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PESTICIDE RESIDUES AND ACUTE DIETARY RISK ASSESSMENT IN POLISH RAW FOOD (2005–2013)

POZOSTAŁOŚCI PESTYCYDÓW I OCENA OSTREGO RYZYKA W POLSKIEJ ŻYWNOŚCI POCHODZENIA ROŚLINNEGO (2005–2013)

Abstract: Food safety is very important for consumers. Fruits, vegetables and cereals are not only the major source of vitamins, minerals, fibre and energy, but can also be a source of many pollutants posing health hazards. Pesticides found in food are just examples of harmful substances affecting food safety. The objective of this paper was to assess short-term health risks assessment based on the concentration of pesticide residues found in agricultural products collected from national food control systems during the period 2005–2013 at the Official Pesticide Residue Laboratory in Bialystok in frame of RASFF (Rapid Alert System for Food and Feed) system. During nine-year testing, totally 2021 fruits, vegetables and cereals were sampled from the north-eastern and central part of Poland and analyzed by gas and liquid chromatography and spectroscopic technique for the presence of 188 active substances of pesticides. Contaminations were not detected in 65.3 % of samples, 31.9 % samples contained residues below the maximum residue levels (MRLs), while 2.8 % of tested samples exceeded MRLs. Among 81 RASFF notifications noted, the greatest number of irregularities concerned exceeding the values of MRL – 41, in 27 cases it was found that a pesticide was not used in accordance with the registration of plant protection product. The highest estimated values for short-term exposure were obtained for plum for the dimethoate, and in the group of toddlers it was 94.6 % ARfD (Acute Reference Dose), and in the adult group it was 23.3 % ARfD.

Keywords: Active substances of pesticides, north-eastern Poland, RASFF notification, food safety

One of the most important factors determining human health is a proper diet, which is a prerequisite for our growth, both physical and mental, general well-being. While a wholesome meal is significant to a consumer's health, one should also note the quality of the food eaten. Fruits and vegetables are key components of a healthy diet. They are

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low fat and low energy-dense foods, relatively rich in vitamins, minerals and other bioactive compounds, as well as being a good source of fibre. A high intake of fruits and vegetables in the diet is positively associated with the prevention of cardiovascular disease, cancer, diabetes and osteoporosis. However, fruits, vegetables and cereals are not only the major source of vitamins, minerals, fibre and energy, but can also be a source of many pollutants posing health hazards. Pesticides, heavy metal, and mycotoxins found in food are just a few examples of harmful substances affecting food safety [1–3]. Other hazards include food-poisoning bacteria (including Salmonella) [4–6], but also an inappropriate diet which can lead to overweight, obesity [7]. Data from literature confirm that one of the drawbacks of using plant protection products (p.p.p.) is their potential risk to human health due to the presence of active substances of pesticide residue in fresh food products [8, 9]. Pesticides have been associated with a wide range of ill health symptoms, ranging from short-term headaches and nausea to cancer, reproductive harm, and endocrine disruption [10]. Moreover, extensive or inappropriate use of p.p.p. by farmers can lead to contamination of various ecosystems [11].

In modern times, the issue of the safety and quality of food is a major public concern, and, if neglected, would seriously endanger consumers' health. Food safety remains a key challenge for the European Union (EU) agriculture, especially when, according to Food and Agriculture Organization of the United Nations (FAO), before 2050 the demand for food will have doubled (especially in countries such as India and China) [12].

The Rapid Alert System for Food and Feed (RASFF) is a significant element in managing food safety. Created by the European Commission in accordance with European Parliament Regulation No. 178/2002 [13] on food law, it is meant to provide a quick response about dangerous food substances that fail to meet with safety requirements. RASFF members include: The European Commission (network administration authority), EU member states, European Food Safety Authority (EFSA), EU candidate countries, other countries as well as international organizations. In RASFF system, a member state sets up a national contact point gathering information on food and feed that happen to pose direct or indirect danger to health. The information is then passed on to the European Commission, which immediately notifies other RASFF members [14].

In Poland, procedures and requirements (in accordance with EU regulations) necessary to ensure food safety, are determined by the Act of 25th August, 2006 [15]. Under this act, relevant inspection authorities and food producers are obliged to monitor active substances concentration levels in food, and then to compare the results with the maximum residue levels (MRLs). In aspect of pesticides, to RASFF system samples with residues greater than the maximum residue levels (the residue is from a pesticide that is registered in Poland, but the amount is greater than the MRL set by EFSA), samples with residues of unregistered pesticides (the residue is from a pesticide that is not registered in Poland for any use) and/or "off label" residues (the residue is from a pesticide that is registered for some uses in Poland, but not for the crop on which it was used) are reported. The RASFF system has been in operation in Poland since 2004, and is coordinated by the Chief Sanitary Inspector (GIS). Notifications provided through RASFF may include information on market notifications (two types: alert and information notifications) and border rejections.

