ARCHIVES OF ENVIRONMENTAL PROTECTION

vol. 37 no. 3 pp. 43 - 54 2011

PL ISSN 2083-4772

PESTICIDE RESIDUES IN APPLES (2005–2010)

BOŻENA ŁOZOWICKA*, PIOTR KACZYŃSKI

Institute of Plant Protection – National Research Institute
Pesticide Residue Laboratory
Chełmońskiego 22, 15-195 Białystok
*Corresponding author's e-mail: B.Lozowicka@iorpib.poznan.pl

Keywords: Pesticide residues, apples, dietary exposure.

Abstract: Fruit and vegetables constitute an essential part of human diet and that is why they should be "safe". Chemical contaminants of plant origin in food, including the pesticide residues, are defined as critical differentiators of quality and food safety. Pesticide residues are found in fruits, vegetables, cereals and herbs chemically protected at low concentrations, but they are one of the elements that affect the quality of healthcare.
The aim of this study was to assess the pesticide residues in apples from the north-eastern Poland (Lubelskie, Podlaskie and Warmińsko-Mazurskie provinces) and get an answer whether any contamination in fruit from the region is similar to that in other countries and whether it can lead to exposure of consumer's health. Also assessed compliance of used pesticides with applicable law and found residues were compared with the Maximum Residue Levels (MRLs). The study showed that 59% of the samples of apples from the north-eastern Poland contain pesticide residues below the MRL, and 7% above the limits. The estimated dietary intake has shown the chronic dietary exposure of the most vulnerable groups – children and adults to the pesticide residues in Polish apples was relatively low and does not constitute a health risk to. The results show that apples from north-eastern Poland are safe.

INTRODUCTION

Plant based food is an integral part of the human diet and as such should be "safe". Chemical contaminants of plant based foods, including pesticide: insecticide, fungicide and herbicide residues are defining factors in determining food quality and safety. Chemical residues occur in small amounts in fruit, vegetables, grains or herbs which have been treated chemically, but they may become one of the elements which influence the health qualities of foods. These residues, in general, are a consequence of chemical application to protect the crops from unwanted pests or occur through their persistence in the environment. These residues should appear in lowest levels possible and should be toxicologically acceptable. Every pesticide used for plant protection has a legally established Maximum Residue Level (MRL). In many developed countries of the European Union efforts have been made to minimize or to prevent the negative effects of excessive and often irrational chemical treatment of agricultural products. Chemical protection of plants from diseases, pests or weeds should be replaced, whenever possible, with alternative methods including biological, physical or agrotechnical and integrated methods.

In Poland, a few research institute have conducted studies to determine the presence of chemical residues in plant based foods as well as the risk to people of these chemical contaminants, and these are fragmentary. Therefore, it became important to conduct a study concerned with the most commonly consumed fruit – apples, and their effect on the health of consumers.

The safety of foods cannot be ascertained without conducting analytical studies. The analysis of chemical residues in plant materials is very difficult, since they occur in very small concentrations (ppm, ppb). Therefore, very specialized methods of sample preparation, as well as methods of instrumental analysis are necessary. Simultaneous analysis of a wide range of pesticides including those belonging to the organochloride, organophosphate, pyrethroid, triazine, triazole, strobilurin, carbamate, ureic, phenolic or neonicotinoid groups is made possible by the use of multi-residue (MR) procedures. The results of the analytical studies, their credibility and reliability, play an important role in decision making, on the legislative level and regarding health concerns. It is important that the results obtained in the analytical laboratory are of sufficient quality. The document of DG SANCO entitled "Method Validation and Quality Control Procedures for Pesticide Residues Analysis in Food and Feed" (SANCO 2009) deals with the identification of pesticide residues.

The aim of this study was to ascertain the occurrence of chemical pesticide residues in apples from north-eastern Poland and to obtain an answer whether residue levels in the fruit from this region are similar to those in other regions of Poland and of the European Union, as well as to asses if they pose a risk to the health of the consumers. Additionally, adherence to legal regulations regarding the use of chemical compounds in crop cultivation was ascertained, as well as conformity of the levels of detected residues to the legally established Maximum Residue Levels (MRLS) in Poland and the EU.

MATERIALS AND METHODS

Study samples

Samples of apples (222) from north-eastern Poland (Lubelskie, Podlaskie, Warmińsko-Mazurskie) were obtained under the official control of residues of plant protection products conducted in 2005–2010 by the Ministry of Agriculture and Rural Development, implemented in cooperation with regional inspectorates of Plant Protection and Seed (WIORiN). These samples were collected in September-November by the inspectors according to a predetermined schedule for a given year. The apples were not peeled or washed. The samples of apples were delivered in packaging, which protected them from contamination, damage or loss, properly sealed and labeled, and along with a sampling report, all of which assured the correct identification of the sample.

