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Food Safety Aspects of Pesticide Residues in Spice Paprika

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Abstract**—**Environmental and health safety of condiments used for spicing food products in food processing or by culinary means receive relatively low attention, even though possible contamination of spices may affect food quality and safety. Contamination surveys mostly focus on microbial contaminants or their secondary metabolites, mycotoxins. Chemical contaminants, particularly pesticide residues, however, are clearly substantial factors in the case of given condiments in the *Capsicum* family including spice paprika and chilli. To assess food safety and support the quality of the *Hungaricum* product spice paprika, the pesticide residue status of spice paprika and chilli is assessed on the basis of reported pesticide contamination cases and non-compliances in the Rapid Alert System for Food and Feed of the European Union since 1998.

Keywords**—**Spice paprika, *Capsicum*, pesticide residues, RASFF.

I. Introduction

FOOD safety may become jeopardized by various biological, physical or chemical agents that adventitiously occur at any point of the food supply chain due to natural, accidental or deliberate contamination and that are reasonably likely to cause illness or injury in the absence of their control. To protect consumers, food safety policies in the European Union (EU), codified by law [1], aim to assure a high level of food safety, animal health, animal welfare and plant health within the EU. For this purpose, the EU implements an integrated approach to provide food safety “from farm to fork”, including science-based risk assessment to assure effective risk management measures; effective control systems to guarantee compliance with EU food safety and quality standards; and adequate monitoring of this compliance with alerting mechanisms regarding non-compliance cases to ensure the effective functioning of the internal food market. The main device of such alerting mechanisms is the Rapid Alert System for Food and Feed (RASFF) created in 1979 and amended several times later [1]-[3].

Among chemical agents of agricultural origin posing hazard to food safety, pesticide residues are predominant. These agrochemicals occur in agricultural produce due to improper pesticide application to crop, illegal use of given agrochemicals (use of pesticides not registered for the given crop) or inadequate harvest or storage conditions (e.g. harvest before the end of the waiting period of the last pesticide application; pesticide treatment during storage, etc.). Therefore, crop commodities as raw materials for food production are obviously considered as sources for the occurrence of pesticide residues in processed food. Nonetheless, food products also contain natural substances of plant origin used as condiments: spices and herbs. Spices, used in the whole, broken or ground forms, are defined as “vegetable products or mixtures thereof, free from extraneous matter, used for flavoring, seasoning, and imparting aroma in foods” by the International Standardization Organization (ISO) [4], while herbs are generally defined as fresh or dried leafy parts of various soft-stemmed perennial or annual plants [5]. Although spices are added to processed foods in minor quantities, their contamination definitely contribute to the contamination levels found in food products. Spices and herbs are contained in almost every processed food, including ready-to-eat products, and are often used by the consumer for flavoring purposes. Although hazards posed by contamination in spices mostly apply to dynamic contamination capable to multiplication (e.g. microbial contamination or related substances, particularly for of pathogenic microorganisms), static contamination by given chemical substances (e.g. pesticide residues) cannot be neglected, either. The presence of chemical contaminants is being routinely monitored in condiments by instrumental analysis combined with chemometrics [6] to control spice quality, compliance to market quality requirements and safety to human health.

Belonging to the genus *Capsicum*, spice paprika and chillies have numerous varieties, including hot, mild, fiery and sweet types, with fruits of hanging or standing type and of different shapes (oval, cone or bell) or colors (from green and yellow to different shades of red). These fruits used dried and ground are used as food condiments or culinary supplements [7]. In additional to flavoring uses, paprika varieties contain various amounts of biologically active, beneficial substances. The hot taste is caused by capsaicinoids, related to vanillyl amine, the level of which is measured on the Scoville scale. Other important bioactive compounds are carotenoids and vitamin C.