The objective of this paper is to evaluate the quality of local raw fruits, vegetables and cereals in aspect of active substances presence on the basis of RASFF notifications made during the period 2005–2013 at the Laboratory of Pesticide Residue of the Plant Protection Institute – National Research Institute in Bialystok and to evaluate on that basis the consumer's risk related to short-term exposure.

Materials and methods

Standards

Pesticides (188 active substances) were obtained from Dr. Ehrenstorfer Laboratory (Germany). Standard stock solutions (purity for all standards >95 %) of various concentrations were prepared in acetone and stored in dark below 4 ^{o}C. The tests covered the determination of active substances of pesticides, from 93 in 2005 to 188 in 2013.

Reagents and chemicals

All reagents used were analytical grade. Acetone, *n*-hexane, diethyl ether, toluene, dichloromethane for pesticides residue analysis, florisil (60–100 mesh) and phosphate buffer pH = 8 were provided by J.T. Baker (Deventer, Holland). Acetonitrile, methanol, hydrochloric acid, sodium hydroxide, potassium hydroxide, zinc acetate dihydrategrade, anhydrous sodium acetate, anhydrous tin (II) chloride, ammonium iron (III) sulfate were purchased from POCH (Gliwice, Poland). Silica gel (230–400 mesh) and N,N-dimethyl-1,4-phenylenediammonium dichloride were obtained from Merck (Darmstadt, Germany). The anhydrous sodium sulfate was purchased from Fluka (Seelze-Hannover, Germany). Sodium sulfide nonahydrate and celite were supplied by Sigma-Aldrich (St. Louis, USA). Before use all sorbents were activated at 600 ^{o}C.

Samples

During 2005–2013, in the framework of the official testing of residues of plant protection products conducted by the Ministry of Agriculture and Rural Development, totally 2021 samples of fruits, vegetables, cereals and oilseeds were analyzed for active substances of pesticides. These samples were collected between May–November by the regional inspectors of Plant Protection and Seed according to a predetermined schedule for a given.

Analytical methods

Sample preparation was done using three techniques (Fig. 1): Multi Residue Method (MRM) and two Single Residue Methods (SRM), fully described in our earlier published work [16, 17, 18, 19]. These methods were validated and accredited in