The scope of the study of pesticides was established mainly on the basis of information obtained from agricultural producers, who declared the type of pesticides used in plant protection in sampling reports. The first to be studied among these substances were the compounds most commonly used (e.g. captan) and those relatively persistent within the environment (e.g. DDT). During the study period discussed the occurrence of 127 active substances of pesticides were researched.

Analytical Methods

Standards

Pesticides (127) were obtained from the Dr. Ehrenstorfer Laboratory (Germany) and are listed in Table 1. Pesticide standard stock solutions (purity for all standards > 95%) of various concentrations were prepared in acetone and stored at 4°C. Standard working solutions were prepared by dissolving appropriate amounts of stock solution with a hexane/ acetone (9:1) mixture.

Table 1. Analyzed active substances (common name)

Active substancje (common name)
Insecticides
acetamiprid*, aldrin, alpha-cypermethrin, azinophos-ethyl, azinophos-methyl, beta-cyfluthrin, bifenthrin, bromopropylate, buprofezin, carbaryl, chlorfenvinfos, chlorpyrifos ethyl*, chlorpyrifos methyl, cyfluthrin, cypermethrin*, DDT sum (p,p'- DDE, p,p'- DDD, o,p'- DDT, p,p'- DDT), deltamethrin, diazinon*, dichlorvos, dicofol, dieldrin, dimethoate*, endosulfan (α, β, sulphate), endrin, esfenvalerate, ethion, fenazaquin*, fenitrothion*, fenpropathrin, fenvalerate, fipronil, formothion, α-HCH, β-HCH, HCB, heptachlor, heptachlor epoxide, heptenophos, isofenphos, lambdacyhalothrin, lindane (γ-HCH), malathion, mecarbam, methoxychlor, methidathion, parathion-ethyl, parathion methyl, permethrin, phosalone*, pirimiphos-methyl, pirimicarb*, propoxur, quinalphos, tebufenpyrad, tetradifon, triazophos
Fungicides
acrinathrin, azoxystrobin, benalaxyl, benomyl[1], bitertanol, boscalid*, bromuconazole, bupirimate, captan*, carbendazim*, carbofuran, chlorothalonil, cyprodinil*, cyproconazole, dichlofluanid, dicloran, difenokonazole, dimethomorph, diphenylamine, dithiocarbamates (mancozeb, maneb, methiram, propineb, thiram, ziram)[2]*, fenarimol, fenazaquin, fenhexamid, fludioxonil, flusilazole*, folpet*, imazalil, iprodione, krezoxim-methyl, mepanipyrim, quintozene, metalaxyl, myclobutanil, oxadiksyl, penconazole, pirimethanil*, procymidone, propiconazole, tebuconazole, tecnazene, tetraconazole, tolclofos-methyl, tolylfluanide*, triadimefon, triadimenol, trifloxystrobin*, vinclozolin
Herbicides
atrazine, chlorprofam, lenacil, linuron, metribuzin, napropamide, nitrofen, pendimethalin, profam, promethrin, propachlor, propyzamide, simazine, trifluralin
* compound found [1] determined as carbendazim [2] determined as CS_2

Multi - residue (MR) method of isolation and determination of 119 pesticide residues using gas chromatography

A developed MR method, accredited by the PCA (AB 839), was used for isolation and determination of pesticide residues in apple samples. The apple samples were initially cut up and then mixed. A technique based on Matrix Solid Phase Dispersion (MSPD) was used to isolate pesticide residues. The extraction process was conducted simultaneously with purification using adsorption column chromatography. Extracts obtained from the samples were analyzed for pesticide residue presence through comparison with available mixture standards of pesticides, using a gas chromatography (GC). GC analysis was performed with a gas chromatograph Agilent (Waldbronn, Germany) model 7890A equipped with electron capture (EC) and nitrogen-phosphorous (NP) detectors non-polar column HP-5 (5%-phenyl)-methylpolysiloxane and Chemstation chromatography manager data acquisition and processing system (Hewlett-Packard, version A.10.2). Retention times of resulting peaks were compared with those of the standards. When the chromatogram of an extract showed no peaks with the same (or similar) retention times as those shown by the standards, it was concluded that within the studied range the concentration of the residue fell below the level of detection (LOD). However, if the chromatogram of the extract analyzed did contain peaks with retention times similar to those of a standard, then the presence of a given analyte was confirmed on columns with different polarity. If the Maximum Residue Level (MRL) of a given analyte was exceeded, the analysis of the sample was repeated (both extract preparation and instrumental analysis).