The EU represents one of the largest markets for spices and herbs in the world. The leading spice consumer countries are Germany, the UK, Romania and Hungary responsible for 19%, 16%, 14% and 12% of the total consumption of spices in the EU in 2007, respectively. The most consumed spices in the EU are pepper, paprika and pimento [8]. The vast majority of spices are imported into the EU, only a few spices are produced within the EU, including spice paprika representing 62% of the EU spice production, with main producers of Hungary and Romania. Therefore, food safety of spice paprika is a major issue in food safety not only for these producer countries, but also to all European consumers.

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II. Pesticides Authorized in the European Union for Spice Paprika Cultivation

Overall 50 pesticide active ingredients have been registered in the EU in paprika cultivation. Of these, 1, 7, 14, 22 and 6 are authorized as seed treatment, soil disinfectants, fungicides, insecticides and herbicides, respectively. The apparent overwhelming predominance of insecticides is explained by pest composition and pesticide market issues.

Botanical insecticides (Neem cake, garlic extract), substances of natural origin (abamectin), as well as their combination with synthetic insecticides (pro-insecticide diafenthiuron), as well as earthworm excretory substance extract (Vermiwash) have been suggested for eco-friendly pest control and sustainable production of chilli [9], [10]. The spray administration of jasmonic acid in chilli has also been proposed as a possible alternative of pesticide applications, found to be most effective in two time spray at 0.5 mM concentration [11].

Official maximum residue levels (MRLs) for pesticide residues are specified in *Codex Alimentarius* [12] and other documents [13] for given commodities, including paprika/ chilli (genus *Capsicum*) (HS code 09420) crushed or ground fruit of genus *Capsicum* (HS code 09042090). MRLs for pesticides in products of plant and animal origin are defined as the highest permitted concentration of residues of pesticides legally authorized in or on foodstuffs and food for animals. As defined by law, all food products that contain residues of any given pesticide (the parent compound and its metabolites, and/or breakdown or reaction products found) authorized for the given commodity above the MRL or any given pesticide not authorized for the given commodity at any concentration have to be rejected from consumption or trade.

III. Rapid Alert System for Food and Feed

The Rapid Alert System for Food and Feed (RASFF), established in 1979 [2], operates in all EU member states through their national food safety authorities. The system operates on the basis of authority statements on execution measures of the alert system for food and feed safety. Within the system, member states report to the European Commission (EC), without delay, any hazards affecting human health directly or indirectly originated from food and feed products or commodities that have been identified through RASFF. The system, operated by the EC, establishes a direct contact among the EC, the European Food Safety Authority (EFSA) and relevant authorities of the member states. Any identified hazard related to food and feed and reported to the EC is promptly transferred to all RASFF members. To date RASFF has been proven to be an effective instrument to exchange information in real-time within EU member states.