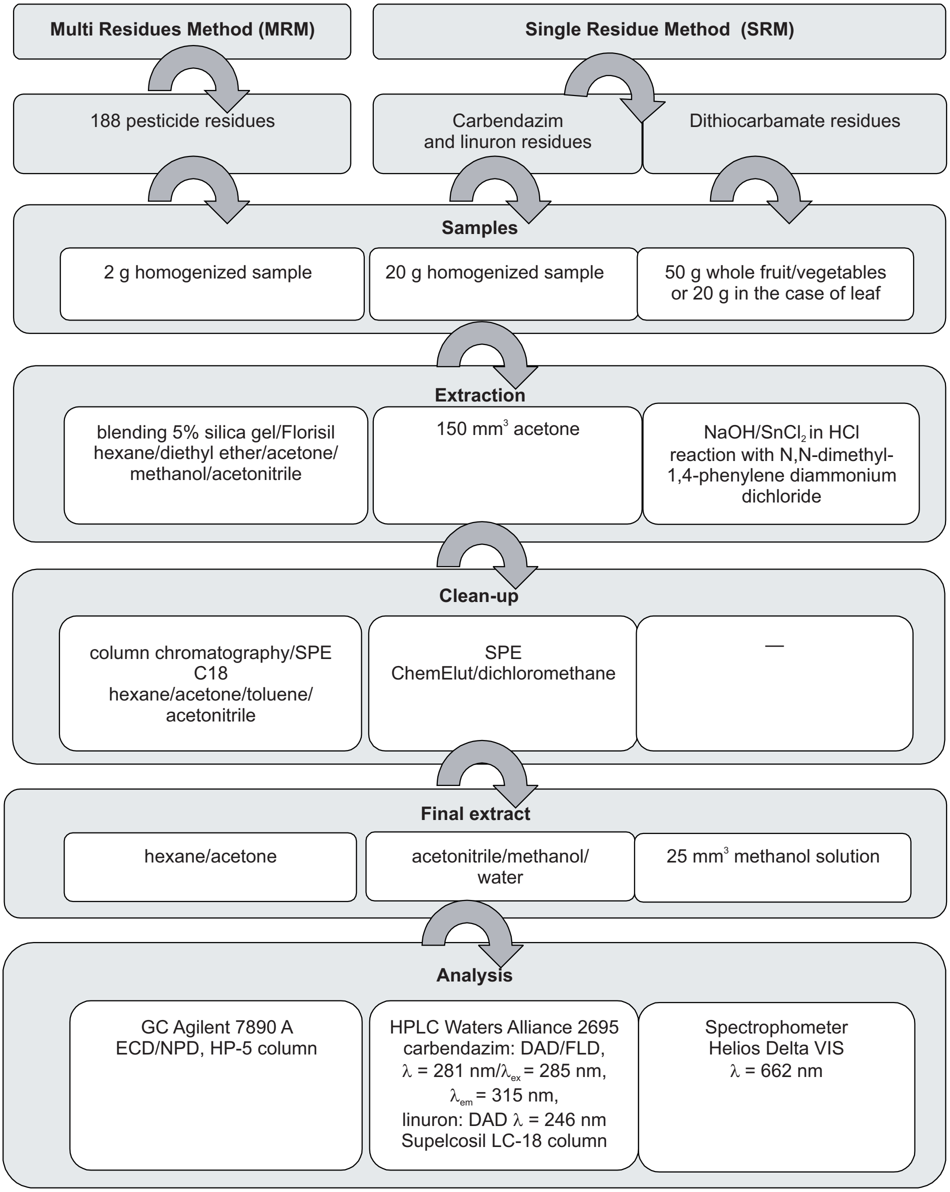

Fig. 1. Scheme of sample preparation procedures
Legend: MSPD – matrix solid phase dispersion; GC – gas chromatography; HPLC – high-performance liquid chromatography; ECD/NPD – electron capture detector/nitrogen phosphorus detector; DAD – diode array detector; FLD – fluorescence detector

accordance with PN-EN ISO/IEC 17025 [20] by the Polish Center of Accreditation, PCA.

Quality check

To be sure about the quality of results, the Laboratory has accreditation PN/EN ISO IEC 17025 and regularly take a part with satisfactory performance in external proficiency assessment schemes in proficiency testing schemes organized and run by the Food Analysis Performance Assessment Scheme (FAPAS; Central Science Laboratory in York) and by the European Commission (University of Almeria). Participation in EC tests is mandatory for all Official Laboratory undertaking the analysis of these commodities for the official controls on pesticide residues, using of validated methods and the employment of suitably qualified persons to carry out analysis.

Risk assessment

Non-compliances related with exceeding of MRLs was assessed in relation to national and EU legislation [21, 22], in the case of detection of active substance of forbidden p.p.p. on the market according to plant protection act [23]. The evaluation was conducted for the general population of consumers (adults) and critical population, children aged from 1.5 to 4 years, as the group most vulnerable to the effects of exposure to active substances of pesticide residues.

Short-term exposure was estimated by comparing single intake of the highest detected residue of plant protection products to a set volume ARfD (Acute Reference Dose).

Short-term exposure was calculated according to the following formula [24]:

$$ESTI = \sum \frac{F \cdot HR \cdot P}{\text{mean\_ weight}}$$

where: *ESTI* – Estimate of Short-Term Intake;
F – full portion consumption data for the commodity unit;
HR_P – the highest residue level.

The risk assessment of consumer health exposure associated with consumption of crops containing pesticide based on the available epidemiological studies conducted for the two sub-populations in the database of food consumption: the British model, Pesticides Safety Directorate [25], consumption at 97.5 percentile. In Poland there is no complete data for this populations, hence the need to use other available sources. Values of ARfD are elaborated by European Food Safety Authority (EFSA) of EU [26] or Federal Institute for Risk Assessment (BfR), Germany [27].

Results and discussion

In 2005–2013, 2021 crop samples were tested. Contaminations were found in 34.7 % of the samples. 31.9 % samples contained residues below the maximum residue levels (MRLs), while 2.8 % of tested samples exceeded MRLs and in 65.3 % were not detected. Detailed data referring to particular years are shown in Table 1.

Table 1

Occurrence of pesticide residues in samples analyzed during the years 2005–2013

Year	Samples without residues	% to total samples	Samples with detected residues below MRL	% to total samples	Samples with detected residues above MRL	% to total samples
2005	161	8.0	108	5.3	4	0.2
2006	164	8.1	51	2.5	3	0.1
2007	129	6.4	79	3.9	6	0.3
2008	182	9.0	76	3.8	18	0.9
2009	173	8.6	90	4.5	5	0.2
2010	198	9.8	63	3.1	6	0.3
2011	90	4.5	33	1.7	3	0.1
2012	95	4.7	22	1.1	0	0
2013	128	6.3	120	5.9	12	0.6
Total	1320	65.3	644	31.9	57	2.8

During the researched period from among the 81 notifications noted at the Laboratory of Pesticide Residue in Bialystok (Fig. 2), the largest number of notifications was made in the year 2008 – 21. In 2013, seventeen RASFF notifications were made, and it was the second highest score in 9-year period. Year 2012 was the only year when no notifications were recorded.