Single method (SM) of isolation and determination of dithiocarbamates (mancozeb, maneb, methiram, propineb, thiram, ziram), carbendazim, and linuron residues.

A modified colorimetric method [1] was used for the determination of dithiocarbamate residues (express as CS_2). At the extraction stage a MSPD technique with silica gel purification was used to identify carbendazim residues, while instrumental determination was done using a liquid chromatography technique (Waters Alliance 2695 chromatograph) with photodiode (Waters 2996) and fluorescent detectors (Waters 2475). An SPE technique was used at the extraction stage for the determination of linuron, while instrumental identification was done with liquid chromatography (Waters Alliance 2695 chromatograph) with a photodiode detector (Waters 2996) [10].

Method Validation

Method validation was conducted according to the requirements of the European Commission contained in the SANCO's "Quality Control Procedures for Pesticide Residues Analysis" [20, 21] and the "Method Validation and Quality Control Procedures for Pesticide Residues Analysis in Food and Feed" [19] (http://www.crl-pesticides.eu/) as well as in the requirements of the standard PN-EN ISO/IEC 17025 [13].

Risk of consumer chronic exposure to the pesticide residues detected in apples

Consumption data play a major role in the dietary risk assessment of residues in food. As this may vary considerably depending on eating habits, estimates are used. The data concerning residues for a risk estimation were obtained in 2005–2010 by the Pesticide Residue Laboratory in Bialystok of the official control of pesticides residues. The studies included 127 compounds in 212 apple samples proceeding from of north-eastern Poland. This risk was calculated through the comparison of residues found in apples to the established acceptable daily intake (ADI) values. The level of residue concentration in a product was determined as the arithmetic mean of all the results obtained. The results under limit of detection (LOD) of analytical methods used for intake calculations were taken as LOD values. Values of ADI are elaborated by Joint FAO/WHO Meeting on Pesticides Residues [24], European Food Safety Authority (EFSA) of European Union or Federal Institute for Risk Assessment (BfR), Germany [2]. For consumer residues intake estimation new model from Pesticides Safety Directorate (PSD) of the Department for Environment, British Food and Rural Affairs, were applied [14].

Calculations were performed using a Chronic and Acute Consumer ver. 1.1. with built-in consumption database for two sub-populations: small children (1.5–4 years of age, 14.5 kg) and adults (19–64 years of age, 76 kg) accepting consumption at the level of the 97.5 percentile. Apple consumption by adults is 0.155 kg/day and by children 0.216 kg/day.

Chronic (long-term) risk was calculated as:

$$EDI = \sum \frac{F_i \times RL_i \times P_i}{mean\_body\_weight}$$

where:
EDI – Estimated Daily Intake,
F_i – food consumption data,
RL_i – residue level to the commodity,
P_i – correction value that takes into account the reduction or increase in residue which might occur on storage or processing.

RESULTS AND DISCUSSION

Between the years 2005–2010 a total of 212 apple samples from north-eastern Poland were analyzed, in which the frequency of occurrence of pesticide residues was ascertained, as well as the types of pesticide active substances. Based on the analytical studies

Table 2. Detected pesticide residues in apples (2005–2010)

No.	Active substance	Mode of action	Samples with residues						Range of residues [mg/kg]
			total		<MRLs		>MRLs		
			n	%	n	%	n	%	
1	Acetamipirid	I	10	4.7	10	4.7	-	-	0.01–0.03
2	Boscalid	F	1	0.5	1	0.5	-	-	0.23
3	Captan	F	73	34.4	73	34.4	-	-	0.02–0.13
4	Carbendazim	F	2	0.9	2	0.9	-	-	0.04–0.07
5	Chlorpiryfos ethyl	I	4	1.9	4	1.9	-	-	0.01–0.03
6	Cypermethrin	I	2	0.9	2	0.9	-	-	0.02
7	Cyprodinil	F	8	3.8	4	1.9	4	1.9	0.01–0.1
8	Diazinon	I	5	2.4	1	0.5	4	1.9	0.02–0.03
9	Dimethoate	I	4	1.9	1	0.5	3	1.4	0.01–0.1
10	Dithiocarbamates	F	57	26.9	57	26.9	-	-	0.05–0.57
11	Fenazaquin	I	2	0.9	2	0.9	-	-	0.05–0.06
12	Fenitrothion	I	2	0.9	-	-	2	0.9	0.02
13	Flusilazole	F	4	1.9	1	0.5	3	1.4	0.02–0.09
14	Folpet	F	1	0.5	1	0.5	-	-	0.04
15	Phosalone	I	4	1.9	-	-	4	1.9	0.03–0.25
16	Pirimethanil	F	23	10.8	19	9.0	4	1.9	0.01–0.48
17	Pirimicarb	I	24	11.3	24	11.3	-	-	0.01–0.12
18	Tolylfluanide	F	19	9.0	19	9.0	-	-	0.02–0.29
19	Trifloxystrobin	F	4	1.9	4	1.9	-	-	0.01–0.1

