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INSIGHT INTO THE LEVEL OF PESTICIDE RESIDUES IN VEGETABLES

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ABSTRACT

The liquid chromatography tandem-mass spectrometry (LC–MS/MS) with ESI was applied for the detection of 55 pesticide residues in vegetables, extracted with QuEChERS. The average recoveries for all analites were 79.4-119.8% (RSDs 3.71-17.42%). The LC-MS/MS was used for the simultaneous residue determination of 55 pesticides in the vegetables. The validated method which uses the LC-MS/MS provides a very high sensitivity, good reproducibility, appropriate linearity and can be applied with the high reliability to the analysis of investigated pesticide residues in vegetable samples. The LOQs of 0.01 mg/kg confirm that the method is appropriate for the determination of pesticide residues in all investigated vegetables according to the regulations of the Serbian and EU MRLs. The multiple detections were confirmed in eight analysed samples. The most frequently detected pesticides were acetamiprid, metalaxyl-M and pyriproxyfen. In only one watermelon sample the concentrations of carbendazim (0.134 mg/kg) and tefluthrin (0.304 mg/kg) were above the MRLs, but all the other detections were below the MRLs.

INTRODUCTION

The environmental analysis helps to protect the natural environment and human health through testing contaminants, such as pesticides, metals and other hazardous toxins and pollutants in air, water, soil and food (Mansour and Gad, 2010). The food safety is a major public concern worldwide and the food consumption has been identified as the major pathway for human exposure to certain environmental contaminants, accounting for >90% of intake compared to the inhalation or dermal routes of exposure (Mansour et al., 2009).
According to the status list of all active substances on the EU market (doc. 3010), more than 1100 pesticides are currently registered. Pesticides are used by farmers to improve or safeguard yields, to improve or protect quality of the produce, and to minimize labor input (Hercegova et al., 2006). Unfortunately, the use of agrichemicals at various stages of cultivation and during post-harvest storage play an important role in food protection and quality preservation (Sannino et al., 2004), considering the fact that they enter the chain of nutrition. During the last decades, the increasing demand of food safety has stimulated research regarding the risk associated with the consumption of foods contaminated by pesticides, heavy metals and toxins (Mansour et al., 2009). Therefore, thorough monitoring of

pesticide residues is crucial for the proper assessment of human exposure to these compounds through foods.

As a source of vitamins, minerals, proteins and carbohydrates, vegetables play an important role in human nutrition. Therefore, a high quality of vegetables is very important for human health (Maksimović et al., 2012). So, the objective of this study was to investigate the pesticide residues in vegetable samples collected from domestic farmers. The data collected are to be used as a reference point for future monitoring as well as for providing a basis for developing sustainable natural resources management practices and for taking preventive measures to minimize human health risks.

MATERIALS and METHODS

Plant material

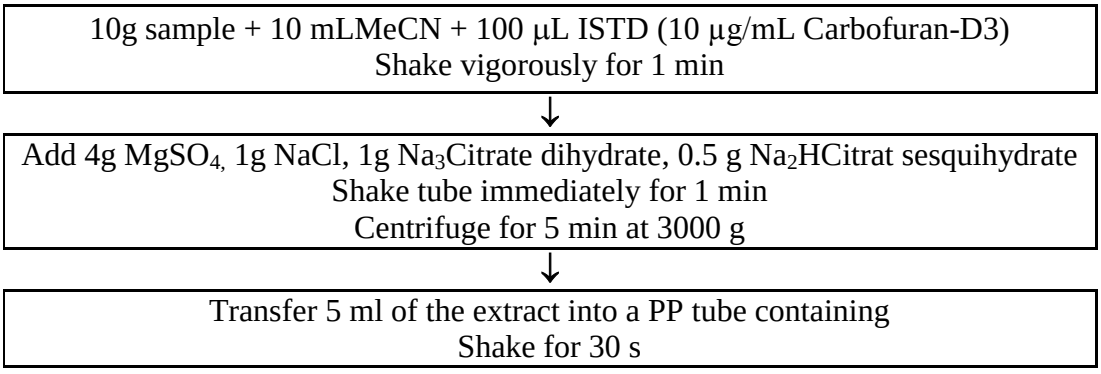
The sum of twelve vegetable samples were analysed on the pesticide residues. The samples were collected directly from farmers from Rivnica and Novi Slankamen: four pepper (*Capsicum annuum* L.) samples, belonging to 4 different cultivars (Kiowa, Domestic, Ringo and Bella Donna), three tomato (*Lycopersicum esculentum*) samples, belonging to three different cultivars (Ferdelance, Garder and Domaci) and three cucumber (*Cucumis sativus*) samples, belonging to three different cultivars (Virginia, Kaman and Solatio). One watermelon and one melon sample were collected from Rivnica.

