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Pesticide residues levels in honey from apiaries located of Northern Poland

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ABSTRACT

Concentration levels of 30 pesticide residues were measured in honey samples collected from apiaries in northern part of Poland (Pomerania) using method based on the QuEChERS extraction followed by liquid chromatography–tandem mass spectrometry with electron spray ionization (LC–ESI–MS/MS). In 29% of the samples were found positive for at least some of the target compounds. Concentration of bifenthrin, fenpyroximate, methidathion, spinosad, thiamethoxam, and triazophos exceeded maximum residue levels (MRL) in five samples (11%), the kind of the residues being correlated to agriculture practices in the region. The maximum values of these pesticides were 14.5, 16.3, 25.7, 20.6, 20.2 and 20.3 ng/g respectively. Profenofos was the most abundant at concentration ranged from <LOQ to 17.2 ng/g.

1. Introduction

Honey produced by honey bees (*Apis mellifiera*) from pollen, plant nectars, and/or honeydew is composed of over 300 chemical substances which belong to different chemical compound groups. These are mainly carbohydrates, water, polysaccharides, fatty acids, proteins, minerals, dyes, fragrances, enzymes, hormones and vitamins in amounts depending on the plant from which the honey was made (Kujawski & Namieśnik, 2008). Honey bees can bring many pollutants deposited on plants into the hive. Therefore, plant protection products used in agriculture can not only cause mass poisoning of bees but may also enter bee products, especially honey (Aliferis, Tarantilis, Harizanis, & Alissandrakis, 2010) affecting its quality, properties and posing a particular threat to human health (Mukherjee, 2009). Pesticides are significant group of xenobiotics affecting the biota. Regulation 396/20 of the European Parliament and of the Council established values of the maximum residue levels (MRLs) of pesticides in products of plant and animal origin (Regulation (EC), 2005). Since September 1st 2008, the European Commission set new MRLs of some pesticides in honey, which are in range of 10 and 50 ng/g.

Honey bees and their products (honey, beeswax and pollen) are used as indicators of environmental pollution with radioactive elements (Tonelli et al., 1990), heavy metals (Conti & Borté, 2001), or pesticides (Celli et al., 1996). Sample preparation and isolation/enrichment of the target compounds are very important analysis steps because the pollutants are present in honey at very low concentration levels. Solid phase extraction (SPE) (Amendola, Pelosi, & Dommarco, 2011; Blasco et al., 2003; Blasco, Lino, et al., 2004; Debayle, Dessalces, & Grenier-Loustalot, 2008; Pang et al., 2006) and liquid–liquid extraction (LLE) (Kujawski & Namieśnik, 2011; Rissato, Galhiane, de Almeida, Gerenutti, & Apon, 2007) are the most common extraction and purification techniques used in the determination of pesticide residue in honey. Other extraction techniques, such as supercritical fluid extraction (SFE) (Rissato, Galhiane, Knoll, & Apon, 2004), matrix solid phase dispersion (MSPD) (Sánchez-Brunete, Albero, Miguel, & Tadeo, 2002), solid phase micro extraction (SPME) (Blasco, Fernandez, Pico, & Font, 2004; Blasco, Font, & Pico, 2008; Campillo, Penalver, Aguinaga, & Herńandez-Córdoba, 2006; Das & Kaya, 2009), and stir bar sorptive extraction (SBSE) (Rissato et al., 2004; Yu & Hu, 2009) have been developed to reduce the amount of reagents and time spend on sample preparation. In recent years, QuEChERS (quick, easy, cheap, effective, rugged and safe) developed in 2003 (Anastassiades, Lehotay, Stajnbaher, & Schenck, 2003), become very popular technique for determination of pesticide residues in food. QuEChERS has also found application in the determination of pesticide residues in bee products (Blasco, Vazquez-Roig, Onghena, Masia, & Picó, 2011; Lombardo-Agüí, García-Campña, Gámiz-Gracia, & Cruces-Blanco, 2012; Wiesta et al., 2011). It involves two steps, extraction based on partitioning between an aqueous and an organic layer via salting-out, and dispersive SPE for further