F – fungicide; I – insecticide;

of the plant material being studied a number of samples have been distinguished: samples free of residues, samples with residues of permitted pesticides below and above permitted boundary limits, as well as those in which substances not recommended for use for a given crop were detected (Tab. 2). Results were interpreted according to Regulation of the Minister of Health [17, 18] and the Directives of the European Parliament and the European Commission [5].

Nineteen compounds were detected 249 times in apple samples (10 fungicides (F) and 9 insecticides (I)). Respectively, ten fungicides occurred in the samples within a range of frequency of 0.6% to 35%, and nine insecticides occurred within the range of frequency of 0.6% to 11% (Fig. 1).

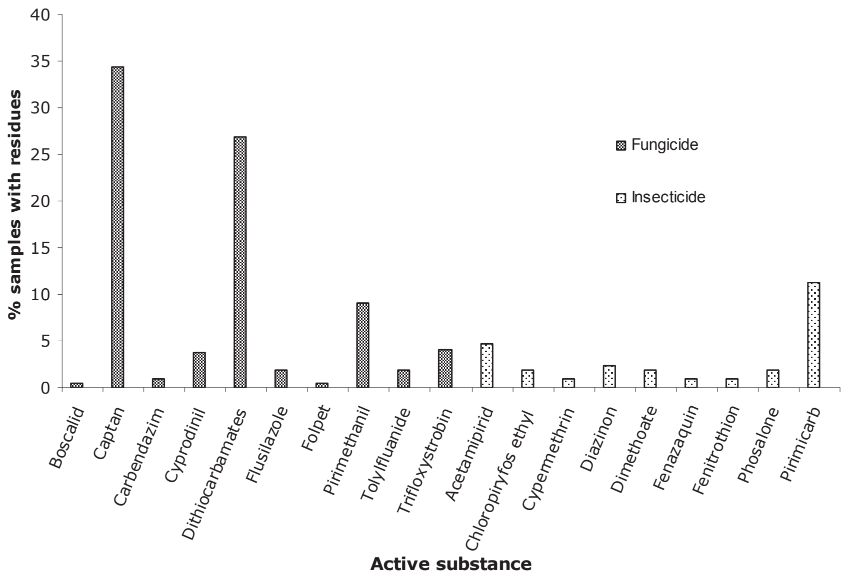

Fig. 1. The frequency of pesticides detection

Among the compounds detected there were significantly more fungicides (83%). The active substances found in apples were: pirimicarb (I, 24 times), acetamipirid (I, 10), diazinon (I, 5), dimethoate (I, 4), chlorpyrifos ethyl (I, 4), phosalone (I, 4), fenazaquin (I, 2), fenitrothion (I, 2), cypermethrin (I, 2), boscalid (F, 1) and captan (F, 73), dithiocarbamates (F, 57), tolylfluanide (F, 19), pirimethanil (F, 23), cyprodinil (F, 8), flusilazole (F, 4), trifloxystrobin (F, 4), carbendazim (F, 2), folpet (F, 1). Plant protection products used in 2005–2010 for apple protection with detected active substances are presented in Table 3.

Seventy two of the 212 apples (32%) did not contain residues. Most of the analyzed samples (59%) contained pesticide residues under Maximum Residue Level (Fig. 2).

