pesticide residue content in 108 samples of apples. The pesticide residues were determined by gas chromatography with NPD, ECD and GLC – MS. The samples were tested for the content of 75 pesticides with LOD of 0.001 to 0.005 mg/kg which were lower than MRLs according to the EU standards. The relative standard deviation was lower than 19% for all the tested compounds. In the apple samples taken during 2004, the percentage of the samples positive to the pesticide residue content was 51.85% and the most frequent contaminants were ∑ HCH and endosulfan. In the analyzed samples, taken during 2005, out of 70.91% samples in which the pesticide residues were detected, endosulfan was present in 41.03%, captan in 35.9%, chlorpyrifos in 20.51% and parathion in 17.95%. The content of the procymidone and lambda-cyhalothrin residues were over the EU MRLs. During 2006 all apple samples were residue-free. Out of 13 samples analyzed in 2007, five contained the pesticide residues below the EU MRLs with the most frequently detected dithiocarbamate.*

Key words: *Apple, pesticides, residues, GLC, monitoring*

S. LAZIC, M. PUCAREVIC', V. BURSIC, N. OSTOJIC', S. VUKOVIC, Faculty of Agriculture, Trg Dositeja Obradovica 8, Novi Sad, SERBIA; 'Institute of Field and Vegetable Crops, Maksima Gorkog 30, Novi Sad, SERBIA. ***ПЕСТИЦИДНИ ОСТАТЪЦИ В ЯБЪЛКИ ОТ ПАЗАРА НА РЕПУБЛИКА СЪРБИЯ ЗА ПЕРИОДА 2004–2007 Г.***

Резюме: *Проучването обхваща определяне съдържанието на пестицидни остатъци в 108 проби от ябълки с газова хроматография с детектори NPD, ECD и GC-MS. Пробите са изследвани за съдържание на 75 пестицида с граници на откриване от 0,001 до 0,005 mg/kg, които са по-ниски от максимално допустимите концентрации (МДК) съгласно европейските стандарти. Относителното стандартно отклонение е по-ниско от 19% за всички анализирани съединения. В проби от ябълки, взети от 2004 г. процентът на положителните проби за съдържание на пестицидни остатъци е 51,85% като най-чести замърсители са ∑ HCH и ендосулфан. В анализираните проби, взети през 2005 г., от 70,91% проби, в които са открити остатъчни количества от пестициди, ендосулфан е наличен в 41,03%, каптан в 35,9%, хлорпирифос в 20,51% и паратион в 17,95%. Количествата на остатъците от процимидон и ламбда-цихалотрин са над европейските МДК. През 2006 г. не са установени пестицидни остатъци в пробите от ябълки. От 13 проби, анализирани през 2007 г., 5 съдържат остатъци с количества по-ниски от МДК, като най-често откривани са дитиокарбаматите.*

Ключови думи: *ябълки, пестициди, остатъчни вещества, GLC, мониторинг*

The residues of pesticides in fruit are the consequence of their direct application in the agricultural production. In order to comprehend in what condition the pesticide residues in fruit are and how hazardous they are to human health, it is essential to carry out a long-lasting monitoring of their residue content and to create a data base and a base of contaminant contents. As food is one of the most important factors of the environment it directly affects human health and existence. That is why it must be of a high safety quality. Within that framework the role of fruit in nutrition is significant. According to the latest data, the fruit con-

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sumption has reached almost 170 kg per person a year. (Gebara et al., 2007). Fruit is a significant source of nutrition which provides the human body with the necessary and useful compounds such as the vitamins (C, B complex vitamins, precursors of vitamin A), minerals (K, Mg, Fe, Cu), fibres and other matters which have a positive effect on the human body.

These matters are unstable so that it is recommendable to consume fresh fruit (not treated thermically). On the other hand it needs to be emphasized that fresh fruit consumption entails a certain risk of being exposed to the residue of the pesticides which have been used for protection during the production and storage. At present, the pesticides are widely used for fruit protection. Their excessive use can jeopardize human health so that the content of their residues in the agricultural products used in the nutrition of people and animals must be checked on. The programmes of monitoring the pesticide residues in food which are continuously carried out ensure that the consumers are not exposed to the intolerable level of pesticide residues. There are other ways of inappropriate use of pesticides such as intolerable high doses or disregard of the time interval between the last pesticide treatment of plant species and harvesting – PHI, which can be prevented by a regular monitoring of the pesticide residues (Pucarevi?, 2008).

