PESTICIDE RESIDUES IN ENVIRONMENTAL AND PRODUCE SAMPLES FROM ECOLOGICAL AND CONVENTIONAL PAPRIKA CULTIVATION FIELDS

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Abstract
To support environmental and food safety of spice paprika production, paprika growing sites in intensive and ecological cultivation have been sampled and analyzed for pesticide residues in Hungary. Two sites of three producers in each cultivation mode were sampled in early summer. Soil samples have been collected at three different points from two or three depth levels, thus, altogether 42 soil samples have been collected at six intensive cultivation fields (ICFs) and 23 soil samples from ecological cultivation fields (ECFs). Pesticide residues in soil extracts have been determined by gas chromatography coupled with mass spectrometry (GC-MS). In soils from ICF sampling sites pesticide active ingredients trifluralin, tefluthrin, chlorpyrifos and DDT were detected together with certain decomposition products (DDE, DDD). Harvested paprika samples were collected in September from four ICFs and from one ECF. Biological samples, prepared by a modified QuEChERS extraction method and analyzed for pesticide residues by GC-MS, contained no detectable amounts of pesticide active ingredients and metabolites, even when plants were grown in ICF on soil containing pesticide residues.

Introduction
Spices used for flavoring in food industry and households are often contaminated with organic microcontaminants [1, 2] or microorganisms [3] of agricultural origin. As a result, production and trade of spices deserve special attention in the assurance of environmental and food safety. Traceability of spice contamination cases is difficult as possible occurrence patterns are very complex. In case of spice paprika mycotoxins, illegal dye utilization, pesticide residues, non-pathogenic microorganisms and heavy metals are the main risk sources. The third biggest hazard factor has been pesticide residues [4], being the reason for 27 various pesticide active ingredients and one metabolite notifications between 2005 and 2015 [2] within the Rapid Alert System for Food and Feed (RASFF) of the European Union [5]. In the present work, our aim was to find out if there are quantitative pesticide residue differences between intensive cultivation mode and organic farming method among different paprika growers in Hungary.

Experimental
In field studies six sites of three paprika producers practicing intensive cultivation mode and two organic farmers in the Southern region of Hungary have been involved (Figure 1). Soil and surface water contamination has been studied in two sampling regimes in June/July and in September. Altogether 42 soil samples have been collected at six intensively cultivated sampling sites (two sites of each producer, three different points from two or three depths). Soil samples from organic farmers have been collected also at three different points from two or three depths (0-20, 20-40, 40-60 cm) and one additional point was sampled (23 samples). Soils of all intensively cultivated fields and a single organic field were sampled in the same way in September, thus, 49 soil samples were collected in this regime. In addition, 6 samples from

surface water in these fields, partly used for irrigation purposes, were also obtained, in each sampling regime. Harvested paprika samples were collected in September from four intensive cultivation fields and from two organic cultivation fields as well.

Water samples were prepared and determined by GC-MS by the multiresidue pesticide analysis method applied by survey authorities in Hungary [6] and modified and validated in our laboratory [7, 8]. Acidic ingredients, including chlorophenoxy acid type herbicides, were eluted from graphitized carbon black solid phase extraction cartridges in a second fraction and were then subjected to derivatization to silyl esters using *t*-butyldimethylsilyl *N*,*N*-dimethylcarbamate as a derivatizing agent [9]. GC-MS analysis was performed on a Varian Saturn 2000 workstation equipped with a Varian CP 8200 autosampler (Varian Inc., Walnut Creek, CA, USA). Quantification of the selected pesticides was performed using matrix-matched calibration. The estimated values of the limits of detection (LODs) were in the range 0.4–5.5 ng/L. Pesticide residues in soil and plant extracts were also determined by GC-MS, paprika samples were prepared by a modified QuEChERS extraction method.

