

ORIGINAL ARTICLE

PESTICIDE RESIDUES IN RAW AGRICULTURAL PRODUCTS FROM THE SOUTH-EASTERN REGION OF POLAND AND THE ACUTE RISK ASSESSMENT

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ABSTRACT

Background. The use of pesticide leads to the increase in quantity and quality of yields, but may also result in presence of toxic contaminants in food products.

Objective. The aim of this study was to evaluate presence of pesticide residues in raw agricultural products from the south-eastern region of Poland, to verify their compliance with the maximum residue levels' (MRLs) as specified in the EU regulations concerning products present in the market, and to assess the acute risk related to consumption of these products. **Material and Methods.** Samples of raw agricultural products were obtained from production farms as a part of an official premarket monitoring of pesticide residues conducted on behalf of the Ministry of Agriculture and Rural Development, implemented in cooperation with the regional Inspectorates of Plant Health and Seed Inspection. The scheduled tests covered determination of 243 chemicals included in residue definitions for purposes of pesticide residues monitoring in or on food of plant origin (229 pesticides). **Results.** In 2015, a total of 328 samples of raw commodities collected from the south-eastern region of Poland were analysed for the presence of pesticide residues. Pesticide residues were detected in 84 samples (25.6%), while in 7 samples (2.1%) they exceeded MRLs. Violations of MRLs concerned 2 samples of Peking Cabbage, 3 samples of dill, 1 sample of raspberry and 1 sample of spinach. The pesticide residues were most often found in: fruit (38.3% of all fruit samples), herbs (35.3%) and vegetables (20.0%). The assessed acute exposure did not exceed the 100% acute reference dose (ARfD) in any sample. **Conclusions.** Monitoring of pesticide residues in the agricultural crops prevents penetration of products with MRLs exceeded or containing unacceptable pesticide residues into the market, thus protecting consumers' health.

Key words: pesticide residues, agricultural products, risk assessment, multiresidue method

STRESZCZENIE

Wprowadzenie. Stosowanie pestycydów prowadzi do wzrostu ilości i jakości plonów, ale może skutkować występowaniem szkodliwych zanieczyszczeń w żywności.

Cel. Celem badań była ocena występowania pozostałości pestycydów w produktach rolnych pochodzących z południowowschodniej Polski w odniesieniu do najwyższych dopuszczalnych poziomów pozostałości (NDP) określonych w rozporządzeniu UE dla produktów obecnych na rynku oraz oszacowanie ostrego ryzyka związanego ze spożyciem tych produktów.

Materiał i metody. Próbki produktów rolnych zostały pobrane z gospodarstw produkcyjnych w ramach urzędowej kontroli pozostałości pestycydów w produkcji pierwotnej, prowadzonej na zlecenie Ministerstwa Rolnictwa i Rozwoju Wsi, realizowanej we współpracy z wojewódzkimi Inspektoratami Ochrony Roślin i Nasiennictwa. Program kontroli obejmował oznaczenie 243 substancji chemicznych ujętych w definicji pozostałości do celów monitorowania pozostałości pestycydów w żywności pochodzenia roślinnego (229 pestycydów).

Wyniki. W 2015 roku wykonano analizy 328 próbek płodów rolnych na obecność pozostałości pestycydów. Pozostałości tych substancji wykryto w 84 próbkach (25,6%), przy czym w 7 próbkach (2,1%) przekroczyły one poziom NDP. Przekroczenia dotyczyły 2 próbek kapusty pekińskiej, 3 próbek kopru ogrodowego, 1 próbki malin oraz 1 próbki szpinaku. Najczęściej pozostałości stwierdzano w próbkach owoców (38,3% wszystkich próbek owoców), ziół (35,3%) i warzyw (20,0%). Dla żadnej z próbek, oszacowane ostre narażenie nie przekroczyło wartości 100% ostrej dawki referencyjnej – ARfD.

Wnioski. Kontrola pozostałości pestycydów w produktach rolnych zapobiega wprowadzaniu na rynek produktów zawierających pozostałości powyżej NDP lub zawierających substancje niedozwolone, a tym samym chroni zdrowie konsumentów.

Słowa kluczowe: pozostałości pestycydów, uprawy rolne, oszacowanie ryzyka, metoda wielopozostałościowa

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INTRODUCTION

The yield from plant production is continually exposed to harmful organisms. It is essential to protect plants and plant products against such organisms, to prevent yield reduction or damage, and to ensure high quality of harvested products and high agricultural productivity. Different methods are available in this area, including non-chemical methods covering practices such as use of resistant varieties, crop rotation, mechanical weeding, biological control, as well as chemical methods, such as use of plant protection products. One of the most common methods for protecting plants and plant products against harmful organisms is the use of active substances in plant protection products. However, a possible consequence of their use may be the presence of residues in treated products, in animals feeding on those products and in honey produced by bees exposed to those substances [2, 9, 12, 17, 21].

According to the European Commission Regulation, substances may only be included in plant protection products when it has been demonstrated that they are clearly beneficial for plant production while having no foreseeable harmful effect on human or animal health or any unacceptable environmental impact [3].

In Poland, the regulatory compliance in the use of plant protection products is supervised by the Inspectorates of Plant Health and Seed Inspection, on behalf of the Ministry of Agriculture and Rural Development. As part of this supervision, pesticide residues levels in agricultural crops are monitored every year, including analyses performed, inter alia, by the Laboratory of Pesticide Residue Analysis in Rzeszow.

