

REVIEW

Pesticide residues in spice paprika and their effects on environmental and food safety

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Summary

Environmental and food safety of spices used for flavouring in food production, or for culinary purposes in catering and at households, receive relatively low attention, particularly in low volume spice trade networks, even though potential spice contaminants may exert adverse effects on food safety and quality. Contamination surveys of spices generally focus on microbial impurities or mycotoxins. Yet, pesticide residues are also prevalent chemical contaminants in spices of the *Capsicum* species, including chilli and spice paprika. To avoid human exposure to pesticide residues through food, maximum residue levels (*MRLs*) have been established for each authorized pesticide active ingredient in given commodities, yet high variability is seen in *MRLs* even among *Capsicum* products. The official notification network of the European Union on food and feed contamination, Rapid Alert System for Food and Feed (RASFF), systematically reports on cases of non-compliance of food products with the corresponding food safety requirements since 1998. To assess environmental and food safety and to maintain the quality of the “Hungaricum” spice paprika products, the levels of pesticide residues as contaminants in spice paprika and chilli are discussed on the basis of RASFF alerts and notifications, and on the basis of other contamination cases reported in the scientific literature.

Keywords

spice paprika; *Capsicum*; pesticide residues; Rapid Alert System for Food and Feed; maximum residue level

Several physical, chemical or biological agents have potential adverse effects on food and environmental safety. These agents may emerge at any stage of the food supply production chain in consequence of accidental, natural or intentional contamination. Therefore, in the absence of control, these factors potentially induce illnesses and injuries. To protect consumers, food safety policies of the European Union (EU) ensure a high level of food safety, animal welfare, animal health and plant health. In the interest of the promotion of appropriate food safety in EU, an integrated concept “from farm to fork” is applied, with science-based risk assessment to ensure efficient risk management. Competent control systems are applied to warrant compliance with quality standards and food safety requirements, as well as a suitable monitoring system of this compliance at place with alerting mechanisms as regards to non-compliance

incidents to support the proper operation of the internal food markets. As a surveying and reporting mechanism, Rapid Alert System for Food and Feed (RASFF), established in 1979 and having been revised several times later [1–3], is the most important vehicle of this EU food safety approach.

Current intensive agriculture relies on various agrochemicals that are hazardous substances per se. Their residues may appear in agricultural products due to illegal application of pesticides (e.g. application of not registered pesticides in the given crops), incorrect use of agrochemicals to given crops (e.g. application of pesticides at dosages above the level authorized for the given crop) or improper conditions of harvesting and storage (e.g. application of pesticides during storage, insufficient withdrawal period applied between the date of the last pesticide treatment and harvesting). Crop commodities used as

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raw materials for food production are evidently deemed as sources of pesticide residues in the food products.

In addition to crop commodities, various natural compounds of plant origin, herbs and spices applied as condiments also reach food products, along with their potential contaminants. International Standardization Organization (ISO) determines spices used in broken, ground or whole forms like “vegetable products or mixtures thereof, free from extraneous matter, used for flavouring, seasoning, and imparting aroma in foods”, while herbs are defined as the dried or fresh leafy parts of non-arboreal perennial or annual plants [3, 4]. Even though processed food products contain low quantities of condiments, contaminants present in spices may increase the detected level of food contamination. The majority of processed foods, including ready-to-eat products, contain herbs and spices. Furthermore, consumers apply condiments for flavouring or colouring often after cooking, processing or any other form of heat treatment. As ecological (organic) farming has improved continuously since the early 1990s, the demand for spices and herbs produced by organic farming is increasing in EU in the intention of the consumers to avoid pesticide residue-type contaminants, and a full range of organic spices and herbs is available at both regional levels and at the level of supermarket chains, although the quantities consumed vary by products and regions [5]. Contaminants in condiments may occur as dynamic contamination, i.e. capable to multiply (e.g. microbial contamination, especially with food-borne pathogenic microorganisms) [6] or as static contamination by various chemical compounds (e.g. mycotoxins, pesticide residues) [7, 8]. Dynamic contamination is determined by classical microbiological and molecular biological methods, while static contaminants are monitored mostly by instrumental analysis facilitated by chemometrics [9] for qualitative and quantitative determination of contaminant levels and for authentication of spices and herbs.

Spice paprika and chillies of genus *Capsicum* have been used in dried or ground form as culinary condiments or supplements since about 7500 BCE [10], and since they reached Europe in the fifteenth century [11], they have been cultivated in various types and varieties, as sweet, hot, mild and fiery species, with fruits of various shapes (e.g. bell, oval, cone), colours (e.g. yellow, green, shades of red), orientation (standing or hanging) or of various bioactive component content. *Capsicum* species are classified into three main types, *C. annuum*, *C. frutescens* and *C. pubescens*, on the basis of taxonomic and genetic

characteristics. The varieties are typically of high pigment content ranging from 1000 mg·kg⁻¹ to 8000 mg·kg⁻¹ [11], and the colour of paprika is used as a facile quality descriptor, expressed by the extractable colour level by ASTA (American Spice Trade Association) [12]. Moreover, *Capsicum* species can be classified on the basis of the content of capsaicin, varying from 0 mg·kg⁻¹ to as high as 18600 mg·kg⁻¹, being responsible for the pungency of spice paprika [11].

The trade of herbs and spices by EU represents a substantial, if not the greatest, proportion of the world market. As for per capita consumption of condiments in EU, Germany, United Kingdom, Romania and Hungary are the leading consumers, representing 19%, 16%, 14% and 12% of the total consumption, respectively [13], with pimento, pepper and paprika being the most consumed condiments. Import to EU of spice paprika is the second largest segment among the imported spices and herbs, the main importers being Germany and Spain, responsible for 24% and 20% of the total spice paprika import, respectively. Spice paprika, produced mostly in Hungary and Romania, represents 62% of paprika condiment production in EU. Consequently, the aspects of food safety of spice paprika are essential for the producer member states to maintain their business position, as well as for all consumers in EU to be able to rely on a guaranteed food safety status maintained. This paper surveys pesticide active ingredients and formulated pesticides that can be used in paprika cultures on the basis of current EU regulations (regulating active ingredients) and on the basis of recent Hungarian authorization measures (regulating formulated plant protection products), similar to the regulations of other member states in EU. Residue levels reported in spice paprika by RASFF since 1998 are also reviewed.

Pesticide authorization in the European Union

Plant protection products (PPPs) are governed in EU by Regulation (EC) 1107/2009 [14]. A rather important characteristic of the pesticide registration policy is that pesticide active ingredients are authorized at EU level, while formulated PPPs and their use on given crop commodities are registered at member state level.