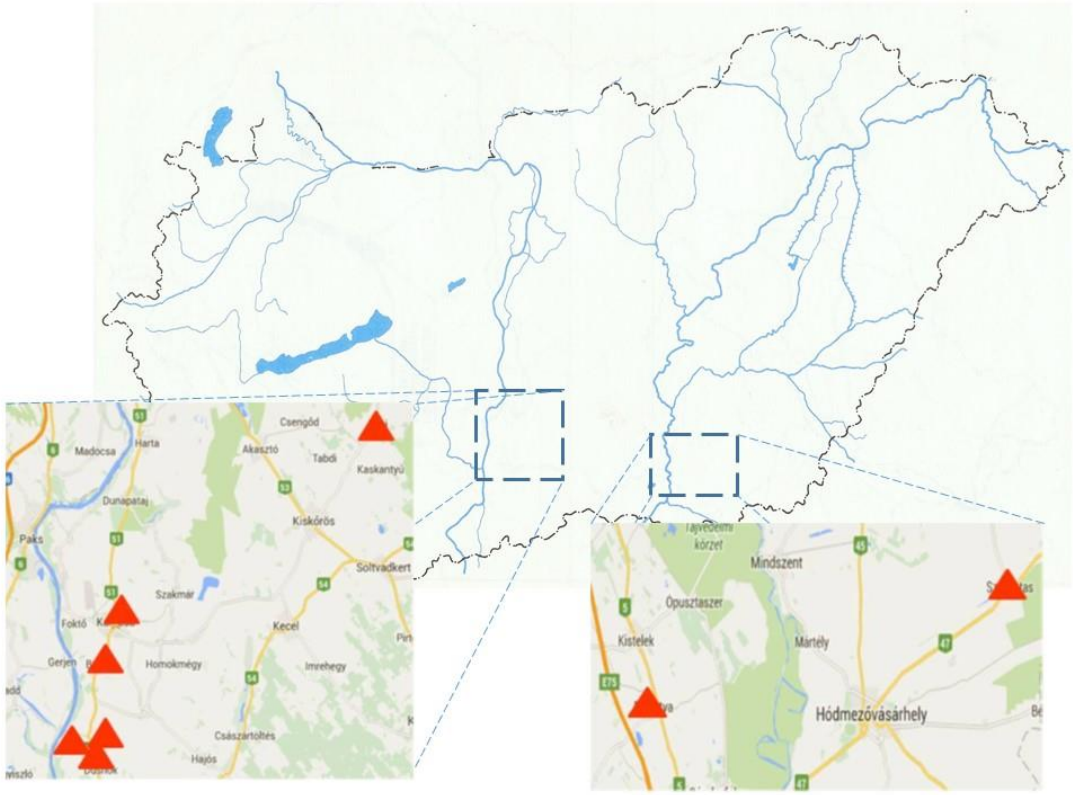

Figure 1. Sampling sites at intensive (6) and ecological (2) cultivation fields

Results and discussion

In soils from intensive cultivation fields as sampling sites pesticide active ingredients trifluralin, tefluthrin, chlorpyrifos and DDT together with their decomposition products (DDE and DDD) have been identified, whereas in some cases traces of diazinon and atrazine, and in a single case metolachlor have been detected, but not quantified. Trifluralin has been measured in soil samples collected at five sites. Although not always occurring, most of the samples contained this pollutant. Contamination levels detected in soils in the Summer and Autumn sampling regimes are listed in Table 1, the chemical structures of the contaminating pesticide active ingredients

detected are depicted in Figure 2.

Table 1. Concentration of pesticides (µg/g soil) found in soil samples collected in June (upper row, normal font) and September (bottom row, *Italics font*) from intensively cultivated fields.

Sampling site	Pesticide/metabolite/residue					
	trifluralin	tefluthrin	chlorpyrifos	DDT	DDE	DDD
1	0.021-0.072	–	–	–	–	–
	0.002-0.049	–	–	–	–	–
2	0.027-3.201	0.106-0.277	–	–	–	–
	0.038-0.358	*0.037-0.195*	–	–	–	–
3	0.013-0.029	–	–	–	–	–
	–	–	–	–	–	–
4		–	0.595-16.610	–	–	–
		–	–	–	–	–
5	–	0.071-0.441	–	0.040-0.865	0.030-0.051	0.044-0.572
	0.011-0.019	*0.027-0.306*	–	*0.057-0.756*	*0.007-0.040*	*0.007-0.031*
6	0.024-0.057	0.188-0.864	–	1.353-4.805	0.046-0.471	1.141-8.351
	–	*0.007-0.154*	–	*0.488-5.699*	*0.028-0.449*	*0.208-1.594*