The aim of this study was to evaluate presence of pesticide residues in raw agricultural products from the south-eastern region of Poland to verify compliance of these products with the maximum residue levels' (MRLs) as specified in the EU regulations for products present in the market [2], and to assess the acute risk related to consumption of these products.

MATERIAL AND METHODS

Samples of raw agricultural crops were collected from production farms as a part of an official premarket monitoring of pesticide residues conducted on behalf of the Ministry of Agriculture and Rural Development, implemented in cooperation with the regional Inspectorates of Plant Health and Seed Inspection. Agricultural products were sampled from the south-eastern region of Poland from 4 voivodeships: Lubelskie, Małopolskie, Świętokrzyskie and Podkarpackie. Sampling was done according to Regulation of the Minister of Agriculture and Rural Development from 27 November 2013 on the sampling of plants, plant products or other objects to test for the presence of residues of plant protection products [15].

The analyses covered the determination of 243 chemicals included in residue definitions for purposes

of enforcement of relevant limits and pesticide residues monitoring in or on food of plant origin (229 pesticides). Limits of quantification for all pesticide/product combinations were sufficient to compare the results with MRLs. Accredited methods according to ISO/IEC 17025:2005 [13] were used to determine the presence of pesticide residues. The multiresidue analytical method was based on the residue extraction with acetone and dichloromethane and further purification of the extract on a Florisil column [10, 18]. Residues quantification was carried out with Agilent 6890 and Agilent 7890 gas chromatographs, each equipped with ECD and NPD detectors. Along with the multiresidue method, spectrophotometric determination of dithiocarbamate residues expressed as milligrams of CS, per kilogram [1], and high-performance liquid chromatography (Waters Alliance 2695) with photodiode array detector and fluorescent detector for determination of carbendazim residues, were performed [14]. Test results were confirmed in compliance with the European Commission guidelines [4, 5].

The methods were validated before their use for determination of pesticide residues in the samples. Recovery assays of active substances were carried out on blank samples spiked with target compounds at two concentrations, in five replicates. The methods' trueness and precision parameters in terms of the average recovery and relative standard deviation were calculated and assessed according to the European Union guidelines [4, 5]. The linearity of the chromatographic and spectrophotometric responses were evaluated at five concentration levels. The measurement uncertainty of methods was estimated and was found to be compliant with European Union guidelines [4, 5]. Blank fortified samples were analysed within the framework of quality control/assurance, and methods' repeatability and reproducibility were also verified.

In 2015, The Laboratory participated in proficiency tests organized by The European Union Reference Laboratory for Pesticide Residues in Fruit and Vegetables, University of Almeria, Spain, and The European Union Reference Laboratory for Pesticides in Cereals & Feedingstuff, Technical University of Denmark, achieving satisfactory results.

The obtained results were compared to the MRLs in force in the European Union [2, 7]. According to the guidelines specified in the SANCO (now superseded by SANTE) document for samples under official control, MRL violations were reported for pesticide levels exceeding the MRL, with the method uncertainty (50%) considered [4, 5]. Moreover, the analysis verified whether plant protection products containing detected pesticides were approved for a given crop [16].

The acute exposure was calculated for samples with MRLs violated, using International Estimated Short-Term Intake (IESTI) equations [8].

IESTI for dill, raspberry and spinach was calculated according to the following formula:

$$IESTI = \frac{LP \times HR}{bw}$$

while IESTI for Peking cabbage was calculated according to the following formula:

$$IESTI = \frac{LP \times HR \times v}{bw}$$

where:

- LP highest large portion reported (97.5th percentile of eaters), in kg of food per day;
- HR highest residue in sample, in mg/kg;
- V variability factor the factor applied to the composite residue to estimate the residue level in a high-residue unit; defined as the residue level in the 97.5th percentile unit divided by the mean residue level for the lot.

The large portion, the variability factor and the body weight values were taken from the Pesticide Residue Intake Model developed by The European Food Safety Authority (PRIMo model, rev.2), in which the large portion consumption data is provided by the Member States [6]. Calculated IESTI values were compared with toxicological reference values – the acute reference dose (ARfD) or, when this value is not provided, with the acceptable daily intake (ADI). ARfD values (and the ADI value for pyrimethanil) were taken from the EU Pesticide Database [7]. IESTI values below 100% of ARfD are considered as safe for humans.