The active ingredients must be approved for use by the European Commission (EC) to be considered for being marketed in any form of pesticide formulation. In the process of authorization, these substances are evaluated in scientific evidence-based risk assessment by the European Food Safety Authority (EFSA), and debated or commented by the member states. Risk assess-

ment evaluation statements issued by EFSA are the basis of subsequent EC decisions regarding authorization. Active ingredients classified as carcinogenic, mutagenic, teratogenic, endocrine disruptor, persistent or bioaccumulative substances cannot be approved [15]. Pesticide active ingredients regularly undergo detailed re-assessment. During the last major re-registration process finished in 2010, the number of registered active ingredients was substantially reduced from 959 to approximately 480 compounds, which are authorized now as pesticide active ingredients or PPPs [16, 17].

In contrast to pesticide active substances, formulated PPPs are authorized by the member states on their territory, in accordance with the corresponding EU rules and regulations. The enabled use of the pesticide formulations in various crop cultures is also determined at member state level.

To avoid over-excessive human exposure to pesticide residues through foodstuffs and the drinking water, maximum residue levels (*MRLs*) have been established for these compounds in different commodities throughout the world, including EU, and the levels of pesticide residues are required to be regularly monitored. *MRL* values are fixed by EC for all food and animal feed on the basis of a complete risk assessment by EFSA [18]. If the levels of residues in case of approved pesticides exceed the determined *MRLs* in the food and animal feed products, measures have to be taken to prevent the use of the contaminated products or crops. In contrast, unpermitted pesticide active ingredients or their metabolites cannot be present in the food or animal feed at any content. These contaminants generally originate from inappropriate technology or earlier environmental contamination [2]. The official *MRLs* of pesticide residues are specified in Codex Alimentarius [19] and other declarations [18, 20] for various commodities.

Pesticides authorized in the European Union for spice paprika cultivation

Currently, 51 pesticide active ingredients are registered in EU for paprika cultivation (Tab. 1). Of these, 22, 15, 7, 7 and 1 are registered as insecticides, fungicides, herbicides, soil disinfectants and seed treatment compounds, respectively. These registered pesticides are dominated by insecticides, explained by the pest composition of the commodity and by the trends of the agrochemicals market [21]. Eco-friendly pest controlling and maintainable production of chilli can be implemented by the use of natural substances (e.g. abamectin), botanical insecticides (e.g. extract of garlic, neem cake), their incorporation with syn-

thetic insecticides (e.g. diafenthiuron pro-insecticide), and the extract of earthworm excretory substances (e.g. Vermiwash) [22, 23]. In chilli commodities, spray application of jasmonic acid has also been advocated as an effective alternative to pesticide treatments, being found to be most efficient at 1.05 mg·ml⁻¹ concentration [24].

As seen, the control of insect pests is an essential part of chemical crop protection technologies in paprika cultivation. Systemic or contact insecticide formulation can be used to control pest in the crop cultivation [25] and numerous formulated insecticide preparations containing the currently registered active ingredients are commercially available for this purpose. The use of the most hazardous insecticide compounds such as organophosphates or chlorinated hydrocarbons has been reduced or banned in recent years [21], and pyrethroids and neonicotinoids remain predominantly in use. Concerns regarding neonicotinoids, as compounds with both lipophilic character and good water solubility, have been raised due to their ability to well dissolve in both lipids and water. Resulting from their systemic characteristics, neonicotinoids are uptaken by plant transport tissues, which potentially leads to contamination by their residues in crops and agricultural products, as well as in foods with high fat content [26, 27]. Uptake and excretion by the plant transport system have been brought to correlation with their significant bee toxicity. In consequence, the use of several neonicotinoid compounds (imidacloprid, thiamethoxam and clothianidin) has been banned in flowering crops by EC for two years [28], and the ban is still in effect as re-assessment of these active ingredients has not yet been finished.

Fungal diseases can cause yield losses in paprika cultivation, similarly as in other crops, therefore the use of contact, translaminar and systemic fungicide formulations is necessary [29]. In paprika cultivation, the most important fungicide substances are the systemic triazoles (e.g. penconazole), strobilurin derivatives (e.g. azoxystrobin) as well as the contact fungicides of dithiocarbamate group [21]. Of particular food safety concern, also for paprika cultivation, are the facts that fungicide residues can be found in food products and animal feeds not only due to pre-harvest, but also due to post-harvest applications [30]. Moreover, several studies confirmed the mutagenic effects of certain fungicidal compounds (e.g. mancozeb, captan, folpet) [31, 32].

Several herbicide active ingredients are registered for weed control in paprika. The most important herbicide substances used in paprika cultures are napropamide, pendimethalin, cloma-

Tab. 1. Pesticide active ingredients registered for paprika cultivation (in 2015) in the European Union and in Hungary.

Active ingredient	Chemical class	Year of registration	Authorized for glasshouse	Authorized for field	MRL (EU) [mg·kg ⁻¹]			MRL (WHO/FAO) [mg·kg ⁻¹]			
					Sweet/bell pepper	Fruit spice	Sweet pepper	Peppers chilli	Peppers chilli (dried)	Spice (fruits and berries)	
Insecticide/acaricide											
<i>B. thuringiensis</i>	Cry toxin	1938	valid	valid	-	-	-	-	-	-	-
Pirimicarb	Carbamate	1970	-	valid	0.5	0.05	-	-	-	20	-
Cypermethrin	Pyrethroid	1975	valid	valid	0.5	-	0.1	2	10	3	0.5
Lambda-cyhalothrin	Pyrethroid	1985	-	valid	0.1	-	-	-	-	-	0.03
Esfenvalerate	Pyrethroid	1986	-	valid	0.05	0.1	-	-	-	-	-
Abamectin	Avermectin	1985	valid	-	0.07	0.05	0.09	0.005	0.5	-	-
Emamectin-benzoate	Avermectin	1997	-	valid	0.02	0.02	-	-	0.2	-	-
Lufenuron	Benzoylphenylurea	1990	valid	-	1	0.02	0.8	-	-	-	-
Pyridaben	Pyridazine	1990	2015	2015	0.5	0.05	-	-	-	-	-
Imidacloprid	Neonicotinoid	1991	valid	-	1	0.05	-	-	10	-	-
Thiamethoxam	Neonicotinoid	1991	valid	-	0.7	0.05	-	-	7	-	-
Thiacloprid	Neonicotinoid	1999	valid	-	1	0.05	1	-	-	-	-
Acetamiprid	Neonicotinoid	1995	valid	-	0.3	-	-	-	2	-	-
Pymetrozine	Pyridylmethyleneamino-triazinone	1993	valid	valid	3	0.1	-	-	-	-	-
Tebufenpyrad	Pyrazole	1993	-	valid	0.5	0.1	-	-	-	-	-
Pyriproxyfen	Juvenile hormone mimic	1995	valid	-	1	0.05	-	-	-	-	-
Methoxyfenozide	Diacylhydrazine	1996	valid	-	2	0.05	-	-	20	-	-
Spinosad	Spinosyn	1997	valid	valid	2	0.1	-	-	3	-	-
Bifentazate	Biphenylcarbazate	2000	valid	-	3	0.1	2	3	-	-	-
Indoxacarb	Oxadizine	2000	valid	valid	0.3	0.05	-	-	-	-	-
Flonicamid	Nicotinamide	2005	valid	valid	0.3	0.1	-	-	-	-	-
Chlorantraniliprole	Diamine	2006	valid	-	1	0.02	-	-	5	-	-
Fungicide											
Sulphur	Inorganic	historic use	-	valid	-	-	-	-	-	-	-
Copper hydroxide	Inorganic	1968	valid	valid	-	-	-	-	-	-	-
Copper oxychloride	Inorganic	early 1900s	valid	valid	5	40	-	-	-	-	-
Copper sulphate	Inorganic	historic use	-	valid	-	-	-	-	-	-	-
Captan	Perchloromethylmercap to derivative	1949	-	valid	0.03	0.1	-	-	-	-	-
Mancozeb	Dithiocarbamate	1961	-	valid	5	-	1	-	20	-	-
Iprodione	Dicarboximide	1974	-	valid	7	0.05	-	-	-	-	-