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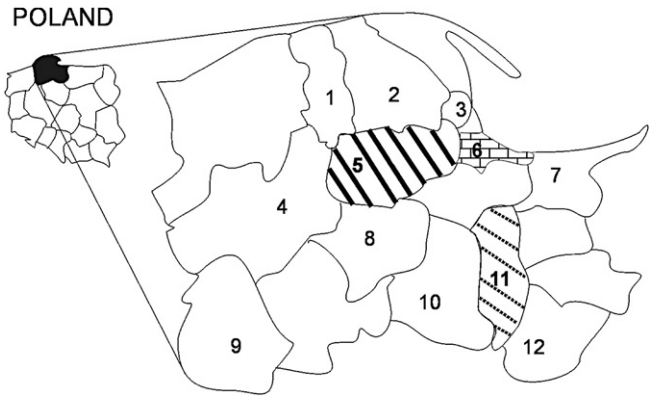

Fig. 1. Location of sample collection area in the districts of Pomerania (Poland): 1-Lebork, 2-Wejherowo, 3-Gdynia, 4-Bytów, 5-Kartuzy, 6-Gdańsk, 7-Nowy Dwór, 8-Kościerzyna, 9-Człuchów, 10-Starogard Gdański, 11-Tczew, 12-Kwidzyn (the shaded areas indicate regions where the MRLs were exceeded – see Results and discussion).

clean-up using combinations of $MgSO_4$ and different sorbents, such as C18, primary–secondary amine (PSA) or graphitized carbon (GCB) to remove interfering substances (Anastassiades et al., 2003)

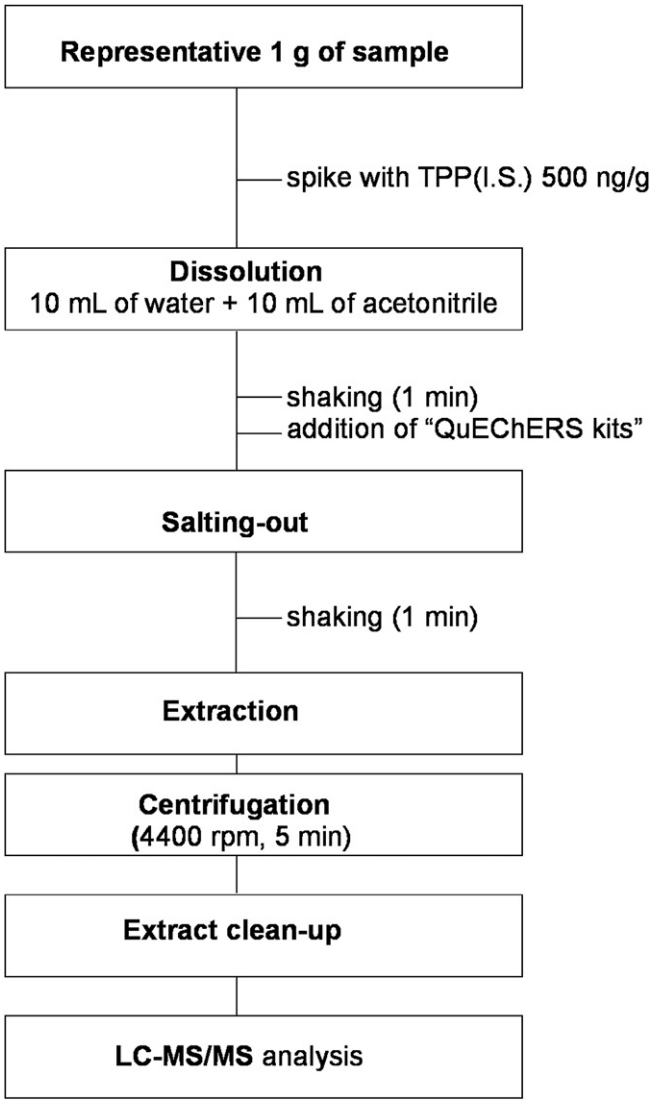

Fig. 2. Analytical procedure work-up flow chart.