Table 1. Pesticide residues detected in analysed samples

			1				Mean	
Crop	No. of analysed samples	No. of samples with residues < MRLs	No. of samples with residues > MRLs	Active substance (category)	No. of positive samples	Range min– max or value [mg/kg]	(medium- bound option) ± SD [mg/kg]	MRL [mg/ kg]
				Fruits		•		
Apple	3	1	0	captan (F)	1	<0.02-0.04	0.02 ± 0.02	3.0
Apple	5		0	pirimicarb (I)	1	<0.01-0.03	0.01 ± 0.01	2.0
				captan ^a (F)	2	<0.02-0.59	0.05 ± 0.14	4.0
Apricot	16	3	0	cypermethrin (I)	1	<0.01-0.03	0.01 ± 0.01	2.0
				dithiocarbamates ^a (F)	1	<0.05-0.43	0.05 ± 0.10	2.0
			0	difenoconazole (F)	1	<0.01-0.04	0.01 ± 0.01	0.2
Black currant	7	2		dithiocarbamates (F)	1	<0.05-0.73	0.13±0.27	5.0
				trifloxystrobin (F)	1	<0.01-0.01	0.01 ± 0.00	1.0
		5	0	captan (F)	3	<0.02-0.14	0.04 ± 0.05	5.0
Cherry	7			difenoconazole (F)	2	<0.01-0.05	$0.02{\pm}0.02$	0.3
				tebuconazole (F)	1	<0.02-0.27	$0.04{\pm}0.10$	1.0
				triadimenol (F)	3	<0.01-0.03	0.01 ± 0.01	0.1
Gooseberry	1	1	0	difenoconazole (F)	1	0.03	_	0.1
Gooseberry				trifloxystrobin (F)	1	0.05	_	1.0
	5	3	0	azoxystrobin ^a (F)	1	<0.01-0.02	0.01 ± 0.01	2.0
				cyprodinil (F)	1	<0.01-0.12	0.03 ± 0.05	3.0
Grape (table)				dithiocarbamates (F)	1	<0.05-0.11	0.04 ± 0.04	5.0
				folpet ^a (F)	2	<0.01-0.22	0.05 ± 0.09	0.02
				pyrimethanil (F)	1	<0.01-0.30	0.06 ± 0.13	5.0
Decel	8	1	0	captan ^a (F)	1	<0.02-0.04	0.01 ± 0.01	4.0
Peach	0	1	0	pirimicarb ^a (I)	1	<0.01-0.02	0.01 ± 0.01	2.0
Raspberry				boscalid (F)	11	<0.01-1.04	0.07 ± 0.18	10.0
		17	1	captan ^a (F)	1	<0.02-0.02	0.01 ± 0.00	10.0
				cyprodinil (F)	6	<0.01-0.40	0.04 ± 0.10	3.0
	47			fenazaquin ^{a, b} (I)	1	<0.01-0.06	0.01 ± 0.01	0.01
				fenhexamid (F)	2	<0.05-1.42	0.07 ± 0.23	10.0
				fludioxonil (F)	4	<0.01-0.32	0.03 ± 0.08	5.0
				folpet ^a (F)	1	<0.01-0.28	0.01 ± 0.04	10.0
				iprodione (F)	3	<0.02-1.42	$0.04{\pm}0.21$	30.0
				pyrimethanil (F)	9	<0.01-0.23	0.02 ± 0.04	10.0
				pyraclostrobin (F)	4	<0.02-0.20	0.02 ± 0.04	3.0
				spirodiclofen (I)	2	<0.01-0.04	0.01 ± 0.01	0.02