Tab. 1. continued

Active ingredient	Chemical class	Year of registration	Authorized for glasshouse	Authorized for field	MRL (EU) [mg·kg ⁻¹]		MRL (WHO/FAO) [mg·kg ⁻¹]				
					Sweet/bell pepper	Fruit spice	Sweet pepper	Peppers chilli	Peppers chilli (dried)	Spice (fruits and berries)	
Metolaxyl	Acylalanine	1979	NA	NA	0.5	0.1	-	-	10	-	
Penconazole	Triazole	1983	valid	-	0.2	0.1	-	-	-	-	
Myclobutanil	Triazole	1986	valid	valid	0.5	0.05	-	-	20	-	
Tebuconazole	Triazole	1988	NA	NA	0.6	-	1	-	10	-	
Difenoconazole	Triazole	1989	valid	-	0.8	0.3	-	-	5	-	
Azoxystrobin	Strobilurin derivate	1996	valid	-	3	0.3	-	-	30	-	
Iprovalicarb	Valinamide carbamate	1999	NA	NA	0.01	0.05	-	-	-	-	
Fenpyrazamine	Pyrazole	2012	valid	-	3	0.01	-	-	-	-	
Herbicide											
Napropamide	α -Naphthylxypropionamide	1969	-	valid	0.1	0.05	-	-	-	-	
Pendimethalin	Dinitroaniline	1974	-	valid	0.05	0.05	-	-	-	-	
Clomazone	Isoxazolidinone	1980	-	valid	0.01	0.05	-	-	-	-	
Fluazifop-P	Aryloxyphenoxypropionate	1983	-	valid	0.01	0.03	-	-	-	-	
Propaquizafop	Aryloxyphenoxypropionate	1987	-	valid	0.05	0.05	-	-	-	-	
Quizalofop-P-terfuryl	Aryloxyphenoxypropionate	1989	-	valid	0.4	0.05	-	-	-	-	
Clethodim	Cyclohexanedione	1987	-	valid	0.5	0.1	-	-	-	-	
Soil disinfectant											
Dazomet	Dithiocarbamate	1897	-	valid	0.1	0.02	1	-	20	-	
Chlorpyrifos	Organophosphate	1965	-	2015	0.01	1	2	-	20	1	
Fosetyl	Organophosphate	1977	valid	-	130	400	-	-	-	-	
Fosthiazate	Organophosphate	1992	valid	-	0.02	0.05	-	-	-	-	
Oxamyl	Carbamate	1974	valid	-	0.01	0.05	2	-	-	0.07	
Propamocarb	Carbamate	1978	-	valid	3	0.05	3	-	10	-	
Tefluthrin	Pyrethroid	1986	-	valid	0.05	0.05	-	-	-	-	
Seed treatment											
Thiram	Dithiocarbamate	1942	-	valid	0.1	0.2	1	-	20	-	

Pesticide active ingredients are authorized by the European Union (EU), formulated pesticide preparations for paprika are registered by the given member state (Hungary). Year of registration is given according to the Pesticide Manual [21]. Authorization is given according to registration status in the given member state (Hungary).

MRL (EU) – maximum residue levels defined by the EU authorities are listed according to the database of European Commission [20]. MRL (WHO/FAO) – maximum residue levels defined by the World Health Organization (WHO) and the Food and Agriculture Organization of the United Nations (FAO) are listed according to the Codex Alimentarius [19].

NA – not applied (the active ingredient is authorized by EU, but not registered in the given member state (Hungary)).

zone and clethodim [21]. These compounds can be classified on the basis of mode of action, selectivity, the method and the timing of application. According to the timing of the treatments, herbicides can be applied to soil before planting and in pre-emergent or post-emergent mode. Being phytotoxic to *Capsicum* species (as to other plants), glyphosate cannot be applied at post-emergence timing on paprika [33]. Due to its root colonization by soil fungi [34], the phytotoxic effect was readily followed by monitoring the shikimic acid level as a bioindicator in mycorrhized *C. annuum* L. [35]. However, glyphosate is commonly applied at pre-emergence timing for weed control in *C. annuum* [36–38]. Moreover, it was evidenced that glyphosate can be transferred to paprika plants through the rhizosphere [39]. Through its effect on mycorrhizal fungi, glyphosate also affects earthworms and the soil ecosystem [40].

The EU Rapid Alert System for Food and Feed

The national food safety authorities of the member states of EU systematically monitor agricultural produce and food commodities for compliance with the current official *MRLs* for pesticide residues. To facilitate information exchange among member states and the public, the Rapid Alert System for Food and Feed (RASFF) of EU was established in 1979 [41]. RASFF has proven to be a prominent device to report non-compliances in agricultural commodities and food products with food safety regulations, to ensure a direct and real-time exchange of information among countries in EU, and to assist sustenance of an outstanding food safety status.

Definition of pesticide residues

It is essential to underline that the vocational and legal definition specifies pesticide residues as “one or more substances present in or on plants or products of plant origin, edible animal products or elsewhere in the environment and resulting from the use of a plant protection product, including their metabolites and products resulting from their degradation or reaction” [42]. Residues of each pesticide are listed in RASFF, unless specified otherwise, are combined as content values of the active ingredient and all metabolites. In listed cases, certain metabolites may be reported separately, as often seen e.g. for 2-chloro-ethanol as a soil disinfectant metabolite (Tab. 2), or for aminomethylphosphonic acid (AMPA), a common metabolite of the herbicide active ingredient glyphosate. This results in two main consequences: (1) Residue levels listed for a given active ingredient in RASFF cannot be considered as

actual residual contents of the given active ingredient, but are, *per definitionem*, the combined contents of the given active ingredient and all its metabolites detected in the given sample; (2) The toxicological assessment of the actual residue levels seen in RASFF requires careful evaluation, as metabolites and degradation products of pesticide may occasionally be more hazardous than the pesticide active ingredient itself. Examples include ethylenethiourea (ETU) as a metabolite of alkylene-bis-dithiocarbamates, metamidophos as a metabolite of acephate, or the *N*-decarboxymethylated metabolite of indoxacarb [43–45].