MATERIAL AND METHOD

Our study comprised the determination of the pesticide residue content in 108 samples of apples from the market of the Republic of Serbia taken during 2004–2007 (27 samples were analyzed in 2004, 55 samples in 2005, 30 samples in 2006 and 13 samples in 2007).

The pesticide analysis was carried out by the multiresidual method after Fillion et al. (2000). To put it briefly, the samples were homogenized with acetonitril and sodium chloride. The clean-up was performed by using the SPE C-18, the eluate was collected in cuvettes with sodium sulphate. After that, the eluate was cleaned up again by Envi Carb + Amino propyl columns. Then, it was evaporated to 2 ml with the acetone twice and evaporated to dryness and diluted in acetone. For the identification and quantification of pesticides the gas chromatography with electron capture detector (ECD), nitrogen/phosphorus detector (NPD) and Mass Spectrometry were used.

The residue concentration of the positive samples was calculated by the calibration curve, generated from the peak area obtained by the results of the standard analysis.

RESULTS AND DISCUSSION

Since the pesticides are widely used for fruit protection at present, their excessive use can jeopardize human health so that the content of their residues must be checked on.

The analysis of the 27 samples of apples from 2004 showed that the pesticide residues in the 14 samples with the most frequently present ΣHCH (51.85%), endosulfan (28.57%) chlorpyrifos (21.43%) were detected whereas the diazinone, malathion and fenitrothion were present in one sample (not the same one). The content of all the other pesticide residues was below the EU MRLs. In the analyzed samples, taken during 2005, out of 70.91% samples in which the pesticide residues were detected, endosulfan was present in 41.03%, captan in 35.9%, chlorpyrifos in 20.51%, parathion in 17.95%. In two samples the procymidone and dihlorvos respectively were present, and in one sample Σ HCH, malathion, fenitrothion, pirimiphos-methyl, bifenthrin and lambda cyhalotrin were present respectively. Out of seven samples in which the paration was detected, five contained the values of this pesticide over the MRL. The content of the procymidone residue detected in two samples as well as the content of lambda-cyhalothrin found in one sample were over the EU MRLs. All the detected values were below the MRL. During 2006 thirteen samples of apples were analyzed in which no pesti-

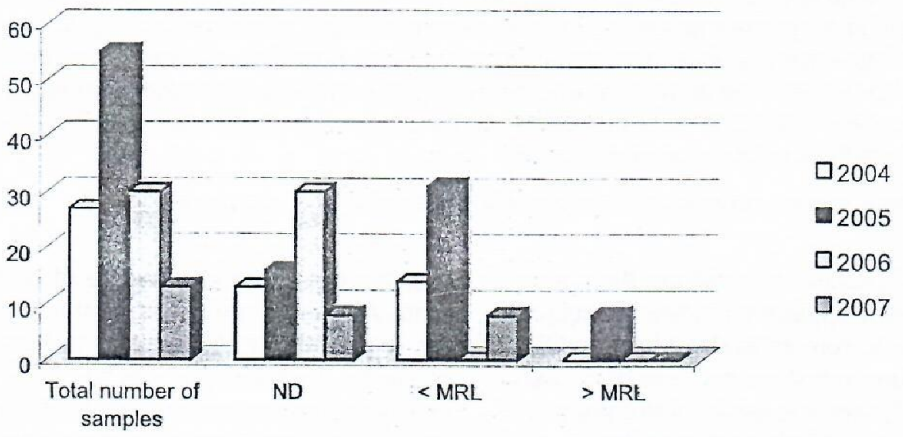

Fig. 1 Pesticide residues in apple samples on the market of the Republic of Serbia 2004–2007
Фиг. 1. Пестицидни остатъци в проби от ябълки от азара на Република Сърбия през 2004–2007 г.

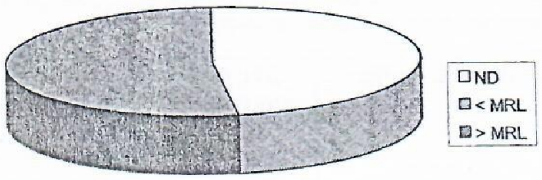

Fig. 2. Distribution of pesticide residues detected in apple samples in 2004

Фиг. 2. Разпределение на пестицидни остатъци открити в проби от ябълки през 2004 г.

cide residues were detected, or residues were not found for they were under the LOD. Out of 13 samples analyzed in 2007, five contained the pesticide residues below the EU MRLs with the most frequently detected dithiocarbamate (60.0%), cypermethrin (40.0%) and amitraz (20.0%). Figure 1 shows the total of pesticide residues in the apple samples during four years from the market of the Republic of Serbia.