1 1				1		0.01.0.00		
	2			cypermethrin (I)	1	<0.01-0.03	0.02±0.02	0.05
Red currant		1	0	difenoconazole (F)	1	<0.01-0.01	0.01±0.00	0.2
				dithiocarbamates (F)	1	<0.05-3.60	1.81±2.53	5.0
				trifloxystrobin (F)	1	<0.01-0.25	0.13±0.17	1.0
				azoxystrobin (F)	1	<0.01-0.02	0.01±0.00	10.0
				boscalid (F)	7	<0.01-0.17	0.03±0.04	10.0
			0	cyprodinil (F)	6	<0.01-0.26	0.03±0.06	5.0
Strawberry	16	12		difenoconazole (F)	1	<0.01-0.02	0.01±0.00	0.4
	10			dithiocarbamates (F)	1	<0.05-0.37	0.05±0.09	10.0
				fludioxonil (F)	6	<0.01-0.18	0.02 ± 0.04	4.0
				pyrimethanil (F)	2	<0.01-0.06	0.01 ± 0.02	5.0
				tetraconazole (F)	2	<0.01-0.01	0.01 ± 0.00	0.2
				boscalid (F)	1	<0.01-0.04	0.01±0.01	4.0
				captan ^a (F)	1	<0.02-0.09	0.02 ± 0.02	5.0
Sweet cherry	15	4	0	deltamethrin (I)	1	<0.01-0.02	0.01 ± 0.00	0.2
				difenoconazole (F)	1	<0.01-0.01	0.01 ± 0.00	0.3
				iprodione (F)	1	<0.02-0.77	0.06 ± 0.20	10.0
				getables, herbs and cerea	ls			
Broccoli	9	1	0	chlorpyrifos (I)	1	<0.01-0.02	0.01 ± 0.01	0.05
Brussels sprout	2	1	0	chlorpyrifos (I)	1	<0.01-0.01	0.01 ± 0.00	0.05
Carrot	2	1	0	boscalid (F)	1	< 0.01-0.01	0.01±0.00	2.0
				chlorpyrifos ^a (I)	1	<0.01-0.01	0.01±0.00	0.1
Celeriac	8	2	0	azoxystrobin (F)	1	< 0.01-0.03	0.01±0.01	1.0
				chlorpyrifos (I)	1	<0.01-0.01	0.01±0.00	0.05
				difenoconazole (F)	1	<0.01-0.01	0.01±0.00	2.0
				linuron (H)	2	< 0.05-0.05	0.03±0.01	0.5
				propiconazole ^a (F)	1	< 0.01-0.02	0.01±0.01	0.05
		3	3	boscalid (F)	2	<0.01-1.10	0.07±0.27	10.0
D.11	1.5			chlorpyrifos ^{a, b} (I)	3	<0.01-0.66	0.08±0.18	0.05
Dill	17			iprodione ^a (F)	1	<0.02-0.10	0.02±0.02	20.0
· /				1' (1 1' h (TT)	2	<0.02-0.55	0.06±0.14	0.6
				pendimethalin ^b (H)	3	0.02 0.00		
Lettuce	4	1	0	cyprodinil (F)	3	<0.01-0.03	0.01±0.01	15.0
Lettuce	4	1	0	cyprodinil (F)			0.01±0.01 0.01±0.00	15.0 1.0
Lettuce	4	1	0	cyprodinil (F) azoxystrobin ^a (F)	1 1	<0.01-0.03 <0.01-0.01	0.01±0.00	1.0
Lettuce	4	1	0	cyprodinil (F) azoxystrobin ^a (F) boscalid (F)	1	<0.01-0.03		
	4			cyprodinil (F) azoxystrobin ^a (F) boscalid (F) chlorpyrifos ^a (I)	1 1 1	<0.01-0.03 <0.01-0.01 <0.01-0.07	0.01±0.00 0.01±0.02 0.01±0.00	1.0 3.0 0.05
Lettuce Parsley root		3	0	cyprodinil (F) azoxystrobin ^a (F) boscalid (F) chlorpyrifos ^a (I) linuron (H)	1 1 1 1 1	<0.01-0.03 <0.01-0.01 <0.01-0.07 <0.01-0.01 <0.05-0.05	0.01±0.00 0.01±0.02 0.01±0.00 0.03±0.01	1.0 3.0 0.05 0.2
				cyprodinil (F) azoxystrobin ^a (F) boscalid (F) chlorpyrifos ^a (I) linuron (H) propiconazole ^a (F)	1 1 1 1 1 3	<0.01-0.03 <0.01-0.01 <0.01-0.07 <0.01-0.01 <0.05-0.05 <0.01-0.03	0.01±0.00 0.01±0.02 0.01±0.00 0.03±0.01 0.01±0.01	1.0 3.0 0.05 0.2 0.05
				cyprodinil (F) azoxystrobin ^a (F) boscalid (F) chlorpyrifos ^a (I) linuron (H) propiconazole ^a (F) tebuconazole ^a (F)	1 1 1 1 1 3 1	<0.01-0.03 <0.01-0.01 <0.01-0.07 <0.01-0.01 <0.05-0.05 <0.01-0.03 <0.02-0.07	0.01±0.00 0.01±0.02 0.03±0.01 0.01±0.01 0.02±0.02	1.0 3.0 0.05 0.2 0.05 0.4
				cyprodinil (F) azoxystrobin ^a (F) boscalid (F) chlorpyrifos ^a (I) linuron (H) propiconazole ^a (F) tebuconazole ^a (F) trifloxystrobin ^a (F)	1 1 1 1 3 1 1	<0.01-0.03 <0.01-0.01 <0.01-0.07 <0.01-0.01 <0.05-0.05 <0.01-0.03 <0.02-0.07 <0.01-0.01	0.01±0.00 0.01±0.02 0.01±0.00 0.03±0.01 0.01±0.01 0.02±0.02 0.01±0.00	1.0 3.0 0.05 0.2 0.05 0.4 0.08