Analytical methods for monitoring pesticide residues in spice paprika

Determination of pesticides in complex matrices, such as paprika, involves sample treatment by various extraction techniques, often including additional clean-up steps. An efficient sample pre-treatment eliminates interfering matrix components (pigments, lipids) that improves limit of detection (*LOD*) and minimizes matrix effects by pesticide/matrix combinations. Steps involved in sample preparation depend on the selectivity of the detection method, and the procedure has to be compatible with the analytical method. Traditional extraction methods (e.g. Soxhlet extraction) are being gradually replaced by faster and more effective techniques, including supercritical fluid extraction (SFE), microwave-assisted extraction (MAE), accelerated solvent extraction (ASE), often performed automatically and coupled to the analytical instrument [46], or solid-phase extraction (SPE) using cartridges or dispersive phases as the most commonly applied method for clean-up purposes. In addition, immunoaffinity clean-up also allows selective removal and elution of a limited range of target compounds. In turn, application of multiple-analyte affinity columns is restricted mainly to preliminary clean-up prior to immunoanalytical (ELISA) determination and/or prior to determination of mycotoxins. Currently, the QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe) sample preparation method is the most widely used procedure for determination of pesticide residues in food matrices [47], validated for hundreds of pesticides in different food commodities and applied also to complex and highly pigmented spice matrices (red chilli, black and white pepper) [48]. This simple flexible method, easily adjustable to various targets and matrices, originally consisted of an initial extraction step with acetonitrile followed by partitioning after the addition of salts (anhydrous magnesium sulphate and sodium chloride) and, thereafter,

Tab. 2. Pesticide active ingredients and a metabolite reported in the European Union (EU) Rapid Alert System for Food and Feed (RASFF) in spice paprika since 1998.

Active ingredient	Chemical class	Year of ban in EU or in Hungary	Pesticide residues reported by EU RASFF in spice paprika				
			Year	Reporting country	Country of origin	Commodity	Residue level [mg·kg ⁻¹]
Insecticide/acaricide							
Dicofol	Chlorinated hydrocarbon	NU	2010	UK	Dominica	chilli	4.2
			2010	FR	Dominica	chilli, fresh	0.98
Endosulfan	Chlorinated hydrocarbon	2007	1999	FI	ES	paprika, sweet	NR
			2011	FR	Dominica	paprika, fresh	0.1
Acephate	Organophosphate	2006	1999	FI	ES	paprika, sweet	NR
			2008	BE	India	chilli	0.26
Chlorpyrifos	Organophosphate	–	2001	EL	India	chilli, ground	0.41
			2002	NL	Thailand	paprika	1.0
			2004	ES	India	chilli, ground	0.14
			2011	IT	Thailand	chilli, fresh	1.2
Dimethoate	Organophosphate	–	2009	BE	Uganda	chilli	0.05
			2013	UK	Egypt	chilli	0.08
Ethion	Organophosphate	NU	2000	IT	India	chilli	NR
			2001	DE		chilli, ground	NR
			2001	DE		chilli, ground	4.06
			2001	IT		chilli	0.82
			2001	IT		chilli	2.38, 4.06
			2001	UK		chilli, ground	11.8, 12.6
			2001	DE	UK	chilli, ground	3.83, 5.37
			2001	EL	India	chilli, ground	2.01, 2.34
			2003	ES	India	paprika, ground	0.77
			2008	BE	India	chilli	2.0
			2010	DE	UK	chilli, ground	0.02
			2011	IT	Egypt	paprika, hot, fresh	0.27
			2013	FI	Thailand	chilli, dry	0.57
			2013	IT	India	chilli, fresh	0.19
Formothion	Organophosphate	1998	2011	DE	Dominica	chilli, fresh	0.22
Methamidophos	Organophosphate	2008	1999	FI	ES	paprika, sweet	NR
			1999	FI	ES	paprika, sweet	NR
			2000	FI	ES	paprika, sweet	NR
			2002	NL	Thailand	paprika	0.36
			2002	NL	Thailand	paprika	0.44
			2002	FI	Thailand	chilli	0.93
			2010	DE	UK	chilli, ground	0.09
2015	CR	Laos	chilli	0.03			
Omethoate	Organophosphate	NU	2009	BE	Uganda	chilli	0.04
			2013	UK	Egypt	chilli	0.12
Phosalone	Organophosphate	2009	2003	ES	India	paprika, ground	1.33
Profenofos	Organophosphate	NU	2002	NL	Thailand	paprika	1.2
			2002	NL	Thailand	paprika	0.23
			2011	IT	Thailand	chilli, fresh	0.51, 0.93
Prothiophos	Organophosphate	NU	2002	NL	Thailand	paprika	0.21
			2002	NL	Thailand	paprika	0.24
Triazophos	Organophosphate	2004	2001	EL	India	chilli, ground	0.23, 0.27
			2004	HU	Brazil	paprika, ground	0.52, 0.76