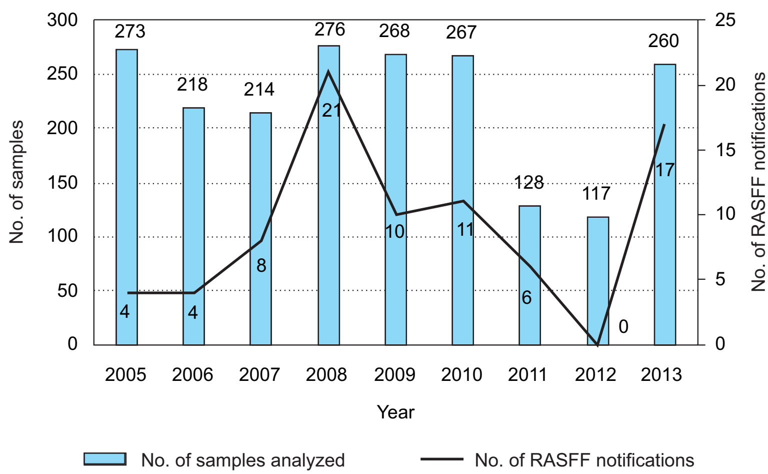

Fig. 2. RASFF notifications in 2005–2013

The greatest number of irregularities concerned exceeding the values of MRL – 41, in 27 cases it was found that a pesticide was not used in accordance with the registration, and in 13 cases simultaneous excess of MRL and the use of non-registered pesticides have occurred.

Data of the National Sanitary Inspectorate had shown that, the National Contact Point in 2013, during the official control in the country 270 RASFF notifications received (in 2012 – 443, in 2011 – 384, in 2010 – 219, in 2009 – 248, in 2008 – 292, in 2007 – 257, in 2006 – 193, in 2005 – 102 notifications) [27]. The number of notifications reported during the official control increased systematically until 2012 (with the exception of the years 2009 and 2010, when a slight decrease was recorded), and then in 2013 the number decreased by ca. 27 %. The decrease in the number of notifications may be indicative of an improving quality of agricultural-food products present in the trade volume within the territory of our country [14] or it may be an isolated occurrence. As follows from RASFF Annual Report [28], Poland sent 120 notifications in 2013, which places it on the 7th position among the notifying entities. The largest number of notifications was sent to the European Commission in 2013 by Contact Points situated in Italy (534 notifications), in Germany (331 notifications), United Kingdom (327 notifications), Netherlands (264 notifications) and France (249 notifications). Petroczi et al [29] revealed, that in the years 2000–2009, 60 % of the RASFF notifications were made by Italy, Germany, the UK and Spain.

The most frequent hazards reported to the RASFF system in north-eastern Poland in 2013 (similarly to the year 2010, 2009, 2008, 2007, 2006, 2005) included fruit contamination (Fig. 3). Only in 2011 more notifications for vegetables were recorded.

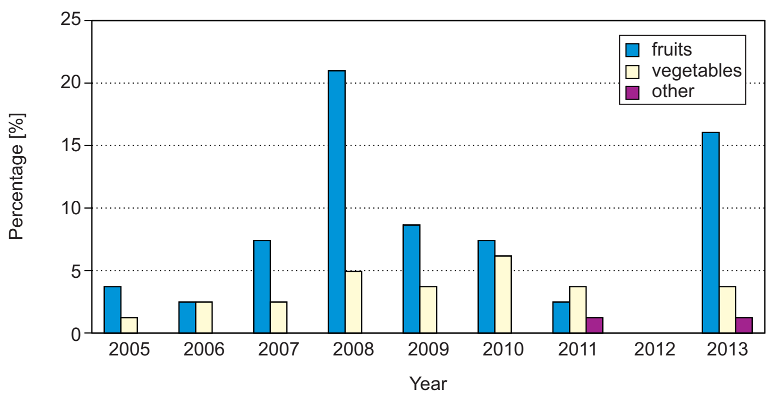

Fig. 3. Number of notifications according to the food products in 2005–2013

Notifications of the fruits constituted 69.1 %, vegetables and cereals, oilseeds were 28.4 % and 6.5 %, respectively. The results another authors confirm that fruits are the group of crops where the producers use chemical p.p.p. most frequently [30, 31]. The largest number of notifications concerned samples of currants (34.6 %) and apples (22.3 %). Currants belong to the group of fruits where exceeding of the MRL [32] and using of the unauthorised chemical p.p.p. were the most frequently detected. The maximum residue level was exceeded in 25 currant samples, including alpha–cypermethrin (two samples: 0.08; 0.1 mg/kg, MRL = 0.05 mg/kg), cypermethrin (three samples: 0.09; 0.14; 0.22 mg/kg, MRL = 0.05 mg/kg), difenoconazole (one sample: 0.43 mg/kg, MRL = 0.05 mg/kg), endosulfan (one sample: 0.28 mg/kg, MRL = 0.05