				cyprodinil (F)azoxystrobina (F)boscalid (F)chlorpyrifosa (I)linuron (H)propiconazolea (F)tebuconazolea (F)trifloxystrobina (F)alpha-cypermethrina (I)	1 1 1 1 1 3 1 1 1 1	<0.01-0.03 <0.01-0.01 <0.01-0.07 <0.05-0.05 <0.01-0.03 <0.02-0.07 <0.01-0.01 <0.01-0.04	0.01±0.00 0.01±0.02 0.01±0.00 0.03±0.01 0.01±0.01 0.02±0.02 0.01±0.00 0.01±0.01	1.0 3.0 0.05 0.2 0.05 0.4 0.08
				cyprodinil (F)azoxystrobina (F)boscalid (F)chlorpyrifosa (I)linuron (H)propiconazolea (F)tebuconazolea (F)trifloxystrobina (F)alpha-cypermethrina (I)azoxystrobin (F)	1 1 1 1 3 1 1 1 3	<0.01-0.03 <0.01-0.01 <0.01-0.07 <0.05-0.05 <0.01-0.03 <0.02-0.07 <0.01-0.01 <0.01-0.04 <0.01-0.10	0.01±0.00 0.01±0.02 0.03±0.01 0.02±0.02 0.01±0.00 0.01±0.00 0.01±0.01 0.01±0.02	1.0 3.0 0.05 0.2 0.05 0.4 0.08 1.0 5.0
				cyprodinil (F)azoxystrobina (F)boscalid (F)chlorpyrifosa (I)linuron (H)propiconazolea (F)tebuconazolea (F)trifloxystrobina (F)alpha-cypermethrina (I)azoxystrobin (F)bifenthrinc (I)	1 1 1 1 3 1 1 1 3 1 1 3 1	<0.01-0.03 <0.01-0.01 <0.01-0.07 <0.01-0.01 <0.05-0.05 <0.01-0.03 <0.02-0.07 <0.01-0.01 <0.01-0.04 <0.01-0.10	0.01±0.00 0.01±0.02 0.03±0.01 0.02±0.02 0.01±0.00 0.01±0.00 0.01±0.02 0.01±0.02	$\begin{array}{c} 1.0 \\ 3.0 \\ 0.05 \\ 0.2 \\ 0.05 \\ 0.4 \\ 0.08 \\ 1.0 \\ 5.0 \\ 0.05 \\ \end{array}$
Parsley root				cyprodinil (F)azoxystrobina (F)boscalid (F)chlorpyrifosa (I)linuron (H)propiconazolea (F)tebuconazolea (F)trifloxystrobina (F)alpha-cypermethrina (I)azoxystrobin (F)bifenthrinc (I)chlorpyrifosa (I)	$ \begin{array}{c} 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 3 \\ 1 \\ 1 \\ 1 \\ 1 \\ 3 \\ 3 \\ 1 \\ 3 \\ 3 \\ 1 \\ 3 \\ 3 \\ 1 \\ 3 \\ 3 \\ 1 \\ 3 \\ 3 \\ 1 \\ 3 \\ 1 \\ 3 \\ 1 \\ 3 \\ 1 \\ 3 \\ 1 \\ 3 \\ 1 \\ 3 \\ 1 \\ 3 \\ 1 \\ 3 \\ 1 \\ 3 \\ 1 \\ 3 \\ 1 \\ 3 \\ 1 \\ 3 \\ 1 \\ 3 \\ 1 \\ 3 \\ 1 \\ 1 \\ 3 \\ 1 \\ 3 \\ 1 \\ 3 \\ 1 \\ 3 \\ 1 \\ 1 \\ 1 \\ 3 \\ 1 \\ 3 \\ 1 \\ 3 \\ 1 \\ 1 \\ 1 \\ 3 \\ 1 \\ 1 \\ 1 \\ 3 \\ 1 \\ 1 \\ 1 \\ 3 \\ 1 \\ $	<0.01-0.03 <0.01-0.01 <0.01-0.07 <0.05-0.05 <0.01-0.03 <0.02-0.07 <0.01-0.01 <0.01-0.04 <0.01-0.10 <0.01-0.10 <0.01-0.22	0.01±0.00 0.01±0.02 0.01±0.00 0.03±0.01 0.01±0.01 0.02±0.02 0.01±0.00 0.01±0.02 0.01±0.02 0.01±0.02	1.0 3.0 0.05 0.2 0.05 0.4 0.08 1.0 5.0 0.05 0.5
Parsley root	11	3	0	cyprodinil (F)azoxystrobina (F)boscalid (F)chlorpyrifosa (I)linuron (H)propiconazolea (F)tebuconazolea (F)trifloxystrobina (F)alpha-cypermethrina (I)azoxystrobin (F)bifenthrinc (I)chlorpyrifosa (I)cypermethrina (I)	1 1 1 1 3 1 1 3 1 3 1 3 1	<0.01-0.03 <0.01-0.01 <0.01-0.07 <0.05-0.05 <0.01-0.03 <0.02-0.07 <0.01-0.01 <0.01-0.04 <0.01-0.10 <0.01-0.10 <0.01-0.22 <0.01-0.12	0.01±0.00 0.01±0.02 0.03±0.01 0.02±0.02 0.01±0.00 0.01±0.00 0.01±0.02 0.01±0.02 0.01±0.02 0.02±0.05 0.01±0.03	$\begin{array}{c} 1.0 \\ 3.0 \\ 0.05 \\ 0.2 \\ 0.05 \\ 0.4 \\ 0.08 \\ 1.0 \\ 5.0 \\ 0.05 \\ 0.5 \\ 1.0 \\ \end{array}$
Parsley root				cyprodinil (F)azoxystrobina (F)boscalid (F)chlorpyrifosa (I)linuron (H)propiconazolea (F)tebuconazolea (F)trifloxystrobina (F)alpha-cypermethrina (I)azoxystrobin (F)bifenthrinc (I)chlorpyrifosa (I)cypermethrin (I)deltamethrin (I)	1 1 1 1 3 1 1 1 3 1 3 1 1 1 1	<0.01-0.03 <0.01-0.01 <0.01-0.07 <0.01-0.01 <0.05-0.05 <0.01-0.03 <0.02-0.07 <0.01-0.01 <0.01-0.04 <0.01-0.10 <0.01-0.10 <0.01-0.22 <0.01-0.12 <0.02-0.02	0.01±0.00 0.01±0.02 0.01±0.00 0.03±0.01 0.02±0.02 0.01±0.00 0.01±0.01 0.01±0.02 0.01±0.02 0.02±0.05 0.01±0.03 0.01±0.00	$\begin{array}{c} 1.0\\ 3.0\\ 0.05\\ 0.2\\ 0.05\\ 0.4\\ 0.08\\ 1.0\\ 5.0\\ 0.05\\ 0.5\\ 1.0\\ 0.5\\ 1.0\\ 0.5\\ \end{array}$