The determination of pesticide residues in honey is based mainly on gas chromatography (GC) and liquid chromatography (LC) (Rial-Otero, Gaspar, Moura, & Capelo, 2007).

This paper reports the levels of 30 pesticide residues found in honey samples collected in northern region of Poland (Pomerania) in the year 2010. The target compounds were chosen on the basis of

Table 1
Multiple reaction monitoring of the studied compounds (dynamic MRMs, delta retention time 1 min, except for alachlor 2 min).

Compound	MW [g/mol]	Precursor ion (*m*/*z*)	Product ions (*m*/*z*)		t_r [min]	Collision energy [V]
			Quantifier ion	Qualifiers		
Alachlor	269.1	270.1	238.0	162.1	17.01	13
				117.0		61
Azinphos-ethyl	345.1	346.1	132	77.0	16.71	41
				51.0		5
Azinphos-methyl	317.0	318.0	132	77.0	14.67	37
				51.0		77
Bifenthrin	422.1	440.2	181.0	165.0	28.94	77
				115.0		141
Carfentrazone-ethyl	411.1	412.1	345.9	383.9	18.42	9
				365.9		13
Chloridazon	221.0	222.0	77.0	65.1	7.06	77
				51.1		41
Coumaphos	362.0	363.0	226.9	334.9	19.43	9
				306.9		13
Diazinon	304.1	305.1	169.1	153.1	19.19	17
				96.9		33
Dimethoate	229.0	230.0	124.9	198.9	6.70	5
				170.9		9
Dimoxystrobin	326.2	327.2	205.0	116.0	18.24	17
				58.1		29
Fenpyroximate	421.2	422.2	366.0	107.0	26.84	61
				77.0		101
Haloxyfop-R-methyl	375.1	376.1	315.9	91.0	22.32	29
				65.1		69
Heptenophos	250.0	251.0	127.0	125.0	14.17	9
				89.0		33
imidacloprid	255.1	256.1	209.0	175.0	5.70	13
				84.0		13
Indoxacarb	527.1	528.1	149.9	292.9	23.13	9
				248.9		9
Methidathion	302.0	303.0	145	85.1	14.42	13
				58.1		29
Methiocarb	225.1	226.1	169.0	121.1	15.30	13
				77.0		41
Methomyl	162.1	163.1	88.0	106.0	3.64	9
				58.1		21
Omethoate	213.0	214.0	124.9	182.9	2.19	9
				154.9		9
Oxamyl	236.1	237.1	72.1	90.0	2.95	9
				56.1		49
Oxydemeton-methyl	246.0	247.0	168.9	124.9	3.43	17
				109.0		25
Pirimicarb	238.1	239.1	72.0	182.1	13.25	9
				56.0		53
Profenofos	372.0	373.0	302.8	344.8	23.79	9
				128.0		49
Pyrazophos	373.1	374.1	222.0	238.0	20.90	17
				148.0		53
Qualiafos	298.1	299.1	96.9	271.0	18.14	9
				243.0		9
Spinosad A	731.5	732.5	98.1	98.1	28.38	73
				142.1		29
Spinosad D	745.5	746.5	142.1	98.1	29.00	29
				142.1		77
Temephos	466.0	467.0	124.9	418.9	25.31	13
				404.9		9
Thiamethoxam	291.0	292.0	211.0	181.0	4.05	17
				131.9		17
Triazophos	313.1	314.1	162.1	77.1	16.32	57
				65.1		73
TPP (IS)	326.1	327.1	152.0	77.0	19.48	41
				51.0		89