mg/kg), esfenvalerate (two samples: 0.1; 0.15 mg/kg, MRL = 0.02 mg/kg), fenazaquin (ten samples: 0.03; 0.04; 0.05; 0.09; 0.11; 0.13; 0.19; 0.22; 0.24; 0.25 mg/kg, MRL = 0.01 mg/kg in 2007–2008 and MRL = 0.1 mg/kg in 2009–2013), fenitrothion (four samples: 0.03; 0.02 mg/kg, MRL = 0.01 mg/kg), flusilazole (one sample: 0.05 mg/kg, MRL = 0.02 mg/kg), procymidone (one sample: 0.024 mg/kg, MRL = 0.02 mg/kg) and tolylfluanid (one sample: 0.03 mg/kg, MRL = 0.02 mg/kg). The use of unauthorised products by producers were connected mainly with the lack of appropriate products registered for protection of a given type of crops. For example, from the group of fungicides: flusilazole (1), azoxystrobin (1) and tolylfluanid (1) in currants were detected. From the group of insecticides: fenazaquin (3) and endosulfan (2) were detected. These results confirm problems with the chemical protection of minor crops [33]. Moreover, the large number of notifications concerning apples results, among other factors, from the fact that this type of fruit due to its predominance in consumption is one of the most frequently tested product [34–41].

In total, 30 different active substances of pesticides, belonging to 18 different chemical groups, were found (Table 2).

Table 2

Active substances of pesticides detected in analysed samples from north-eastern and central Poland

<table>
<tr><th>Category</th><th>Chemical group</th><th>Active substance name</th><th>Samples</th><th>Range [mg/kg]</th><th>Commodity</th></tr>
<tr><td rowspan="14">A/I</td><td>Unclassified</td><td>Fenazaquin</td><td>13</td><td>0.030–0.250</td><td>Currant, apple</td></tr>
<tr><td rowspan="6">Organophosphate</td><td>Diazinon</td><td>8</td><td>0.010–0.270</td><td>Lettuce, apple, radish, mushroom, pear, carrot</td></tr>
<tr><td>Fenitrothion</td><td>7</td><td>0.020–0.060</td><td>Currant, apple</td></tr>
<tr><td>Chlorpyrifos</td><td>6</td><td>0.010–0.560</td><td>Apple, broccoli, carrot, parsnip</td></tr>
<tr><td>Dimethoate</td><td>6</td><td>0.020–0.320</td><td>Apple, plum, pear, cucumber</td></tr>
<tr><td>Phosalone</td><td>3</td><td>0.030–0.250</td><td>Apple</td></tr>
<tr><td>Pirimiphos-methyl</td><td>1</td><td>0.240</td><td>Rape</td></tr>
<tr><td rowspan="2">Organochlorine</td><td>Endosulfan</td><td>2</td><td>0.030–0.280</td><td>Currant</td></tr>
<tr><td>DDT</td><td>1</td><td>0.093</td><td>Lupin</td></tr>
<tr><td rowspan="4">Pyrethroid</td><td>Cypermethrin</td><td>3</td><td>0.090–0.220</td><td>Currant</td></tr>
<tr><td>Alpha-cypermethrin</td><td>2</td><td>0.080–0.100</td><td>Currant</td></tr>
<tr><td>Esfenvalerate</td><td>2</td><td>0.100–0.150</td><td>Currant</td></tr>
<tr><td>Bifenthrin</td><td>1</td><td>0.150</td><td>Mushroom</td></tr>
<tr><td rowspan="5">F</td><td rowspan="3">Triazole</td><td>Flusilazole</td><td>7</td><td>0.010–0.290</td><td>Currant, apple</td></tr>
<tr><td>Difenoconazole</td><td>2</td><td>0.270–0.430</td><td>Gooseberry, currant</td></tr>
<tr><td>Tebuconazole</td><td>1</td><td>0.070</td><td>Chinese cabbage</td></tr>
<tr><td>Dicarboximide</td><td>Procymidone</td><td>5</td><td>0.020–0.570</td><td>Currant, lettuce, strawberry, tomato</td></tr>
<tr><td>Anilinopyrimidine</td><td>Pyrimethanil</td><td>4</td><td>0.030–0.200</td><td>Apple, chinese cabbage</td></tr>
</table>

Table 2 contd.

Category	Chemical group	Active substance name	Samples	Range [mg/kg]	Commodity
F	Strobilurin	Azoxystrobin	3	0.050–0.060	Currant, cucumber, parsley root
	Carboxamide	Boscalid	3	0.060–0.230	Apple, pear, sour cherry
	Chloronitrile	Chlorothalonil	3	0.060–8.470	Tomato, chinese cabbage, parsley root
	Benzimidazole	Carbendazim	2	0.010–0.020	Mushroom
	Sulphamide	Tolylfluanid	2	0.030–0.490	Strawberry, currant
		Dichlofluanid	1	18.680	Lettuce
	Phthalimide	Captan	1	0.350	Sour cherry
	Anilinopyrimidine	Cyprodinil	1	0.090	Apple
	Morpholine	Dimethomorph	1	1.040	Tomato
	Hydroxyanilide	Fenhexamid	1	0.220	Sour cherry
	Strobilurin	Trifloxystrobin	1	0.020	Sour cherry
H	Dinitroaniline	Trifluralin	1	0.040	Carrot

I – Insecticide; F – Fungicide; H – Herbicide; A – Acaricide.