Parsley root	11	3	0	cyprodinil (F)azoxystrobina (F)boscalid (F)chlorpyrifosa (I)linuron (H)propiconazolea (F)tebuconazolea (F)trifloxystrobina (F)alpha-cypermethrina (I)azoxystrobin (F)bifenthrinc (I)chlorpyrifosa (I)cypermethrin (I)deltamethrin (I)difenoconazole (F)	$ \begin{array}{r} 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 3 \\ 1 \\ $	<0.01-0.03 <0.01-0.01 <0.01-0.07 <0.05-0.05 <0.01-0.03 <0.02-0.07 <0.01-0.01 <0.01-0.04 <0.01-0.10 <0.01-0.10 <0.01-0.22 <0.01-0.12 <0.02-0.02 <0.01-0.02	0.01±0.00 0.01±0.02 0.01±0.00 0.03±0.01 0.01±0.01 0.02±0.02 0.01±0.00 0.01±0.02 0.01±0.02 0.02±0.05 0.01±0.03 0.01±0.00 0.01±0.00	$\begin{array}{c} 1.0 \\ 3.0 \\ 0.05 \\ 0.2 \\ 0.05 \\ 0.4 \\ 0.08 \\ 1.0 \\ 5.0 \\ 0.05 \\ 0.5 \\ 1.0 \\ 0.5 \\ 1.0 \\ 0.5 \\ 2.0 \\ \end{array}$
Parsley root	11	3	0	cyprodinil (F)azoxystrobina (F)boscalid (F)chlorpyrifosa (I)linuron (H)propiconazolea (F)tebuconazolea (F)trifloxystrobina (F)alpha-cypermethrina (I)azoxystrobin (F)bifenthrinc (I)chlorpyrifosa (I)cypermethrina (I)deltamethrina (I)deltamethrina (I)difenoconazole (F)iprodione (F)	1 1 1 1 3 1 3 1 3 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	<0.01-0.03 <0.01-0.01 <0.01-0.07 <0.01-0.01 <0.05-0.05 <0.01-0.03 <0.02-0.07 <0.01-0.01 <0.01-0.04 <0.01-0.10 <0.01-0.10 <0.01-0.12 <0.02-0.02 <0.01-0.02 <0.01-0.02	0.01±0.00 0.01±0.02 0.03±0.01 0.02±0.02 0.01±0.00 0.01±0.00 0.01±0.02 0.01±0.02 0.02±0.05 0.01±0.03 0.01±0.00 0.01±0.00 0.01±0.00 0.01±0.00	$\begin{array}{c} 1.0 \\ 3.0 \\ 0.05 \\ 0.2 \\ 0.05 \\ 0.4 \\ 0.08 \\ 1.0 \\ 5.0 \\ 0.05 \\ 0.5 \\ 1.0 \\ 0.5 \\ 2.0 \\ 0.7 \\ \end{array}$
Parsley root	11	3	0	cyprodinil (F)azoxystrobina (F)boscalid (F)chlorpyrifosa (I)linuron (H)propiconazolea (F)tebuconazolea (F)trifloxystrobina (F)alpha-cypermethrina (I)azoxystrobin (F)bifenthrinc (I)chlorpyrifosa (I)cypermethrin (I)deltamethrin (I)difenoconazole (F)iprodione (F)lambda-cyhalothrina (I)	1 1 1 1 3 1 3 1 3 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	<0.01-0.03 <0.01-0.01 <0.01-0.07 <0.01-0.01 <0.05-0.05 <0.01-0.03 <0.02-0.07 <0.01-0.01 <0.01-0.04 <0.01-0.10 <0.01-0.10 <0.01-0.12 <0.02-0.02 <0.02-0.02 <0.02-0.10 <0.01-0.02	0.01±0.00 0.01±0.02 0.01±0.00 0.03±0.01 0.02±0.02 0.01±0.00 0.01±0.01 0.01±0.02 0.02±0.05 0.01±0.03 0.01±0.00 0.01±0.00 0.01±0.00 0.02±0.02 0.01±0.00	$\begin{array}{c} 1.0\\ 3.0\\ 0.05\\ 0.2\\ 0.05\\ 0.4\\ 0.08\\ 1.0\\ 5.0\\ 0.05\\ 0.5\\ 1.0\\ 0.5\\ 2.0\\ 0.7\\ 1.0\\ \end{array}$
Parsley root	11	3	0	cyprodinil (F)azoxystrobina (F)boscalid (F)chlorpyrifosa (I)linuron (H)propiconazolea (F)tebuconazolea (F)trifloxystrobina (F)alpha-cypermethrina (I)azoxystrobin (F)bifenthrinc (I)chlorpyrifosa (I)cypermethrina (I)deltamethrina (I)deltamethrina (I)difenoconazole (F)iprodione (F)	1 1 1 1 3 1 3 1 3 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	<0.01-0.03 <0.01-0.01 <0.01-0.07 <0.01-0.01 <0.05-0.05 <0.01-0.03 <0.02-0.07 <0.01-0.01 <0.01-0.04 <0.01-0.10 <0.01-0.10 <0.01-0.12 <0.02-0.02 <0.01-0.02 <0.01-0.02	0.01±0.00 0.01±0.02 0.03±0.01 0.02±0.02 0.01±0.00 0.01±0.00 0.01±0.02 0.01±0.02 0.02±0.05 0.01±0.03 0.01±0.00 0.01±0.00 0.01±0.00 0.01±0.00	$\begin{array}{c} 1.0 \\ 3.0 \\ 0.05 \\ 0.2 \\ 0.05 \\ 0.4 \\ 0.08 \\ 1.0 \\ 5.0 \\ 0.05 \\ 0.5 \\ 1.0 \\ 0.5 \\ 2.0 \\ 0.7 \\ \end{array}$