Figure 2 shows the distribution of pesticide residues in 27 apple samples taken during 2004, the percentage of the samples positive to the pesticide residue content was 51.85%. The pesticide residues under the European Maximum Residue Level (MRL) were in 14 of the samples.

In the analyzed samples, taken during 2005, out of 70.91% samples in which the pesticide residues were detected, figure 3, with 71.43% residue over the EU Marls samples.

During 2006 thirteen samples of apples were analyzed in which no pesticide residues were detected. Out of 13 samples analyzed in 2007, five contained the pesticide residues below the EU MRLs. The results are shown in figure 4.

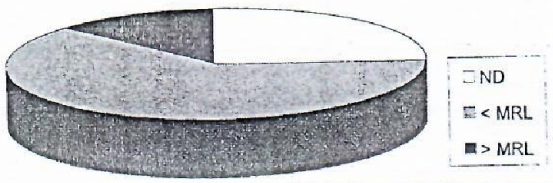

Fig. 3. Distribution of pesticide residues detected in apple samples in 2005

Фиг. 3. Разпределение на пестицидни остатъци открити в проби от ябълки през 2005 г.

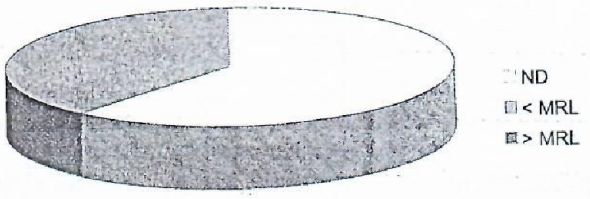

Fig. 4. Distribution of pesticide residues detected in apple samples in 2007

Фиг. 4. Разпределение на пестицидни остатъци открити в проби от ябълки през 2007 г.

Table 1 lists the pesticides detected, their frequency by the concentration level and the number of samples with pesticide residues above the EU MRLs. Most of the residues were present in low concentrations and the detection was below 0.01 mg/kg (31.33%) and 0.05 mg/kg (50.6%).

Multiple residues were detected in nine samples. The details about the pesticides detected and their levels in samples containing two or more residues are presented in table 2.

Vaxevani et al. (2008) presented the results of the four-year monitoring carried out in northern Greece, through the analysis of 1548 samples of fruit and vegetables. Under 2.0% of the analysed samples were over the MRLs values, whereas the pesticide residues were registered in 33.25% on average. The control of the pesticide residues in fruit and vegetables, carried out in Slolvenia during 2006/2007 showed that out of the total of 391 samples, 13 samples exceeded MRLs for acetamiprid, captan, chlorothalonil, cyprodinil, fludioxonil and folpet, 149 samples contained residues equal or lower than MRLs, and no residues were found in 229 samples (Basa Ceasnik et al., 2008). By the analysis of 2305 samples of fruit, vegetables, cereals and others in Slovakia during 2006 and 2007, the most frequently found residues in both years were: chlorpyrifos, thiabendazol, imazalil, maneb group, iprodion and procymidon. Aprox. 20% of all the samples had multiresidual findings and 43% were positive findings (Durcanska et al., 2008). According to the results of the Bulgarian monitoring programme of pesticide residues in a plant production in 2007, 276 samples were analysed. The residues of the pesticides were found in 39% of samples, with 90% of them below the MRLs. Only in 11 samples of tomatoes the level of vinclozolin exceeded the MRLs of 0.05 mg/kg. Chlorpyrifos was the most frequently found pesticide in 11% of samples. In 42 samples there were multiresidual findings. The highest number in a single sample, four pesticides, was found in tomatoes and apples (Mladenova and Shtereva, 2008). The monitoring of the pesticide residues in food, carried out in Lombardia, showed that in 2006 out of the analysed 1024 samples, of which 74 samples represented organic food, the pesticide residues were found in 247 samples and 60 samples had multiresidual fundings. In 28 samples the pesticide residues exceeded the MRLs values. In 10 samples of mint produced in non-European countries, there were intolerably high ammounts of dimethoate, chlorpyrifos and malathion and for that reason they were not allowed onto the national market (Mussida et al., 2007). In Turkey 87 samples were analysed for the pesticide residue content in fruit and vegetables (Tatli et al., 2007). Fifty pesticides which were detected belonged to various chemical compounds: organochlorine,

Таблица 1/Table 1

Остатъци от пестициди, групирани по открити концентрационни нива в проби от ябълки от пазара в Сърбия 2004–2007 г.
Pesticide residues sorted out by concentration level detected in apple samples from the market 2004–2007