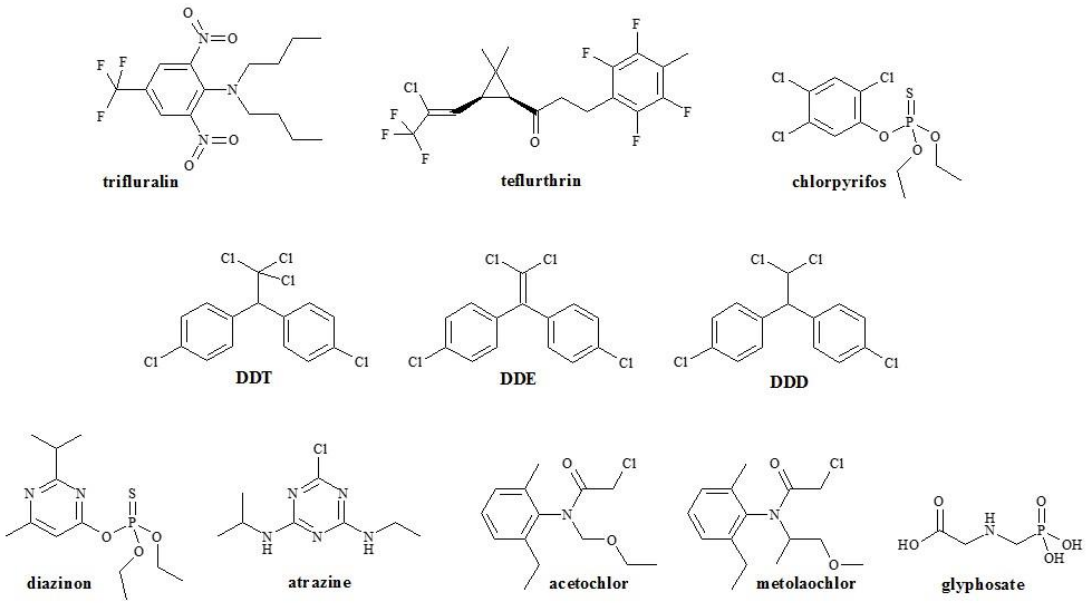

Figure 2. Soil contaminants identified in intensive cultivation fields of spice paprika or of concern in surface water in Hungary

The most common surface water contaminant has been the herbicide active ingredient trifluralin,detected in 50% of the water samples tested at levels of 11-34 ng/L.Although the long banned chlorinated hydrocarbon insecticide active ingredient DDT and its metabolite (DDE) ordegradation product (DDD) appeared at high levels in soilsamples collected at two sites, due to

their low water solubilitythey have not occurred in surface water nearby and or inpaprika harvested from these intensively cultivated fields. Therefore, common reported pesticide contaminants in surface water (e.g. atrazine or acetochlor) [6, 7] have not been detected in the surface water samples collected from paprika cultivation fields, yet currently emerging pollutants, e.g. glyphosate or neonicotinoids [8] (not analyzed in the current study) are expected to become more frequent.

No pesticide residues were detected in paprika extracts, even when plants were grown in polluted soil. This is partially explained by the fact that matrix effects are more substantial in biological (paprika) than in soil samples, but also indicate low absorption/penetration of pesticide active ingredient into paprika fruit, an obvious advantage in food safety. It has to be noted, however, that in contrast to the cultivation field study, pesticide residues occurred in the harvested paprika fruits in a highly intensive cultivation model experiment. Result of this model indicated that the higher the amounts of applied pesticides were, the higher residue levels in soil and in paprika fruits were measured.

Conclusion

The current study allowed, proportionally to its limited scope, a comparative evaluation of spice paprika cultivation under intensive and ecological agronomical conditions in Hungary. Pesticide residues in intensive cultivation fields (ICFs)indicated four major (trifluralin, tefluthrin, chlorpyrifos and DDT) and several minor (diazinon, atrazine, metolachlor, as well as DDT decomposition products DDE and DDD) as soil contaminants, and trifluralin as surface water contaminant. This indicates that mostly past treatments with pesticide active ingredients with more or less persistent characteristics pose hazard of contamination with pesticide residues in environmental matrices. Nonetheless, pesticide residues were not identified (above their limits of detection) in paprika fruit, even if grown under ICF conditions on soil containing pesticideresidues.

Acknowledgements

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References

[1] I. Reinholds, I. Pugajeva, V. Bartkevics, Food Control 60 (2016) 683-689.
[2] Sz. Klátyik, B. Darvas, M. Mörtl, M. Ottucsák, E. Takács, H. Bánáti, L. Simon, G. Gyurcsó, A. Székács, Intl. J. Biol. Biomol. Agric. Food Biotech. Engineer., 10 (3)(2016) 156-159.
[3] L. Eliasson, S. Isaksson, M. Lövenklev, L. Ahrné, Front. Microbiol., 6 (2015)1071.
[4] É. Kónya, E. Szabó, I. Bata-Vidács, T. Deák, M. Ottucsák, N. Adányi, A. Székács, Intl. J. Biol. Biomol. Agric. Food Biotech. Engineer., 10 (3)(2016) 160-166.
[5] European Commission, "The Rapid Alert System for Food and Feed. Annual Reports," 2005-2015, Brussels, Belgium: European Commission, Health and Food Safety Directorate General. *http://ec.europa.eu/food/safety/rasff*
[6] E. Majzik-Solymos, É. Visi, G. Károly, B. Beke-Berczi, L. Győrfi, J. Chromatogr. Sci. 39 (8) (2001) 325-331.
[7] E.Maloschik, A. Ernst, G. Hegedűs, B. Darvas, A. Székács, Microchem. J. 85 (1) (2007) 88-97.

[8] A. Székács, M. Mörtl, B. Darvas, J. Chem. 2015, Article ID 717948, 15 pages
[9] E. Maloschik, M. Mörtl, A. Székács, Anal. Bioanal. Chem. 397 (2) (2010) 537-548.
[10] SPICED Consortium, "Securing the spices and herbs commodity chain," EU-FP7-SEC-2012-1-312631, 2013 *http://www.spiced.eu*