In our study, the most frequently detected group of active substances were insecticides, which comprised 58.3 % of all detections (fenazaquin, diazinon, fenitrothion, chlorpyrifos, dimethoate, phosalone, pirimiphos–methyl, endosulfan, DDT, cypermethrin, alpha-cypermethrin, esfenvalerate, bifenthrin). The largest number of notifications referred to the detection of fenazaquin (13) in samples of currants and apples. Fenazaquin is a non-systemic pesticide used to control mites and other related pests in fruits, vegetables and tea [42]. In turn, 8 concerned the detection of diazinon in samples of lettuce, apples, pears, carrots, mushrooms, radishes, which is a non-systemic organophosphate insecticide used to control pests in fruits, vegetables, ornamentals and other crops [43]. Flusilazole and fenitrothion were identified in 7 samples of currants and apples. Flusilazole is a systemic fungicide used to control fungal diseases in cereals, fruits, vegetables, and nuts [41]; fenitrothion is a non-systemic insecticide used to control various pests in fruit and other crops.

Table 3 shows details for each active substances of pesticides and groups with the same mode of action [44]. These data present carcinogenic properties of captan, procymidone and suggest that thirteen other compounds (bifenthrin, cypermethrin, dimethoate, DDT, endosulfan, boscalid, carbendazim, chlorothalonil, difenoconazole, flusilazole, tebuconazole, tolylfluanid, trifluralin) may have possible carcinogen effect.

Short-term exposure is shown in Table 4. The highest values of short-term exposure were obtained for plum, and for the group of toddlers it was 94.6 % ARfD, and for the adult group it was 23.3 % ARfD. In both cases these values did not exceed the acceptable 100 % threshold. In case of consumption other products, the short-term exposure (ARfD) didn't exceed: 60 % for the group of toddlers and 15 % for the adults.

Table 3

Active substances of pesticides found in samples with corresponding health effects

Substance group	Pesticide	Mode of action	Carcino-gen	Muta-gen	Endocrine disruptor	Reproduction/ development effects	Acetyl choline-sterazy inhibitor	Neuro-toxicant	Respiratory tract irritant	Skin irritant	Eye irritant
Acaricides/ Insecticides											
Pyrethroid	Alpha-cyprmethrin	Non-systemic with contact and stomach action. Sodium channel modulator.	—	—	?	—	X	—	V	V	X
	Bifenthrin	Contact and stomach action with some residual effect. Sodium channel modulator.	?	?	V	?	X	V	—	X	X
	Cyper-methrin	Non-systemic with contact and stomach action. Sodium channel modulator.	?	X	?	?	X	X	V	V	V
	Esfen-valerate	Contact and stomach action. Sodium channel modulator.	X	X	?	?	X	X	—	X	X
Organo-phosphate	Chlorpyrifos	Non-systemic with contact and stomach action. Acetylcholinesterase (AChE) inhibitor.	X	X	?	V	V	V	X	?	?
	Diazinon	Non-systemic with respiratory. Contact and stomach action. Acetylcholinesterase (AChE) inhibitor.	X	?	V	?	V	V	V	V	V
	Dimethoate	Systemic with contact and stomach action. Acetylcholinesterase (AChE) inhibitor.	?	X	?	V	V	X	—	X	V

Table 3 contd.

Substance group	Pesticide	Mode of action	Carcinogen	Mutagen	Endocrine disruptor	Reproduction/ development effects	Acetyl cholinesterazy inhibitor	Neurotoxicant	Respiratory tract irritant	Skin irritant	Eye irritant
Organophosphate	Fenitrothion	Non-systemic. Broad spectrum with contact and stomach action. Acetylcholinesterase (AChE) inhibitor.	X	X	V	—	V	X	—	V	X
	Phosalone	Non-systemic with contact and stomach action. Acetylcholinesterase (AChE) inhibitor.	X	—	—	—	V	V	V	V	V
	Pirimiphos-methyl	Broad-spectrum with contact and respiratory action. Acetylcholinesterase (AChE) inhibitor.	X	—	—	—	V	—	V	V	?
Organochlorine	DDT	Non-systemic stomach and contact action. Sodium channel modulator.	?	V	V	X	V	?	X	X	—
	Endosulfan	Non-systemic with contact and stomach action, acts as a non-competitive GABA antagonist.	?	V	?	—	X	V	—	—	—
Unclassified	Fenazaquin	A mitochondrial electron transport inhibitor with contact action.	X	—	X	?	X	—	V	X	X
Fungicides											
Anilinopyrimidine	Cyprodinil	Systemic. Absorbed through foliage. Inhibits protein synthesis.	X	X	—	?	X	X	V	V	V
	Pyrimathanil	Protective action with some curative properties.	X	—	?	X	X	X	—	X	?