No 3

Tomato				azoxystrobin (F)	4	<0.01-0.03	0.01 ± 0.01	3.0
	20		0	boscalid (F)	2	<0.01-0.21	$0.02{\pm}0.05$	3.0
				chlorpyrifos ^a (I)	1	<0.01-0.11	0.01±0.02	0.5
		8		chlorothalonil (F)	2	<0.01-0.01	0.01±0.00	6.0
				difenoconazole (F)	2	<0.01-0.02	0.01±0.00	2.0
				fenamidone (F)	1	<0.02-0.04	0.01±0.01	1.0
				iprodione (F)	1	<0.02-0.98	0.06±0.22	5.0
Wheat	10	1	0	pirimiphos-methyl (I)	1	<0.01-0.01	0.01±0.00	5.0

SD - Standard Deviation; MRLs - maximum residue levels; I - insecticide, F - fungicide, H - herbicide.

^a Active substance contained in plant protection products not approved for a given crop.

^b Pesticide residue above MRL.

° No plant protection product containing this active substance has been authorized for use in Poland.

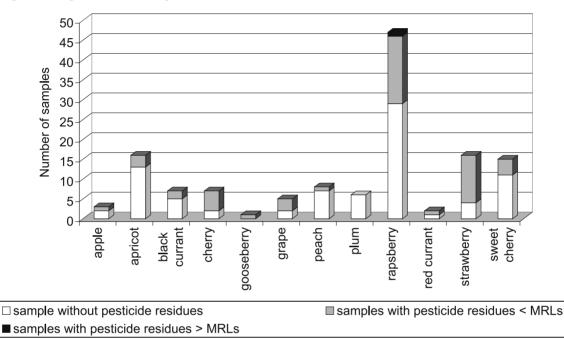


Figure 1. Presence of pesticide residues in specific groups of fruit

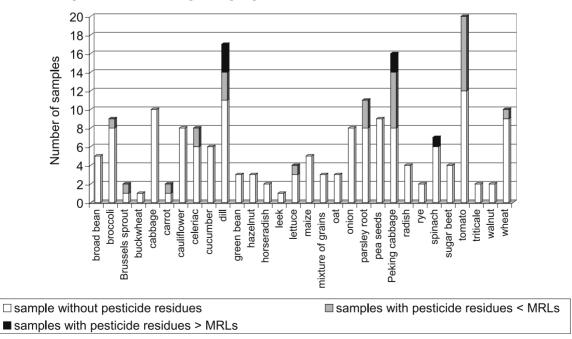


Figure 2. Presence of pesticide residues in specific groups of vegetables, herbs, seeds, nuts and cereals

No 3

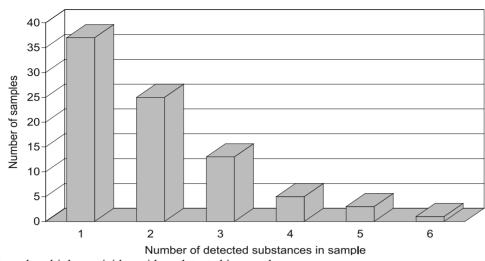


Figure 3. Single and multiple pesticide residues detected in samples

Table 2. International Estimated Short-Term Intake (IESTI) for samples with MRLs violations

		Concentration [mg/kg]	MRL [mg/kg]	ARfD [mg/kg bw]	Model	Λ	Adults			Children				
Сгор	Active substance (category)						LP [kg/ person]	body weight	IESTI [mg/kg bw day]	Intake [% ARfD]	LP [kg/ person]	body weight	IESTI [mg/kg bw day]	Intake [% ARfD]
Dill	chlorpyrifos (I)	0.66	0.05	0.005	1	1	0.0083	62.80	0.00009	1.745	0.1021	17.80	0.00379	75.715
Peking cabbage	pyrimethanil (F)	0.04	0.01	0.17ª	2b	5	0.4500	63.00	0.00143	0.840	0.1270	17.10	0.00149	0.874
Raspberry	fenazaquin (I)	0.06	0.01	0.1	1	1	0.2500	63.00	0.00024	0.238	0.0906	16.15	0.00034	0.337
Spinach	dithiocarbamates ^b (thiram) (F)	2.21	0.05	0.6	1	1	0.5630	63.00	0.01976	3.293	0.4023	17.80	0.04996	8.327

MRLs - maximum residue levels, ARfD - acute reference dose, I - insecticide, F - fungicide, H - herbicide, v - variability factor, LP - large portion, bw - body weight,

^a As the ARfD value is not available, the acceptable daily intake (ADI) value is given.

^b For the risk assessment, CS, level was recalculated as thiram using conversion factor of 1.579.

RESULTS

In 2015, a total of 328 samples: 133 samples of fruit, 130 samples of vegetables, 33 samples of cereals, 17 samples of herbs, 10 samples of seeds and 5 samples of nuts, collected from the south-eastern region of Poland were analysed for the presence of pesticide residues. Pesticide residues were detected in 84 (25.6%) analysed samples while in 7 (2.1%) samples they exceeded MRLs. Violations of MRLs concerned 2 samples of Peking Cabbage, 3 samples of dill, 1 sample of raspberry and 1 sample of spinach. The pesticide residues were most often found in: fruit (38.3% of all fruit samples), herbs (35.3%) and vegetables (20.0%) (Table 1, Figure 1 and 2).

Of 243 analysed substances, 31 were detected in the samples: 19 fungicides, 10 insecticides, and 2 herbicides.