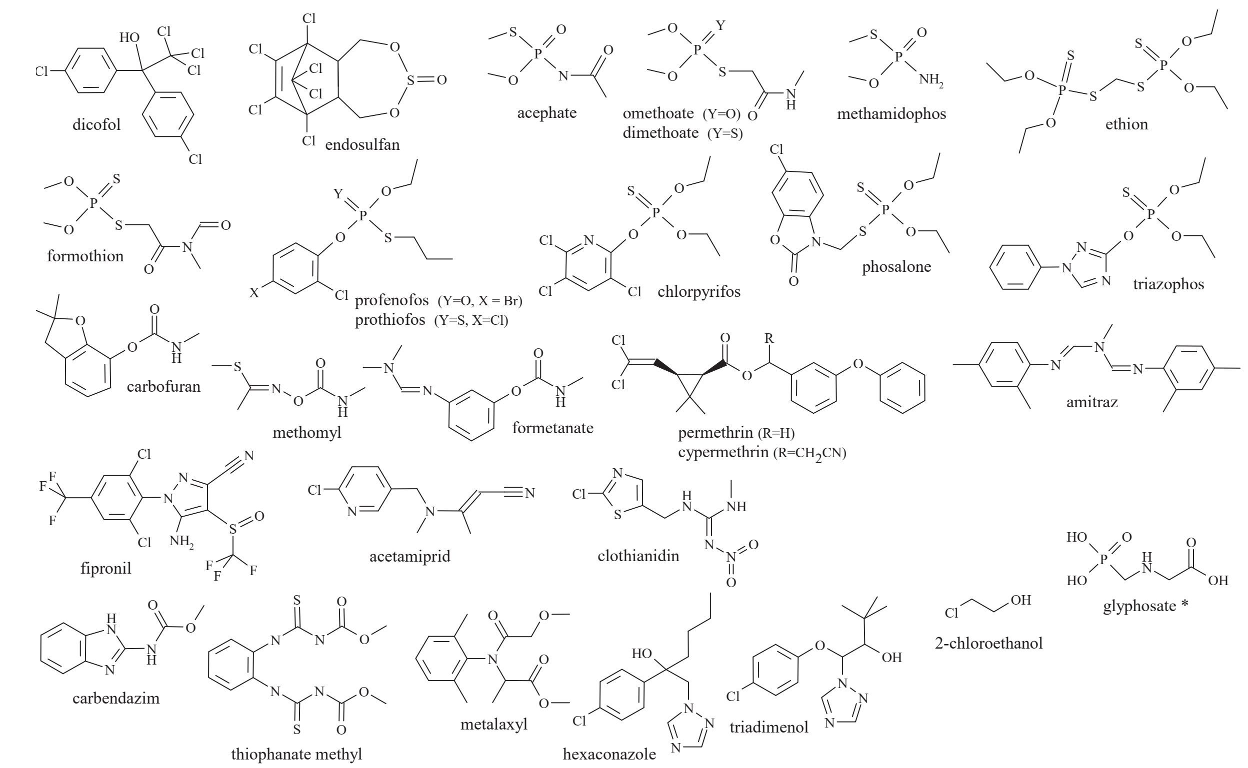

Fig. 1 Pesticide active ingredients complained by the Rapid Alert System for Food and Feed (RASFF) of the European Union (EU) in *Capsicum* species (spice paprika and chilli) until 2015, listed by chemical classification. Insecticides: dicofol, endosulfan, acephate, omethoate, dimethoate, metamidophos, ethion, formothion, profenofos, prothiofos, chlorpyrifos, phosalone, triazophos, cerbofuran, methomyl, formetanate, permethrin, cypermethrin, amitraz, fipronil, acetamiprid, clothianidin. Fungicides: carbendazim, thiophanate methyl, metalaxyl, hexaconazole, triadimenol. Herbicide: glyphosate (* not in RASFF, but used as pre-emergent treatment in paprika). Metabolite: chloroethanol

IV. Pesticide Residues in Spice Paprika Reported by the Rapid Alert System for Food and Feed

Alerts, information notifications and border rejection notifications, along with non-compliance contamination levels found, as well as countries of complaint and of origin specified, are published in the RASFF Annual Reports [14]. (Similarly as determined pesticide residue levels above MRL are listed in the US in the reports of the FDA Residue Monitoring Program [15].) Alerts are hazard warnings regarding findings on products already on the market that do or may necessitate rapid action by member states. Information notifications are hazard warnings regarding findings that do not necessitate rapid action by member states, because the product of complaint has not reached the given member state, its validity expired; it has not reached to or has been removed from the market. Border rejection notifications are hazard warnings regarding rejections of food or feed consignments, transport vehicles or shipments by the competent authorities at the border of the member state. Of the reported RASFF alerts, numerous findings have been related to spice paprika each year.

The EU Rapid Alert System for Food and Feed (RASFF) reported the below ingredients as contaminants in spice paprika (mg/kg) in their Annual Reports [16] and searchable web-portal [17]. Chemical structures of the compounds are seen in Fig. 1, the residue levels reported by RASFF [16], [17] by active ingredient are listed below and are depicted in Fig. 2.