Table 3 contd.

Substance group	Pesticide	Mode of action	Carcinogen	Mutagen	Endocrine disruptor	Reproduction/ development effects	Acetyl cholinesterazy inhibitor	Neurotoxicant	Respiratory tract irritant	Skin irritant	Eye irritant
Benzimidazole	Carbendazim	Systemic with curative and protectant activity. Inhibition of mitosis and cell division.	?	—	?	V	X	X	X	X	X
Carboxamide	Boscalid	Protectant. Foliar absorption. Translocates. Inhibits spore germination and germ tube elongation.	?	—	X	?	X	X	X	X	?
Chloronitrile	Chlorothalonil	Non-systemic. Broad spectrum. Foliar action with some protectant properties. Acts by preventing spore germination and zoospore motility.	?	X	X	—	X	X	V	V	V
Dicarboximide	Procymidone	Systemic with protective and curative properties.	V	—	V	V	X	—	?	X	X
Hydroxyanilide	Fenhexamid	Foliar applied with protective action. Disrupts membrane function. Inhibits spore germination.	X	—	?	X	X	X	X	X	—
Morpholine	Dimethomorph	Systemic with good protective activity. Lipid synthesis inhibitor.	X	X	—	?	X	X	V	V	V
Phthalimide	Captan	Non-systemic with protective and curative action.	V	X	X	—	X	X	—	V	V
Sulphamide	Dichlofluanid	Foliar with protective action	—	—	—	—	X	—	?	?	?

Table 3 contd.

Substance group	Pesticide	Mode of action	Carcinogen	Mutagen	Endocrine disruptor	Reproduction/ development effects	Acetyl cholinesterazy inhibitor	Neurotoxicant	Respiratory tract irritant	Skin irritant	Eye irritant
Sulphamide	Tolylfluanid	Broad spectrum. Multi-site with protective action.	?	—	—	X	X	X	—	V	V
Strobilurin	Azoxystrobin	Systemic translaminar and protectant action having additional curative and eradicant properties. Respiration inhibitor (QoL fungicide).	X	—	—	?	X	X	—	V	V
	Trifloxystrobin	Broad spectrum with preventative and curative action. Respiration inhibitor. (QoL fungicide)	X	—	—	V	X	X	—	V	X
Triazole	Difenoconazole	Systemic with preventative and curative action. Disrupts membrane function - inhibition of demethylation during ergosterol synthesis.	?	—	—	?	X	X	X	V	V
	Flusilazole	Broad spectrum. Systemic with protective and curative action	?	—	—	V	X	X	?	?	?
	Tebuconazole	Systemic with protective. Curative and eradicant action. Disrupts membrane function.	?	—	—	V	X	X	X	X	V
Herbicides											
Dinitroaniline	Trifluralin	Selective. Inhibition of mitosis and cell division.	?	X	V	V	X	—	V	X	X

V – Yes, known to cause a problem; X – No, known not to cause a problem; ? – Possibly, status not identified; – No data.

Table 4

Estimation of short-term (acute) dietary consumer's exposure (2005–2013)

Crop	Active substance	HR [mg/kg]	MRL [mg/kg]	Times exceeded MRL	ARfD* [mg/kg b.w.]	Source	Adults		Children	
							Intake [mg/kg b.w.]	% ARfD	Intake [mg/kg b.w.]	% ARfD
Currant	Alpha-cypermethrin	0.10	0.05	2	0.04	Dir 04/58	0.00016	0.4	0.00036	0.9
Mushroom	Bifenthrin	0.15	0.05	3	0.03	EFSA 11	0.00024	0.8	0.00044	1.5
Carrot	Chlorpyrifos	0.56	0.10	5.6	0.1	Dir 05/75	0.00485	4.9	0.02201	22.0
Tomato	Chlorothalonil	8.47	2.00	4.2	0.6	SCoFCAH Sept 06	0.08838	14.7	0.35077	58.5
Currant	Cypermethrin	0.22	0.05	4.4	0.2	Dir 05/53	0.00035	0.2	0.00079	0.4
Apple	Cyprodinil	0.09	0.05	1.8	0.03	Dir 06/64	0.00135	4.5	0.00648	21.6
Lubin	DDT	0.09	0.05	1.9	Not appl.	JMPR 2000	—	—	—	—
Lettuce	Diazinon	0.27	0.02	13.5	0.025	EFSA 06	0.00266	10.7	0.00326	13.0
Lettuce	Dichlofluanid	18.68	5.00	3.7	Not appl.	—	—	—	—	—
Currant	Difenoconazole	0.43	0.05	8.6	0.16	Dir 08/69	0.00068	0.4	0.00155	1.0
Plum	Dimethoate	0.32	0.02	16	0.01	EFSA 2013	0.00233	23.3	0.00946	94.6
Tomato	Dimethomorph	1.04	0.50	2.1	0.6	Dir 07/25	0.01085	1.8	0.04307	7.2
Tomato	Endosulfan	0.28	0.05	5.6	0.02	JMPR 2006	0.00292	14.6	0.01160	58.0
Currant	Esfenvalerate	0.15	0.02	7.5	0.05	Dir 00/67	0.00024	0.5	0.00054	1.1
Currant	Fenazaquin	0.250	0.10	2.5	0.1	EFSA 2013	0.00039	0.4	0.00090	0.9

Table 3 contd.