Table 3. Plant protection products with detected active substance

No.	Active substance	Plant protection products
1	Acetamipirid	Mospilan 20 SP; Piorun 200 SL
2	Boscalid	Signum 33WG
3	Captan	Captan 50 WP; Captan 80 WG; Kaptan zawiesinowy 50 WP; Kaptan Plus 71,5 WP; Magic Cap 45 WP; Merpan 80 WG; Merpan 50 WP
4	Carbendazim	Cukarb 350 SC
5	Chlorpiryfos ethyl	Chlormezyl 500 EC; Nurelle Max 515 EC; Nurelle D 550 EC
6	Cypermethrin	Cyperkill Super 25 EC; Sherpa 100 EC; Nurelle D 550 EC
7	Cyprodinil	Chorus 75 WG; Switch 62,5 WG
8	Diazinon	Basudin 600 EW; Diazol 500 EW; Grot 250 EC; Basudin 25EC; Diazol 250 EC
9	Dimethoate	Bi 58 Nowy 400 EC; Danadim 400 EC; Dimezyl 400 EC
10	Dithiocarbamates	Dithane M-45 80 WP; Dithane Neo Tec 75 WG; Manconex 80WP; Novozir MN 80 WP; Penncozeb 455 SC; Penncozeb 80 WP; Pennfluid 420 EC; Polyram 70 WG; Promasol Forte 80 WG; Sadoplon 75 WP; Sancozeb 80 WP; Thiram Granuflo 80 WG; Vandozeb 75 WG
11	Fenazaquin	Magus 200 SC
12	Fenitrothion	Owadofos 540 EC; Owadox 1000 EC; Sumithion 500 EC; Sumithion Super 1000 EC
13	Flusilazole	Capitan 400 EC; Punch Bis 400 EC
14	Folpet	Folpan 80 WG; Shavit F 71,5 WP
15	Phosalone	Zolone 350 SC
16	Pirimethanil	Mythos 300 SC; Clarinet 200 SC
17	Pirimicarb	Pirimix 100 PC; Pirimor 500 WG
18	Tolylfluanide	Euparen Multi 50 WG; Folicur Multi 50 WG
19	Trifloxystrobin	Zato 50 WG

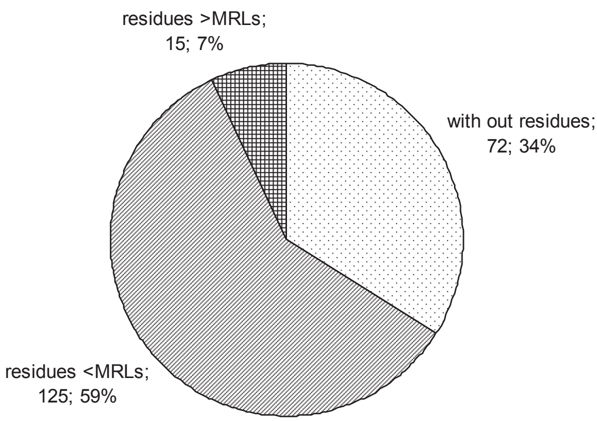

Fig. 2. Pesticide total residues in apples

The MRL was exceeded in 7% (15) of samples for: cyprodinil (0.01; 0.08; 0.1 mg/kg – MRL = 0.05 mg/kg); dimethoate (0.01; 0.05; 0.1 mg/kg – MRL = 0.02 mg/kg); fenitrothion (0.02; 0.02 mg/kg – MRL = 0.01 mg/kg) and diazinon (0.01; 0.02; 0.02; 0.02; 0.03 mg/kg – MRL = 0.01 mg/kg), pirimethanil (0.01–0.48 – MRL = 0.01 mg/kg), flusilazole (0.02; 0.02; 0.03 mg/kg – MRL = 0.01 mg/kg).

Plant protection products not recommended for use in apple orchards containing tolylfluanide or phosalone were present in 4 samples (5%).

Apple samples contained the residue of one compound as well as multiple substances: two, three, four and even six residues (Fig. 3).