Tab. 2. continued

Active ingredient	Chemical class	Year of ban in EU or in Hungary	Pesticide residues reported by EU RASFF in spice paprika				
			Year	Reporting country	Country of origin	Commodity	Residue level [mg·kg ⁻¹]
Triazophos	Organophosphate	2004	2004	HU	Brazil	paprika, ground	0.14
			2010	DE	UK	chilli, ground	0.03
			2009	SE	Thailand	chilli, fresh	0.7
			2012	FI	Thailand	chilli, dry	0.93
			2013	FI	Thailand	chilli, dry	1.4
			2015	BE	Gambia	chilli	1.1
Carbofuran	N-Methylcarbamate	2009	2008	NL	Thailand	chilli	1.2
			2008	BE	Thailand	chilli	0.17
Formetanate	N-Methylcarbamate	NU	2009	FI	Thailand	chilli	6.8
			2012	BG	Turkey	paprika, fresh	0.18
Methomyl	N-Methylcarbamate	–	2007	IT	Morocco	paprika, hot	1.16
			2008	DE	Kenya	chilli fresh	1.0
Cypermethrin	Pyethroid	–	1999	DE	Pakistan	chilli	NR
			2001	EL	India	chilli, ground	1.13, 3.36
			2001	ES	India	chilli	NR
			2003	ES	India	paprika, ground	1.62
			2004	ES	India	chilli, ground	0.51
			2001	DE	India	chilli, ground	6.92
Permethrin	Pyethroid	2007	2011	FR	Dominica	paprika, fresh	0.14
			2011	ES	Dominica	chilli	0.55
			2012	DE	Dominica	chilli	0.47
Fipronil	Phenyl-pyrazole	2013	2015	FR	Dominica	chilli	0.01
Amitraz	Formamidine	2007	2011	FI	Malaysia	chilli, fresh	1.1
Acetamiprid	Neonicotinoid	–	2005	DE	EL	paprika	0.12
			2015	FR	Dominica	chilli, fresh	0.81
Clothianidine	Neonicotinoid		2015	FR	Dominica	chilli	0.22
Fungicide							
Carbendazim	Benzimidazole	2009	2008	BE	India	chilli	1.54
			2011	DE	Dominica	chilli, fresh	0.14
			2015	BE	Dominica	chilli, fresh	0.15
Thiophanate-methyl	Thioallophanate	–	2011	DE	Dominica	chilli, fresh	0.34
			2015	BE	Dominica	chilli, fresh	0.53
Metalaxyl	Phenylamide	2004	2002	NL	Thailand	paprika	0.19
Hexaconazole	Triazole	2009	2008	BE	India	chilli	0.24
Triadimenol	Triazole	2009	2000	IT	Zimbabwe	paprika	NR
			2001	NL	Israel	chilli	0.29
Herbicide							
–	–	–	Residues not found				
Soil disinfectant							
Chlorpyrifos	Organophosphate	–	See among insecticides				
2-Chloro-ethanol	Metabolite	–	2003	DE	DE	paprika, hot	3.64
			2003	DE	ES	chilli, ground	0.17

Registration status is indicated according to legal regulations of Hungary before 2004 or of the European Union (EU) after Hungary joined EU on 1 May 2004. Data reported are statistically not uniform. Chlorpyrifos was still in use in 2015. 2-Chloro-ethanol is a metabolite of ethylene dichloride.

EU country codes: BE – Belgium, BG – Bulgaria, CZ – Czech Republic, DE – Germany, EL – Greece, ES – Spain, FI – Finland, FR – France, HU – Hungary, IT – Italy, NL – The Netherlands, SE – Sweden, UK – United Kingdom.

NU – not in use in Hungary at any time, NR – not reported (detected above limit of detection, but exact content not determined).

subjecting the extract to dispersive SPE (dSPE) [49]. Because low recoveries were recorded for pH-sensitive pesticides (e.g. pymetrozine, imazalil, thiabendazole), acetate [50] or citrate [51], buffering was included. Addition of graphitized carbon black (GCB) dispersive phase to highly pigmented extracts and C18 silica dispersive phase to fatty matrices reduced matrix interferences. Freezing-out was investigated for removal of fatty components [52] and dry ice-partitioning instead of salting out was also developed [53] to improve the recovery of some highly polar pesticides in paprika. Dry ice separates the extract into aqueous and organic solvent (acetonitrile) layers without the need for salting-out and centrifugation, allowing the analysis of the aqueous layer as well. Worthy of note is that the above modifications did not always provide observable benefits [54]. The addition of water to dry food samples is necessary to promote extraction of pesticides in the ground form of spices (e.g. paprika) [52]. As paprika extracts are characterized by complex matrix components, the clean-up step is strongly advisable, yet dSPE is not capable to eliminate strong matrix effects as it only partially removes matrix components. Multi-residue methods for pesticide determination traditionally involved gas chromatography (GC) coupled to mass spectrometry (MS), due to the excellent resolution of capillary GC and the confirmation power of GC-MS based on electron ionization (EI) full scan mass spectra, although selective detectors, such as electron capture detector (ECD), flame photometric detector (FPD) or nitrogen-phosphorus detector (NPD) are also being used in special cases. To improve MS selectivity and sensitivity, tandem MS (MS/MS) is used, as it more effectively removes matrix interferences than single quadrupole MS analysis working in selected ion monitoring (SIM) mode. Very low LODs and simultaneous quantification and confirmation can be achieved due to the high selectivity of triple quadrupole (QqQ) analysers in selected reaction monitoring (SRM) mode. After adequate selection of target precursor and product ions, acquisition of two SRM transitions and evaluation of their quantifier/qualifier ratio confirms the compound detected in the sample [46]. Detection of unknown compounds requires implementation of full-scan technology into routine analysis of pesticide residues in food, in parallel with MS/MS determination of target compounds, allowing detection of broad range of contaminants.

Nowadays, liquid chromatographic (LC) separation is preferred to GC in routine analysis of pesticide residues, because it allows determination of more polar, less volatile and thermally la-

bile pesticides. LC coupled to MS/MS (HPLC-MS/MS) ensures high selectivity and sensitivity even in complex matrices. Although resolution is often lower compared to GC, determination of many GC-amenable pesticides in food samples is possible, and removal of water content from the sample is not necessary. Thus, identification and quantification even at trace levels of hundreds of pesticides are routinely achieved. Thus, LC-MS/MS is routinely employed for identification and quantification, even at trace levels, of hundreds of pesticides. As only previously tuned target pesticides can be detected, careful setting-up the MS/MS method is crucial. Furthermore, the time-shift in LC due to column ageing induces a risk of false negatives.

High-resolution detectors (GC-HRMS or LC-HRMS systems) are also employed for multi-residue pesticide analysis, providing high selectivity in difficult matrices. Application of time of flight (ToF) MS is a powerful tool for qualitative analysis of unknown compounds, enabling high speed data acquisition with high resolution and high mass determination accuracy. A further benefit is that retrospective analysis of samples (data re-processing) for non-targeted analysis of trace components is possible at any time, and identification without reference solution is also achievable. However, the linear detection range is limited, and instrumental LODs are somewhat higher compared to targeted analysis. Therefore, in some cases, the best approach for comprehensive pesticide residue analysis is a combination of different techniques: first a screening method (e.g. ultra-high performance liquid chromatography (UPLC) with ToF detection – UPLC-ToF) for detection of possible targets and their quantitative screening, then confirmation and determination of accurate quantities by another method (e.g. LC-MS/MS). Recently, a method for multi-component analysis of dried paprika and other spices using UPLC coupled to high resolution Orbitrap MS was proposed [52] as a very effective high-throughput technique in full-scan mode, providing better sensitivity than QqQ-MS/MS for quantitative determination of several pesticide contaminants in paprika, and being comparable analytical sensitivity for mycotoxins.

Matrix effects always have to be taken into consideration, particularly in LC methods. Selective detection modes in instrumental analysis do not necessarily eliminate all matrix effects, therefore, labelled internal standards or matrix-matched calibration curves are required for correct quantification in samples. In a study using GC-QqQ, approximately 80% of 130 pesticides in-

vestigated showed signal enhancement in paprika matrix in matrix-matched calibration compared to calibration to standard solutions in organic solvents [46]. Reported limit of quantification (*LOQ*) values for various pesticides in spice commodities are usually in the range of 0.01–0.05 mg·kg⁻¹, the exact values depending on both the physico-chemical properties of the target molecule and the analytical method used, the latter also including the condition of the instrument (e.g. age, maintenance). Use of more selective detection modes (e.g. Orbitrap) results in improvement in *LOQ* by at least one order of magnitude [52].