Общ брой проби Total number of samples – 108 Положителни проби/ Detected samples - 58 Pesticide	Остатъчни количества/Residue, mg/kg					Общ брой детектирания/ Total of detections	Проби с пестицидни остатъци над EU MRLs/ Samples with pesticide residues above the EU MRLs
	<0.01	<0.05	< 0.1	< 0.5	< 1		
Σ HCH	8	0	0	0	0	8	0
Ендосулфан/Endosulfan	18	5	0	0	0	23	0
Каптан/Captan	0	14	0	0	0	14	0
Хлорпирифос/Chlorpyrifos	0	11	0	0	0	11	0
Паратион/Parathion	0	2	0	4	1	7	5
Процимидон/Procymidone	0	0	0	2	0	2	2
Циперметрин Cypermethrin	0	0	1	1	0	2	0
Малатион/Malathion	0	2	1	0	0	3	0
Дихлорфос/Dichlorvos	0	1	1	0	0	2	0
Дитиокарбамат/Dithiocarbamate	0	1	2	0	0	3	0
Ламбда-цихалотрин/Lambda-cyhalothrin	0	0	0	1	0	1	1
Диазинон/Diazinon	0	1	0	0	0	1	0
Фенитротион/Fenitrothion	0	1	0	0	0	1	0
Пиримифос-метил/Pirimiphos-methyl	0	1	0	0	0	1	0
Бифентрин/Bifenthrin	0	0	1	0	0	1	0
Амитраз/Amitraz	0	1	0	0	0	1	0
Общо/Total	26	40	6	8	1	81	8

Таблица 2/Table 2

Проби от ябълки съдържащи 2 или повече пестицидни остатъка
Apple samples containing 2 or more residues

Пестицидни остатъци/Pesticide mg/kg		EU MRL mg/kg
Паратион/Parathion Бифентрин/Bifenthrin	0,466 0,050	0,05 0,3
Паратион/Parathion Ламбда-цихалотрин/Lambda-cyhalothrin	0,0417 0,1052	0,05 0,1
Паратион/Parathion Фенитротион/Fenitrothion	0,5602 0,0757	0,05 0,05
Дихлорфос/Dichlorvos Паратион/Parathion	0,0829 0,1452	0,1 0,05
Дихлорфос/Dichlorvos Паратион/Parathion Процимидон/Procymidone	0,0315 0,1177 0,2333	0,1 0,05 0,02
Хлорпирифос/Chlorpyrifos Каптан/Captan	0,012 0,027	0,5 3,0
Хлорпирифос/Chlorpyrifos Каптан/Captan	0,020 0,016	0,5 3,0
Хлорпирифос Chlorpyrifos Каптан/Captan	0,017 0,018	0,5 3,0
Хлорпирифос/Chlorpyrifos Каптан/Captan	0,010 0,048	0,5 3,0

organophosphorus, syntetic pyrethroid, strobilurine i benzimidazole. The pesticide residues in tomato, artichoke and potato samples were below the LOD. In other samples there was at least one compound minimum. The pesticide residues were not detected in 73.36% of samples, 22.99% were below the MRLs and 3.45% samples contained the residues over the MRLs.

Our analysis dealt with the the determination of the residue content of 75 pesticides in the apple sam-

ples, from the markets of the Republic of Serbia during 2004–2007. Out of 108 samples, the pesticide residues were detected in 58 with endosilfan, captan and chlorpyrifos as the most frequent contaminants. The multiresidues were detected in nine samples while eight samples contained the pesticide residues over the MRLs.

The comparison of the cited data and our results confirms that the high percentage of samples positive to the pesticide residue content is a warning that in the production conditions a continuous and multi-level monitoring of food safety needs to be a regular practice, aiming at the successful prevention of harmful effects of pesticides on the health of people and animals.

CONCLUSION

The analysis of the market samples from the Republic of Serbia shows that out of 108 studied samples 46.3% were residue-free, or they were under the LOD. Only 7.41% of the samples had the concentration of active ingredients above the EU MRLs. The most frequently detected pesticides in the samples were endosulfan 21.3%, captan 12.96% and chlorpyrifos 10.19%. The pesticide residues detected in 53.7% of the analyzed market apple samples, taken during 2004–2007 emphasize that the high percentage of samples positive to the pesticide residue content is a warning that in the production conditions a continuous and multi-level monitoring of food safety needs to be a regular practice aiming at the successful prevention of harmful effects of pesticides on the health of people and animals.

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