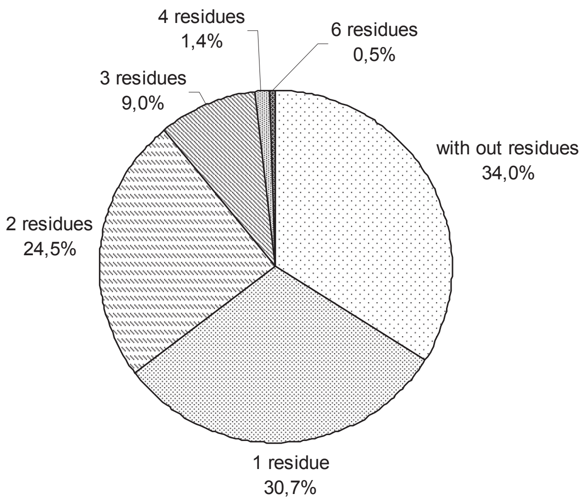

Fig. 3. Percentage of samples with multiresidues

Among all apple samples, 31% (65) contained one pesticde (acetamipiryd, dithiocarbamates, captan, pirimethanil, pirimicarb, tolylfluanide), while two active substances were present in 24.5% of apple samples (52). Captan was identified in 34.4% of samples, at the highest concentration of 0.13 mg/kg and an arithmetic mean of 0.1 mg/kg. Captan is the most frequently detected fungicide in some market basket studies and average concentrations were reported to be relatively high (0.1 mg/kg) [9]. Captan residue levels in other fruit and vegetables also have been measured [3, 6, 15, 16]. Most commonly detected combinations were: captan/pirimicarb, pirimicarb/dithiocarbamates, captan/dithiocarbamates, pirimethanil/dithiocarbamates, flusilazole/dithiocarbamates and pirimicarb/tolylfluanide. The concentration of compounds detected fit within a range of 0.05 to 0.4 mg/kg. 9% of apples (19) contained three residues in concentrations ranging from 0.07 to 0.51 mg/kg, and most often it was the combination of dithiocarbamates/captan. In three samples (1.4%) four residues were found: diazinon/dithiocarbamates/flusilazole/captan (total concentration 0.21 mg/kg), pirimicarb/tolylfluanide/captan/dithiocarbamates in concentration of 0.22 mg/kg, and the combination of dithiocarbamates/fenitrothion/captan/pirimicarb (total concentration 0.71 mg/kg). In one sample (0.5%) six compounds were discovered (chlorpyrifos ethyl/dithiocarbamates/captan/carbendazim/pirimethanil/pirimicarb) in concentration of 0.36 mg/kg.

The assessment of chronic (long-term) health risk for consumers connected with the consumption of apples from north-east Poland containing pesticide residues was conducted on the basis of available epidemiological studies done for the British. There is a lack of full studies done for Polish consumers since these studies only take into account general population and average consumption (50 percentile) [22], and therefore had no practical application in the current study.

During the assessment of the long-term consumer risk the study assumed a cautious approach by using conservative guidelines, which inflated the risk. Nineteen compounds which were taken into account in the calculations are described in Table 4.

Table 4. Chronic dietary exposure to pesticide residues for apples

No.	Active substance	Average residue level [mg/kg]	Acceptable daily intake (ADI) [mg/kg b.w.]	Toddlers [14.5 kg] Consumption [34.5 g/p./d.]		Adults [76 kg] Consumption [59.1 g/p./d.]	
				Intake [µg/kg b.w.]	% ADI	Intake [µg/kg b.w.]	% ADI
1	Acetamipirid	0.01028	0.07	0.153	0.218	0.021	0.030
2	Boscalid	0.01104	0.04	0.164	0.410	0.023	0.056
3	Captan	0.10981	0.1	1.633	1.633	0.224	0.224
4	Carbendazim	0.02033	0.02	0.302	1.511	0.041	0.207
5	Chlorpyrifos ethyl	0.00524	0.01	0.078	0.779	0.011	0.107
6	Cypermethrin	0.02000	0.05	0.297	0.595	0.041	0.082
7	Cyprodinil	0.01165	0.03	0.173	0.577	0.024	0.079
8	Diazinon	0.01024	0.0002	0.152	76.098	0.021	10.438
9	Dimethoate	0.01061	0.001	0.158	15.781	0.022	2.165
10	Dithiocarbamates	0.07571	0.05	1.126	2.251	0.154	0.309
11	Fenazaquin	0.02033	0.005	0.302	6.046	0.041	0.829
12	Fenitrothion	0.01005	0.005	0.149	2.988	0.020	0.410
13	Flusilazole	0.01075	0.002	0.160	7.996	0.022	1.097
14	Folpet	0.02009	0.1	0.299	0.299	0.041	0.041
15	Phosalone	0.01165	0.01	0.173	1.732	0.024	0.238
16	Pirimethanil	0.01877	0.17	0.279	0.164	0.038	0.023
17	Pirimicarb	0.01264	0.035	0.188	0.537	0.026	0.074
18	Tolylfluanide	0.02561	0.1	0.381	0.381	0.052	0.052
19	Trifloxystrobin	0.01052	0.1	0.156	0.156	0.021	0.021
	Sum				120.2		16.5
b.w. – body weight; p. – person; d. – day							

None of the pesticides detected, with the exception of one, posed any consumer health concerns. The residues of diazinon had the highest risk factor determined at 76.1% ADI for small children and 10.4% ADI for adults. This compound, belonging to the organophosphate insecticide group had the lowest ADI value, at 0.0002 mg/kg of all of the pesticides being studied. For children and adults the other compounds showed of 43% and 6.1% of ADI, respectively.