Pesticide residues in spice paprika

As in previous years, herbs and spices occurred within the top 10 product categories of notifications by RASFF in 2014 (altogether 121 notifications during the year) [41]. Within spices, numerous findings were related to spice paprika since 1998 (Tab. 2).

Spice paprika consists of a complex plant matrix. Not only it contains unique alkaloids like capsaicin, but it is also rich in essential oils, red carotenoids, and is characterized by high lipid content. As a result, it occurs to be a difficult sample matrix for chemical analysis, as can be seen in high variability of the analytical data on spice paprika. An international ring trial with nine laboratories across four European countries involved (Croatia, Germany, Spain and the Netherlands) was carried out in 2014 [55]. This used using organic sweet paprika powder, free of incurred residues of pesticides at a level of 0.00001 μg·kg⁻¹, and spiked with 13 different pesticides at contents typically found for the given pesticide, e.g. 360 μg·kg⁻¹ for cypermethrin, 290 μg·kg⁻¹ for procymidone, 220 μg·kg⁻¹ for carbendazim, 190 μg·kg⁻¹ for propamocarb, 150 μg·kg⁻¹ for fenpropathrin, 130 μg·kg⁻¹ for difenoconazole, 80 μg·kg⁻¹ for *N,N*-diethyl-3-methylbenzamide, 50 μg·kg⁻¹ for spiroxamine, 45 μg·kg⁻¹ for endosulfan sulfate, 40 μg·kg⁻¹ for methoxyfenozide, 35 μg·kg⁻¹ for ethion, 30 μg·kg⁻¹ for spinosad and 20 μg·kg⁻¹ for imidacloprid. The survey assessing identification efficacy, trueness and comparability of analytical results among laboratories ended with alarming conclusions: only 56% of the participants (5 out of 9 laboratories) identified all 13 pesticides in the test sample, 44% (4 out of 9 laboratories) reported results of all 13 pesticides within 70–120% of the spiked level, and 56% (5 out of 9 laboratories) found these pesticide levels within a z-score (the ratio of the difference between the nominal and the measured values to the standard deviation of the measured value) at or below 2. The ring trial

was a lower scale repetition of a similar study series in 1982–2009 [56] with the participation of 58–69 laboratories to test for 4 (chlorpyrifos, fenvalerate, procymidone, profenofos) or 5 (bupirimate, metalaxyl, myclobutanil, tetradifon and tolclofos-methyl) compounds out of 73–76 pesticide active ingredients in paprika purée. These surveys resulted in 36–55% of the participants identifying all pesticides in the test sample, 26–41% reporting all pesticides with satisfactory z-scores, and 15–23% achieving their correct identification with accredited analytical methods. The poor efficacy of these ring trials well-illustrates the difficult character of the spice paprika sample material as an analytical matrix.

The complex matrix material of spice paprika requires standardized effective sample preparation processes, the most recent of which being dSPE-based QuEChERS sample preparation technique [50]. This is widely used for determination of pesticide residues in food matrices [47], although reported to be problematic for dithiocarbamates [57]. Widely used for pesticide residue determination, QuEChERS was found to be suitable for parallel determination of pesticide residues and mycotoxin levels in spice paprika from the same pre-treated sample when using UPLC coupled to high resolution Orbitrap MS [52], but appeared unsuitable without further modifications for immunosensoric detection [58]. A modified QuEChERS method on the basis of dry ice-partitioning was found to display substantially lower matrix effects of spice paprika and to provide recoveries above 76% and relative standard deviations less than 20% for 168 pesticides, although certain active ingredients including benfuracarb, carbosulfan, dichlofluanid, probenazole, pymetrozine, tolylfluanid, 4-trifluoronicotinic acid and *N*-(4-trifluoronicotinoyl) glycine remained problematic (allowing recoveries below 70%) [53]. A further modification of the QuEChERS method with the use of multi-walled carbon nanotubes for dSPE was shown to be of utility for simultaneous determination of 227 pesticides in paprika samples by LC with tandem MS [59]. Recoveries were in the range of 70–120% for 199 pesticide active ingredients at a spike level of 40 μg·kg⁻¹, and *LODs* ranging from 0.00004 μg·kg⁻¹ to 0.00405 μg·kg⁻¹. The relative standard deviations for 197 pesticides were below 20% at spike levels of 40 μg·kg⁻¹.

According to a report by a spice company Raps (Kulmbach, Germany) in 1995 (cited by AMAJUOYI [60]), approximately 21% of their imported spice paprika shipment lots were objected due to content of chlorinated hydrocarbons, organophosphates and pyrethroids (249 shipped items

altogether, 45, 35, 15 and 154 items from Greece, Spain, Israel and other countries, respectively). Pesticide residues in imported spice paprika were found at violation rates as frequently as 90.9% between 2004 and 2006 in the United States of America (22 commodity samples analysed), and tolerance violations of 14 cases, including 12 paprika samples from a single country, were recorded out of 37 spice, condiment and flavour samples in 2006 [61]. Dichloro-diphenyl-trichloroethane (DDT) was detected in Korean paprika ($450 \mu\text{g}\cdot\text{kg}^{-1}$) [62].

Organochlorine insecticides (e.g. hexachlorocyclohexane (HCH) isomers, heptachlor, aldrin, γ -chlordane, endosulfan isomers, dieldrin, endrin, DDT and metabolites dichloro-diphenyl-dichloroethane (DDD) and dichloro-diphenyl-dichloroethylene (DDE), methoxychlor, nonachlor), although long removed from registered agricultural use, are still detected in spice paprika in Africa [63, 64]. Organophosphate insecticides (acephate and methamidophos, the latter being also the metabolite of the former), commonly applied for thrips control, were found in spice paprika grown in field cultivation and particularly in greenhouses [65]. Other substances (organophosphates chlorpyrifos, monocrotophos, pyrethroid cypermethrin) were detected in local market samples of paprika in India [66] and in Brazil [67]. Although thermal processing was shown to reduce the levels of organophosphate insecticide (chlorpyrifos, ethion, malathion, methamidophos, parathion, phenthoate, phorate, pirimiphos, pyrazophos, terbuphos, triazophos) residues in *Capsicum*, residual levels as high as 29.6–40% for given active ingredients were also found after different cooking times of up to 60 min [68]. In contrast, drying was shown to cause, as expected, substantial (from 3.52- to 7.50-fold) increase in the levels of ethion, as well as of chlorinated hydrocarbon dicofol and of pyrethroid cypermethrin [69]. In 2015, banned organophosphate insecticides profenofos and phorate were found in dried chilli, green and yellow capsicum in India [70]. Residues of an organophosphate insecticide banned in EU (triazophos) and two registered neonicotinoids (acetamiprid, imidacloprid), as well as nine fungicides (see below), were detected by advanced instrumental analysis in imported and marketed spice paprika grown in Brazil and China, provided by a German spice company Fuchs Gewürze (Dissen am Teutoburger Wald, Germany) [52], significant levels being determined for triazophos ($3 \mu\text{g}\cdot\text{kg}^{-1}$) and for imidacloprid ($5\text{--}12 \mu\text{g}\cdot\text{kg}^{-1}$). Numerous organophosphates were banned due to their toxicity and persistence profile, e.g. profenofos and fipronil,