- Brazil, 2004, triazophos – paprika ground, 0.14, 0.52 and 0.76;
- Egypt, 2013, dimethoate – chilli, 0.08; omethoate – chilli, 0.12; 2011, ethion – hot paprika fresh, 0.27;
- Dominica, 2015, acetamiprid – chilli fresh, 081; carbendazim – chilli fresh, 0.15; clothianidin – chilli, 0.22; fipronil – chilli, 0.01; thiophanate-methyl – chilli fresh, 0.53; 2012, permethrin – chilli, 0.47; 2011, carbendazim – chilli fresh, 0.14; dicofol – chilli fresh, 0.98; endosulfan – paprika fresh, 0.1; formothion – chilli fresh, 0.22; permethrin – chilli, 0.55; paprika fresh, 0.14; thiophanate-methyl – chilli fresh, 0.34; 2010, dicofol – chilli, 4.2; Gambia, 2015, triazophos – chilli, 1.1;
- Germany, 2003, 2-chloroethanol (metabolite) – paprika hot, 3.64;
- Greece, 2005, acetamiprid – paprika, 0.12
- India, 2013, ethion – chilli fresh, 0.19; 2008, acephate – chilli, 0.26; carbendazim – chilli, 1.54; carbofuran – chilli, 0.17; ethion – chilli, 2.0; hexaconazole – chilli, 0.24; 2004, cypermethrin – chilli ground, 0.51; chlorpyrifos – chilli ground, 0.14; 2003, cypermethrin – paprika ground, 1.62; ethion – paprika ground, 0.77; phosalone – paprika ground, 1.33; 2001, cypermethrin – chilli ground, 1.13 and 3.36; chlorpyrifos – chilli ground, 0.41; ethion – chilli ground, 2.34 and 2.01; triazophos – chilli ground, 0.23 and 0.27; 2000, ethion – chilli;
- Israel, 2001, triadimenol – chilli, 0.29;
- Kenya, 2008, methomyl – chilli fresh, 1.0;
- Laos, 2015, metamidophos – chilli, 0.03;
- Malaysia, 2011, amitraz – chilli fresh, 1.1;
- Morocco, 2007, methomyl – hot paprika, 1.16;
- Pakistan, 1999, cypermethrin – chilli;
- Spain, 2003, 2-chloroethanol (metabolite) – chilli ground, 0.17; 2001, cypermethrin – chilli; 2000, methamidophos – paprika sweet; 1999, acephate – paprika sweet; endosulfan – paprika sweet; methamidophos – paprika sweet;
- Thailand, 2013, ethion – chilli dry, 0.57; triazophos – chilli dry, 1.4; 2012, triazophos – chilli dry, 0.93; 2011, chlorpyrifos – chilli fresh, 1.2; profenofos – chilli fresh, 0.51 and 0.93; 2009 formetanate – chilli, 6.8; triazophos – chilli fresh, 0.7; 2008, carbofuran – chilli, 1.2; 2002, chlorpyrifos – paprika, 1.0; metalaxyl – paprika, 0.19; methamidophos – chilli, 0.93, 0.44, 0.36; profenofos – paprika, 0.23; paprika, 1.2; prothiofos – paprika, 0.24, 0.21;
- Turkey, 2012, formetanate – paprika fresh, 0.18;
- Uganda, 2009, dimethoate – chilli, 0.05; omethoate – chilli, 0.04;
- UK, 2010, ethion – chilli ground, 0.02; triazophos – chilli ground, 0.03; 2001, cypermethrin – chilli ground, 6.92; ethion – chilli ground, 12.6 and 11.8, 4.06, 5.37 and 3.83, 0.82, 4.06 and 2.38; methamidophos – chilli ground, 0.09;
- Zimbabwe, 2000, triadimenol – paprika.