The evaluation of consumer health risk connected with the contamination of apples with pesticide residues shows that it did not pose a danger to neither subpopulation of small children or adults. The only noted possible risk for small children was connected with the residues of diazinon.

CONCLUSIONS

There is little information regarding data dealing with pesticides in apples in either Polish or word literature [11]. Despite continuing growth of integrated and ecological production, most apples are still produced using conventional methods. Apple production is undoubtedly connected with a high level of pesticide use. In conventional farming, in Great Britain for example, insecticides, fungicides and herbicides are applied to approximately 92–97% of apple orchard area, growth regulators to 77%, and ureics to 28%. Captan, myclobutanil, penconazole, carbendazim and dithianon are most commonly used fungicides, while chlorpiryfos, thiachloprid and fenoxycarb dominate among insecticides. Many of these pesticides, characterised by high toxicity, are moderately dangerous with possible carcinogenic, endocrinological or toxic effects [4], and act as cholinesterase inhibitors. 19 compounds (insecticides as well as fungicides) were detected in Polish apples. The most common is captan, the fungicide. On the basis of the research it has been concluded that in the case of apple production in north east Poland the levels of all detected pesticide residues occurred at a minimal level of 0.01 mg/kg to 0.09 mg/kg and at the highest levels for pirymethanil at 0.48 mg/kg, and dithiocarbamates at 0.57 mg/kg. Despite common occurrence of pesticide residues, the concentrations encountered were several levels lower than, for example, in apples from Pakistan [12].

In the analyzed apple samples there were found samples containing one residue, samples containing multiple residues, those which contained pesticides both above and below the MRL as well as pesticides which are not recommended for apple production. The assessment of chronic risk for people consuming all detected pesticide residues through all 2005–2010 in 212 apple samples, the fruit of the highest consumption in Poland, shows that they do not pose a danger to their health and the risk is comparable to other countries [7, 8, 23].

REFERENCES

[1] Chmiel Z.: *Spektrofotometryczne oznaczanie śladowych pozostałości dwutiokarbaminianów w materiale roślinnym*, Chemia Analityczna, **24**, 505–511 (1979).

[2] BfR (Bundesinstitut fur Risikobewertung): *Grenzwerte für die gesudheiteitliche Bewertung von Pflanzenschutzmittelrückständenden*, Information Nr. 002/2006 des BfR vom 4. Januar 2006.

[3] Burchat C.S., B.D. Ripley, P.D. Leishman, G.M. Ritcey, Y. Kakuda, G.R. Stephenson: *The distribution of nine pesticides between the juice and pulp of carrots and tomatoes after home processing,* Food Additives and Contaminants, **15**(1), 61–71 (1998).

[4] EPA (Environmental Protection Agency): *Hazard Information on Toxic Chemicals Added to EP CRA Section 313 Under Chemical Expansion*, (http://www.epa.gov/tri/chemical/hazard_cx.htm), Washington, DC 2008.

[5] European Parliament and European Commission Regulation issued on the 23 of February, 2005 no. 396/2005 with subsequent changes (Dz. U. L 70 from 16 of March, 2005) regarding the highest matter (2005).

[6] Fernandez-Cruz M.L., M. Barreda, M. Villarroya, A. Peruga, S. Lianos, J. M. Garcia-Baudin: *Captan and fenitrothion dissipation in field-treated cauliflowers and effect of ousehold processing*, Pest Management Science, **62**(7), 637–645 (2006).