half-life values of these in spice paprika being reported to be 41.0 days and 16.8 days, respectively. Withdrawal periods (waiting periods between the last pesticide treatment and harvest) of 19 days and 5 days were suggested [71], while corresponding values at registered doses for dimethoate and ethion were 2.65 days and 5.63 days, respectively [72]. The pyrethroid cypermethrin has been shown more decomposable in chilli fruits, and its risk assessment indicated a withdrawal period of 1 day to be sufficient at the recommended dosages [73]. A similarly low, 1-day withdrawal period, has been suggested for the neonicotinoid insecticide acetamiprid in chilli [74]. Yet, several neonicotinoids (acetamiprid, clothianidin, dinotefuran, imidacloprid, thiacloprid, thiamethoxam) were reported in Korean paprika, 90.5% of 95 samples analysed being found contaminated, in 82.3% with residues of two or more active ingredients, although in all cases below the Korean and Japanese official *MRLs* [75].

Among fungicides, mancozeb and tebuconazole were found to be most efficient against *Aspergillus flavus* strains found in *Capsicum* powder [76]. Therefore, residues of these compounds are of concern in residue monitoring. A recent survey using advanced instrumental analysis identified residues of seven authorized (azoxystrobin, difenoconazole, iprovalicarb, metalaxyl, myclobutanil, propamocarb, tebuconazole) and two banned (carbendazim, thiabendazole) fungicide active ingredients in spice paprika market samples provided by Fuchs Gewürze [52]. Fungicide residue levels detected in spice paprika were in most cases below the official *MRLs*, except for iprovalicarb ($20\text{--}25 \mu\text{g}\cdot\text{kg}^{-1}$). Levels of other residues were $4.6\text{--}39 \mu\text{g}\cdot\text{kg}^{-1}$, $3\text{--}70 \mu\text{g}\cdot\text{kg}^{-1}$ and $3\text{--}33 \mu\text{g}\cdot\text{kg}^{-1}$ for propamocarb, carbendazim and myclobutanil, respectively.

The officially determined *MRL* values can be found, for given commodities, in various declarations and documents [18–20]. The official *MRLs* for the active ingredients are accepted and registered in Hungary (collected in Tab. 1), including paprika/chilli (genus *Capsicum*) (HS code 09420), crushed or ground fruit of genus *Capsicum* (HS code 09042090) on the basis of databases of the European Commission and the Codex Alimentarius. RASFF is a potent alarming and indicator system in case of the European markets to raise attention if food safety of certain products, mostly those with lengthy and complex trade chains consisting of numerous minor participants [77], such as condiment products. Nonetheless, stern and valid quality control, similar to that applied by global condiment companies, is also required and

strictly monitored “from farm to fork” in the production and distribution of spices. In the case of spices, trade through the internet and by less inspected small-scale manufacturers can be a vehicle of unintentionally or deliberately contaminated products.

The official *MRL* values are derived from the acceptable daily intake (*ADI*) values of residues in a risk assessment process considering the hazard posed by the given substance (i.e. toxicity parameters of the compound) and the level of the exposure through diet, realized by the given commodity containing the contaminating residue. The level of consumption of the given commodity strongly affects *MRL*, as seen in the high variability of *MRL* values among *Capsicum* commodities from raw paprika fruits to ground spice paprika. *MRL* values of given residues may be higher in spice paprika than in raw paprika fruits for two reasons: the increase in the contaminant content in spice paprika during the drying step in the technological process, on the one hand; and spice paprika representing a substantially lower amount in the normal diet than raw paprika, on the other hand. Substantial, up to 80–90% water loss takes place during the drying processes used in spice paprika production [78, 79], which results in an up to ten-fold increase in the residue level in spice paprika compared to that in the paprika fruit as a raw material (decomposition by heat not considered). Further losses of biomass result from removal of the stem from the dried paprika fruit prior to grinding. On the basis of these considerations, one would expect higher *MRLs* for spice paprika than for raw paprika fruit. Indeed, *MRLs* up to 5–10-fold higher for spice paprika were seen for certain pesticide active ingredients, e.g. esfenvalerate (2-fold), fosthiazate (2.5-fold), captan (3.3-fold), iprovalicarb and oxamyl (5-fold), copper compounds (8-fold) and chlorpyrifos (10-fold) (Tab. 1). Yet, in contrast, significantly lower *MRLs* for spice paprika than for raw paprika fruit are set for the majority of pesticide residues (Tab. 1), and the pattern among *MRLs* in various paprika commodities does not appear to be consistent. The permitted *MRL* values can be as low as 60–300-fold lower for spice paprika than for paprika fruit e.g. for bifentazate, iprodione or fenpyrazamine. Variability in *MRLs* may also derive from the differences in detectability of a particular ingredient in different matrices. The legislator, of course, may have numerous aspects to consider, besides the exposure level, e.g. technological features, processing factors or expected decomposition rates. Moreover, certain official *MRLs* may have been established numerous years earlier than

others. Yet, one would expect a more coherent setup among established *MRLs*, unless other reasons justify the existing great differences. Besides that, problematic substances emerge occasionally. Among neurotoxic organophosphate insecticides, ethion has been reported by RASFF at the highest contaminant level (above 12 mg·kg⁻¹), and chlorpyrifos, profenofos and triazophos are also reported at 0.03–1.4 mg·kg⁻¹ levels (Tab. 2). The application of organophosphate formulations, authorized until 2015, has increased after the EU-wide ban of three neonicotinoids (clothianidin, imidacloprid, thiamethoxam) in 2013. In turn, the established *MRLs* for chlorpyrifos, also banned for paprika cultivation in 2016, are still valid, as its residues can still be observed in various paprika commodities and products. Consequently, the establishment of a more logical and coherent set of *MRLs* is urged.