As seen from the contamination profile reported by RASFF, the vast majority of the pesticide residues belong to the class of insecticides, and only a smaller proportion of fungicides along with a fumigant metabolite have been reported as non-compliance cases. The strong dominance of insecticide is explained not only by the pest range damaging spice paprika, but also by the fact that the number of insecticides is overwhelming among pesticides authorized for paprika cultivation. Contamination history obviously reflects pesticide active ingredients having been used over time, rather than the current range of authorized compounds. It is a quite pleasant trend that only two representatives of the persistent (and long-banned) organochlorine insecticides (dicofol, endosulfan) have been reported in RASFF [16], [17], indicating that uptake of residual DDT contamination in soil by paprika plants doesn't seem to occur. The largest group within insecticides is the organophosphate family, along with N-methylcarbamates of the same mode of action in insects, and two members of these families (ethion and formethanate) have been reported at outstandingly high concentrations (12.6 and 6.8 mg/kg, respectively). Similarly, high residue level of the pyrethroid insecticide cypermethrin (6.92 mg/kg) has also been reported. It is noteworthy that the controversial group of neonicotinoids (acetamiprid, clothianidine) is emerging.

Although RASFF provides an effective warning system for the EU market, attention has been called to jeopardized food safety of goods with long and complex trade chains with high numbers of small scale participants [18], such as in the case of trade of spice products. Global spice companies have strict quality control measures at place, and closely follow the product path from farm to fork. Small craft producers, however, importing and exporting possibly *via* the internet, could be mediators of accidental or intentional contamination.

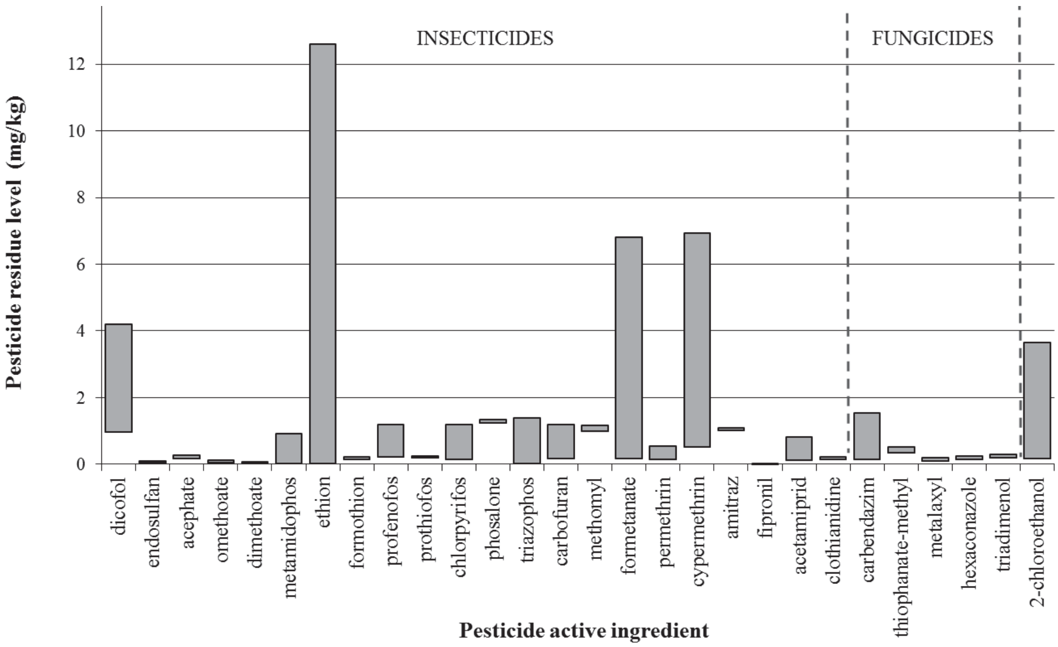

Fig. 2 Pesticide residue levels reported by the Rapid Alert System for Food and Feed (RASFF) of the European Union (EU) in *Capsicum* species (spice paprika and chilli) until 2015 (grey rectangles indicate ranges of detected concentrations)

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