[7] Inigo-Nunez S., M.A. Herreros, T. Encinas, A. Gonzalez-Bulnes: *Estimated daily intake of pesticides and xenoestrogenic exposure by fruit consumption in the female population from a Mediterranean country (Spain)*, Food Control, **21**(4), 471–477 (2010).
[8] Katz J.M., C.K. Winter: *Comparison of pesticide exposure from consumption of domestic and imported fruits and vegetables*, Food and Chemical Toxicology, **47**, 335–338 (2009).
[9] Krol W.J., T. Arsenault, M.J.I. Mattina: *Reduction of pesticide residues on produce by rinsing*, Journal of Agricultural and Food Chemistry, **48**(10), 4666–4670 (2000).
[10] Łozowicka B., P. Kaczyński: *Determination of carbendazim, linuron and glyphosate residues by HPLC method,* Polish Journal of Environmental Studies, **18**(2B), 100–104 (2009).
[11] Łozowicka B.: *Pesticide residues in fresh apples produced under conventional and integrated crop management cultivation*, Environmental Protection and Natural Resources, **35**(36), 306–310 (2008).
[12] Parveen Z., M.I. Khuhro, N. Rafiq: *Evaluation of multiple pesticide residues in apple and citrus fruits 1999–2001*, Bulletin of Environmental Contamination and Toxicology, **73**(2): 312–318 (2004).
[13] PKN (Polski Komitet Normalizacyjny): *PN-EN ISO/IEC 17025:2005. Ogólne wymagania dotyczące kompetencji laboratoriów badawczych i wzorcujących*, PKN 2005.
[14] PSD (Pesticides Safety Directorate): *New intake calculation models for consumer intake assessments.* http://www.detergents.gov.uk/approvals.asp?id=1687, (2006).
[15] Rawn D.F.K. , S.C. Quade, W.F. Sun, A. Fouguet, A. Belangec, M. Smith: *Captan residue reduction in apples as a result of rinsing and peeling*, Food Chemistry, **109**(4), 790–796 (2008).
[16] Rawn D.F., S.C. Quade, J.B. Shields, G. Conca, W.F. Sun, G.M. Lacroix, M. Smith, A. Fouquet, A. Belanger: *Variability in captan residues in apples from a Canadian orchard*, Food Additives and Contaminants, **24**(2), 149–155 (2007).
[17] Regulation of the Minister of Health issued on the 16 of April, 2004 regarding the highest allowable level of pesticides which can occur in foods or on their surface (Dz. U. 2004, Nr 85, pos. 801 with subsequent changes) (2004).
[18] Regulation of the Minister of Health issued on the 16 of May, 2007 regarding the highest allowable level of pesticides which can occur in foods or on their surface (Dz. U. 2007, Nr 119, pos. 817 with subsequent changes) (2007).
[19] SANCO: *Method Validation and Quality Control Procedures for Pesticide Residues Analysis in Food and Feed. Document No. SANCO/2007/3131,* 31 October 2007.
[20] SANCO: *Quality Control Procedures for Pesticide Residues Analysis. Document N° SANCO/10232/2006,* 24 March 2006.
[21] SANCO: *Quality Control Procedures for Pesticide Residues Analysis*. *Document N° SANCO/10476/2003,* 5 February 2004.
[22] Szponar L., W. Sekula, E. Rychlik, M. Oltarzewski, K. Figurska: *The Household Food Consumption and Anthropometric Survey in Poland*. Project Report TCP/POL/8921(A), National Food and Nutrition Institute, Warszawa 2003.
[23] Tariq M.I., A. Shahzad, I. Hussain, N. Sultana: *Pesticides exposure in Pakistan: A review*, Environment International, **33**(8), 1107–1122 (2007).
[24] WHO (World Health Organization): *Inventory of ICPS and Rother WHO Pesticides evaluations and summary of toxological evaluations performed by the Joint Meetingon Pesticide Residues (JMPR)*, WHO/PCS/02.3 (www.who.int.pcs), (2003).

Received: March 14, 2011; accepted: July 14, 2011.

BADANIA POZOSTAŁOŚCI ŚRODKÓW OCHRONY ROŚLIN W JABŁAKCH (2005–2010)

Żywność pochodzenia roślinnego, stanowiąca niezbędny element diety człowieka, powinna być bezpieczna. Zanieczyszczenia chemiczne w żywności pochodzenia roślinnego, w tym pozostałości środków ochrony roślin, są określane jako krytyczne wyróżniki jakości i bezpieczeństwa żywności. Pozostałości środków ochrony roślin występują w owocach, warzywach, zbożach czy ziołach chronionych chemicznie w niewielkich stężeniach, ale są też jednym z elementów mogących mieć wpływ na jakość zdrowotną. Celem pracy była ocena występowania pozostałości pestycydów w jabłkach pobranych w ramach urzędowej kontroli z północno-wschodniej Polski (lubelskie, podlaskie, warmińsko-mazurskie) w latach 2005–2010 oraz uzyskanie odpowiedzi, czy te zanieczyszczenia mogą powodować narażenie zdrowia konsumentów. Ponadto oceniono prawidłowość stosowania środków ochrony roślin z obowiązującymi przepisami prawa oraz dokonano porównania oznaczonych stężeń z najwyższymi dopuszczalnymi poziomami (NDP) w Polsce i UE.

Przeprowadzone badania wykazały, że 59% próbek jabłek pochodzących z północno-wschodniej Polski zawiera pozostałości środków ochrony roślin poniżej NDP, a 7% powyżej granicznych limitów. Oszacowane narażenie zdrowia konsumentów na znalezione pozostałości jest jednak znikome i nie stanowi zagrożenia najbardziej wrażliwej grupy zarówno dzieci, jak i dorosłych.