Environmental and (eco)toxicological aspects of pesticide residues

The aspects of food and environmental safety and good agricultural practices (GAPs) cannot be separated from each other. GAPs ensure a high level of safety and quality of agricultural food and animal feed products [80]. Reported non-compliances with the approved *MRL* values generally originate from improper agricultural technologies. Therefore, pesticide residues found in food and animal feed commodities are strongly dependent on the agricultural practice used, improper or illegal pesticide application, climatic conditions at the production site, as well as harvest and storage conditions. Pesticide residue levels or mycotoxin content exceeding the corresponding *MRL* values are obvious cases of legal non-compliances, but do not necessarily represent immediate health risks as *MRLs* are normally calculated with a 100-fold safety factor [18, 81].

Although pesticides provide effective control of various agricultural pest damages, they are also regarded as dangerous environmental contaminants due to their leaching, drifting, surface runoff from treated sites, foliar spray applications and unintended overspray, especially if reaching surface water. Furthermore, they can also bind to the surface of soil compartments that results in reduced dissolution rates, and the formulated compounds may persist in various environmental matrices [82–85]. Pesticide residues from crops or these matrices may reach drinking water, enter the food processing chain, and occur as food contaminants. These interrelated characteristics of environmental and food safety are also reflected in the “farm to fork” food safety concept of EU, and consequently, environmental and food contamina-

tion by pesticides [2].

Among pesticide active ingredients at present authorized for paprika cultivation, certain insecticide, fungicide and herbicide active ingredients are of environmental concern. Among insecticides, the most ecotoxic classes, chlorinated hydrocarbons and organophosphates have been superseded from practice, and currently neonicotinoids appear to be the most environmentally problematic, particularly when used as a coating material on seeds of guttating plants. Although *Capsicum* species do not strongly guttate, and neonicotinoids are used on them in spray applications, investigation of this most widely used insecticide compounds on paprika plants is a further novel challenge for ecotoxicology. Due to their physico-chemical properties (e.g. water solubility, persistence), neonicotinoids can be accumulated in soils and can be detected in surface water. They may appear in concentrations harmful to pollinator organisms, like honey bees (*Apis mellifera*) [86, 87]. Therefore, the use of neonicotinoids is restricted in flowering crops in EU [28]. Another problematic pesticide active ingredient is glyphosate, commonly applied for pre-emergence control of weeds in *C. annuum*, contributes to the chemical pressure on the environment and habitats [36–40]. Several scientific studies recently raised concerns about this worldwide used active ingredient, and about the surfactants used in glyphosate-based formulations, in

particular polyethoxylated tallowamine (POEA). Furthermore, scientific evidence is available on the negative environmental and agronomic impact of glyphosate [40, 88–90]. Nowadays, the presence of glyphosate in surface water is a globally observable phenomenon due to its good water solubility and widespread use, resulting from increasing environmental contamination particularly on cultivation areas of glyphosate-tolerant genetically modified crops. This is a concern that may deteriorate with emerging bioeconomy [91].

In our investigation of pesticide residues in various environmental and paprika fruit samples originating from intensively cultivated fields in the Southern region of Hungary, Bács-Kiskun County near Kalocsa, pesticide residues were not detected in the collected paprika samples [85]. In the soil samples, tefluthrin, trifluralin and DDT (with decomposition products: DDD and DDE) and, in one case, chlorpyrifos contamination were detected; in some soil samples, atrazine, diazinon and, in one case, metolachlor were determined, but were not quantified (Tab. 3). In contrast, no detectable pesticide residues were found as soil contaminants from paprika cultivation fields managed under ecological (organic) farming. As a surface water contaminant, trifluralin has been detected in the range of 0.011–0.034 mg·l⁻¹ in 50% of the collected water samples. However, pesticide residues were not detected in the investigated paprika sam-

Tab. 3. Content of pesticide residues found in soil samples from intensively cultivated field in two sampling regimes.

Location	Sampling time	Trifluralin	Tefluthrin	Chlorpyrifos	DDT	DDE	DDD
		[μg·kg ⁻¹]					
Site 1	Summer	0.021–0.072	–	–	–	–	–
	Autumn	0.002–0.049	–	–	–	–	–
Site 2	Summer	0.027–3.201	0.106–0.277	–	–	–	–
	Autumn	0.038–0.358	0.037–0.195	–	–	–	–
Site 3	Summer	0.013–0.029	–	–	–	–	–
	Autumn	~ LOD	–	–	–	–	–
Site 4	Summer	–	–	–	–	–	–
	Autumn	–	–	–	–	–	–
Site 5	Summer	~ LOD	0.071–0.441	0.044–0.572	0.044–0.572	0.040–0.865	0.030–0.051
	Autumn	0.011–0.019	0.027–0.306	0.007–0.031	0.007–0.031	0.057–0.756	0.007–0.040
Site 6	Summer	0.024–0.057	0.188–0.864	1.141–8.351	1.141–8.351	1.353–4.805	0.046–0.471
	Autumn	–	0.007–0.154	0.208–1.594	0.208–1.594	0.488–5.699	0.028–0.449

Six cultivation sites near Kalocsa in the Southern region of Hungary (Bács-Kiskun County, Hungary). Summer and autumn sampling were carried out in June and September, respectively.

Trifluralin, tefluthrin, chlorpyrifos, dichloro-diphenyl-trichloroethane (DDT) and its metabolites dichloro-diphenyl-dichloroethane (DDD) and dichloro-diphenyl-dichloroethylene (DDE) were investigated in soil samples. Content is expressed as micrograms per kilogram of soil.

LOD – limit of detection.

ples. A half of the soil samples from intensive cultivation fields were contaminated with tefluthrin, which is one of the most hazardous pyrethroids applied by pest control technology in soils. The investigated water samples were not polluted by this compound presumably due to its low water solubility. Similarly, DDT and its degradation product (DDD) or metabolite (DDE) occurred in soils at high contents at two sites. As a result of their high persistence due to their low water solubility, these compounds were not detected in surface water and paprika samples. Consequently, the residues of persistent compounds could be detected in environmental matrices for a long time after pesticide treatments [85]. The next level in our investigations is the assessment of ecotoxic consequences of these residues. In the scope of this approach, adverse effects of glyphosate and POEA on several aquatic test organisms (e.g. *Daphnia magna* [89], algae species, natural freshwater biofilm communities) are being explored.

In case of (eco)toxicology, co-exposure to pesticide active ingredients and to surfactants used in their formulations often lead to additive or synergistic toxicological effects. Various co-formulants and other additives used in the formulation of pesticides was long considered as inactive i.e. inert ingredients from the biological point of view and, thus, simpler environmental risk assessment was considered to be sufficient in their case according to the valid legislation compared to the active ingredients [92, 93]. Numerous studies showed additive, synergistic or antagonistic effects between the active ingredient and the additives in formulated products. Moreover, toxicity was evidenced for various additives (e.g. detergents) and, therefore, thorough toxicological evaluation of the surfactants and other additives is necessary for proper environmental risk assessment of formulations used in agriculture [88–90, 94].

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