Sample analyses

Pesticide residue determination: Agilent 1100 Series HPLC system with Zorbax XDB C18 analytical column of 50×4.6mm and 1.8 μm particle size (Agilent Technologies) was used. For LC analysis, an Agilent 1200 HPLC system with a binary pump was used. For the mass spectrometric analysis, an Agilent 6410B Triple-Quad LC/MS system was used. Agilent by MassHunter Workstation Software version B.04. QQQ Agilent Technologies, 2011 were applied for the method development and data acquisition.

Validation: The method was validated according to SANCO/12571/2013. The limit of detection - LOD was determined as the lowest concentration giving a response of three times the average baseline. The ratio signal/noise in the obtained chromatograms for the LOD was calculated by MassHunter Qualitative Software. The linearity was checked using matrix matched standards (MMS) at the concentrations of 5.0, 10.0, 25.0, 50.0 and 100.0 ng/mL. The recovery was checked by enriching 10 g of a blank sample with the mixture of pesticide standard of 10 μg/ml in the amount of 100 and 50 μL (final mass concentration 0.10 and 0.05 mg/kg) and with the mixture of pesticide standard of 1 μg/mL in the amount of 100 μl (final mass concentration 0.01 mg/kg) with the addition of the internal standard carbofuran-D3.

Figure 1. QuEChERS extraction



Centifuge for 5 min at 3000 g

↓

Transfer 200 μL into a vial, evaporate to dryness
Reconstitute in 200 μL of mobile phase

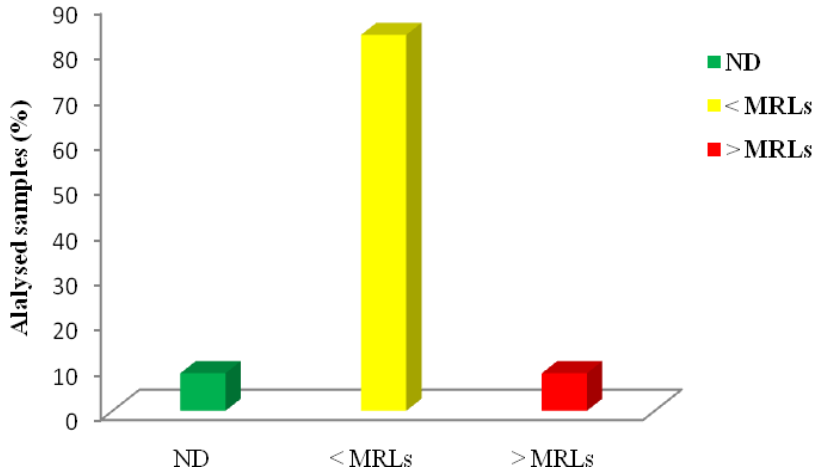
↓

LC-MS/MS

RESULTS

The LC-MS/MS was used for the simultaneous residue determionation of 55 pesticides in the vegetables. The validated method which uses the LC-MS/MS provides a very high sensitivity, good reproducibility, appropriate linearity and can be applied with the high reliability to the analysis of investigated pesticide residues in vegetable samples. The LOQs of 0.01 mg/kg confirm that the method is appropriate for the determination of pesticide residues in all investigated vegetables according to the regulations of the Serbian and EU MRLs.
The distribution of pesticide residues in the analysed vegetable samples was shown on graphic 1 (ND-non detection samples, <MRLs – detections below the MRLs, >MRLs – detections above the MRLs).

Graphic 1. Pesticide detections in vegetable samples.



The multiple detections were confirmed in eight analysed samples (66.67%), while 25% of analysed samples were with single detection. The most frequently detected pesticides were acetamiprid, metalaxyl-M and pyriproxyfen. In only one sample (watermelon) the concentrations of carbendazim (0.134 mg/kg) and tefluthrin (0.304 mg/kg) were above the MRLs, but all the other detections were below the MRLs (Regulation EC No 396/2005).

CONCLUSIONS

- The data processing of the analysed vegetables indicates that the tomato is the vegetable with the most pesticide detections.

- The watermelon is the only vegetable with the values of the MRLs exceeding the regulated MRLs.
- By comparing the pesticide contents in vegetable samples from the previous years, with the analysis results, it can be concluded that the number of samples with the detection above the MRLs was reduced, but that in the production a continuous and multilevel monitoring of food safety must be kept aiming at the successful prevention of harmful pesticide effects on human and animal health.

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Regulation (EC) No 396/2005 of the European Parliament and of the Council (2005) on maximum residue levels of pesticides in or on food and feed of plant and animal origin andamending Council Directive 91/414/EEC.

and SANCO/12571/2013, Guidance document on analytical quality control and validation procedures for pesticide residues analysis in food and feed.