Crop	Active substance	HR [mg/kg]	MRL [mg/kg]	Times exceeded MRL	ARfD* [mg/kg b.w.]	Source	Adults		Children	
							Intake [mg/kg b.w.]	% ARfD	Intake [mg/kg b.w.]	% ARfD
Currant	Fenitrothion	0.06	0.01	6	0.013	EFSA 06	0.00009	0.7	0.00022	1.7
Currant	Flusilazole	0.29	0.02	14.5	0.005	Dir 06/133	0.00046	0.9	0.00104	2.1
Apple	Phosalone	0.25	0.05	5	0.1	EFSA 06	0.00374	3.7	0.01801	18.0
Apple	Pyrimethanil	0.20	0.01	20	Not appl.	Dir 06/74	—	—	—	—
Rape	Pirimiphos-methyl	0.24	0.05	4.8	0.15	EFSA 05	0.00144	1.0	0.00324	2.2
Currant	Procymidone	0.57	0.02	28.5	0.012	DAR 07	0.00090	7.5	0.00205	17.1
Strawberry	Tolylfluanid	0.49	0.02	24.5	0.25	Dir 06/06	0.00129	0.5	0.00240	1.0

HR – Highest residue, MRL – Maximum Residue Limit, ARfD – Acute Reference Dose, b.w. – body weight; * ARfD values are derived from the pesticide database [45].

All RASFF notifications made during the period 2005–2013 at the Laboratory of Pesticide Residue in Bialystok had the character of information notifications. The estimated health risk assessment was acceptable, therefore notifications were not passed on to the European Commission.

Conclusions

Presented research concerns the evaluation of quality of local raw fruits, vegetables cereals and oilseeds in aspect of active substances presence on the basis of RASFF notifications made during the period 2005–2013. The estimated that acute exposure was highest for the dimethoate, however, it was lower than 100 % ARfD. No products were found in which consumption may have negative health effects. The present study shows that although fruits and vegetables from the region of Poland contain many contaminations, their consumption does not pose a danger to the health of adults and children. Nevertheless, studies on pesticide residues should still be developed and should include more and more active substances and various species of vegetables, fruits, cereals and processed goods of plant origin.

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POZOSTAŁOŚCI PESTYCYDÓW I OCENA OSTREGO RYZYKA W POLSKIEJ ŻYWNOŚCI POCHODZENIA ROŚLINNEGO (2005–2013)

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Abstrakt: Bezpieczeństwo żywności jest bardzo ważne dla konsumentów. Owoce, warzywa i zboża są nie tylko ważnym źródłem witamin, minerałów, błonnika i energii, ale również mogą być źródłem wielu zanieczyszczeń mogących stanowić ryzyko dla zdrowia. Pestycydy znajdujące się w żywności to tylko przykłady szkodliwych substancji wpływających na bezpieczeństwo żywności. Celem niniejszej pracy była ocena krótkoterminowego zagrożenia zdrowia na podstawie stężenia pozostałości pestycydów w płodach rolnych pobranych w ramach urzędowej kontroli w okresie 2005–2013 w ramach systemu RASFF (System Wczesnego Ostrzegania o Niebezpiecznej Żywności i Paszach). W dziewięcioletnim okresie badań łącznie 2021 próbek owoców, warzyw i zbóż pobrano z północno-wschodniej i środkowej części Polski i analizowano pod kątem obecności 188 substancji czynnych pestycydów techniką chromatografii gazowej, cieczowej i spektrofotometryczną. Wolnych od zanieczyszczeń było 65,3 % próbek, 31,9 % próbek zawierało pozostałości poniżej, a w 2,8 % powyżej najwyższych dopuszczalnych poziomów (NDP). Spośród 81 powiadomień informacyjnych RASFF, najwięcej nieprawidłowości dotyczyło przekroczenia wartości NDP – 41, w 27 przypadkach stwierdzono, że pestycyd nie był używany zgodnie z rejestracją środka ochrony roślin. Najwyższe oszacowane wartości krótkotrwałego narażenia zdrowia uzyskano dla śliwki dla dimetoatu, w grupie małych dzieci – 94,6 % ARfD (Ostra Dawka Referencyjna) i dorosłych – 23,3 % ARfD.

Słowa kluczowe: Substancje aktywne pestycydów, północno-wschodnia Polska, powiadomienia informacyjne RASFF, bezpieczeństwo żywności