The most commonly detected fungicides included: boscalid (7.6%), cyprodinil (4.3%), pyrimethanil (4.3%), azoxystrobin (3.4%) and difenoconazole (3.4%), while chlorpyrifos (3.7%) was the most commonly found

insecticide, and its residues were found only in vegetable and dill samples. Residues of herbicides were found only in 6 samples: linuron was detected in 3 samples (2 samples of celery root and 1 sample of parsley root) and pendimethalin was found in 3 samples of dill (Table 1). In 22 (6.7%) samples, analyses also revealed presence of 34 substances contained in plant protection products not approved for a given crop (Table 1). These substances can be used in Poland, but for other crops. In one sample of Peking cabbage bifenthrin was detected. This active substance is approved in the EU, but no plant protection product containing this active substance has been authorized for use in Poland.

Over half of the samples with residues contained multiple residues, with up to 6 in one sample (Figure 3). Those multiple residues were found most frequently in Peking cabbage, raspberry, strawberry, tomato, and parsley root.

Pesticide residues were not detected in the following samples (number of analysed samples in the brackets): barley (8), broad bean (5), buckwheat

(1), cabbage (10), cauliflower (8), cucumber (6), green bean (3), hazelnut (3), horseradish (2), leek (1), maize (5), mixture of grains (3), oat (3), onion (8), pea seeds (9), plum (6), radish (4), sugar beet (4), rye (2), triticale (2), and walnut (2).

The acute exposure was estimated for samples with MRLs exceeded. For adults, the maximum value was obtained for consumption of spinach with dithiocarbamate residues, equal to 3.3% ARfD. For children, consumption of this food could result in the acute exposure at the level of 8.3 % ARfD, while in this vulnerable group of consumers, the maximum value of 75.7% ARfD was determined for consumption of dill. As PRIMo model does not provide large portion data for dill consumption, values for celery leaves were used, for which the same MRLs set up apply. The IESTI calculated for dill is overestimated, especially for children (LP = 0.1021 kg/day). In calculations of IESTI for Peking cabbage sample the ADI value was used, because the ARfD value for pyrimethanil is not available. IESTI values were very low and equal to 0.8% ADI for adults and 0.9% ADI for children. For the spinach sample with dithiocarbamate residues, CS₂ levels were recalculated as thiram using the conversion factor of 1.579, because plant protection products with this active substances were applied according to the sampling protocol (Table 2).

None of the analyzed samples could pose the acute health risk to adults or children.

DISCUSSION

Results of this study were interpreted in relation to MRLs requirements set in the EU regulations for products present in the market [2]. Moreover, the analysis verified whether plant protection products containing detected pesticides were approved for a given crop [16]. This study has a preventive nature, protecting the market against products posing a risk to the consumer and not meeting the requirements of relevant legislation. It also aims at verifying whether the producers correctly apply the principles of the Good Agriculture Practices (GAP).

Pesticide residues were detected in 84 (25.6%) analysed samples. This rate is similar to monitoring results obtained for south-eastern Poland (27.9% samples with residues) and for whole country (32.4%) in 2013 [11, 23]. The percentage of raw agricultural products with pesticide residues is lower than percentage of food available on the retail market in Poland (39.7%), where imported food products with a high pesticide content, such as citrus fruits or tea, are also available [21].

MRLs violations were at a similar level (2.1%) as reported by *Nowacka* et. al and *Struciński* et al. (2.0% and 1.8%, respectively) [11, 21], and slightly higher

than the percentage reported by European countries in 2012 and 2013 (1.4%) [19, 20].

Other authors also detected fungicides as the most common residue, followed by insecticide and herbicide residues. Types of detected substances are also very similar [11, 21].

In recent years, an increase in the number of samples containing an active substance present in plant protection products not approved for a given crop is observed, due to reductions in the number of approved plant protection products and changes in the scope of their application [11, 23, 24].

The calculated acute exposure did not exceeded 100% ARfD for any samples with violated MRLs, but results reported by others authors imply that such exposure cannot be excluded. Calculations performed in 2011–2015 by the Risk Assessment Team at the National Institute of Public Health – National Institute of Hygiene shows that out of 127 analytical results non-compliant to a respective MRL value, in 15 cases an estimated short-term exposure exceeded ARfD for children, who are the most vulnerable subpopulation of consumers (ranging from 102% to 2258%). This represents 11.8% of MRL non-compliances. In adults, the exposure expressed per kg of body weight is lower than in children, thus the estimated exposure exceeded ARfD value in 6 cases only (ranging from 100% to 2171%) [22].

Acute risk values calculated for raw agricultural commodities do not necessarily reflect the risk for a consumer that would be calculated for the same products present on market. Levels of pesticide residues in the product available for consumer may change, due to degradation processes.

CONCLUSIONS

- Pesticide residues were detected in 25.6% of analysed raw agricultural products samples, while in 7 samples (2.1%) they exceeded MRLs. Violations of MRLs concerned 2 samples of Peking Cabbage, 3 samples of dill, 1 sample of raspberry, and 1 sample of spinach.
- 2. The pesticide residues were most often found in: fruit (38.3% of all fruit samples), herbs (35.3%) and vegetables (20.0%).
- 3. The calculated acute exposure did not exceed 100% ARfD for any sample, but such exposure could not be excluded.
- 4. Monitoring of pesticide residues in the agricultural crops at premarket stage should be continued, to protect the market against the penetration by products with unacceptable residues of pesticides, and to protect consumers against the excessive exposure to pesticide residues.

Conflict of interest

The authors declare no conflict of interest.

Acknowledgements

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