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Consumer exposure to pesticide residues in apples from the region of south-eastern Poland

Ewa Szpyrka · Anna Kurdziel · Magdalena Słowik-Borowiec · Magdalena Grzegorzak · Aneta Matyaszek

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Abstract The production of apples in Poland is the largest among the countries of the European Union, and therefore, the consumption of these fruits is high in our country. The aim of this study was to determine the presence of pesticide residues in Polish apples and to assess if these residues pose a risk to the health of the consumer. Furthermore, compliance with legal regulations concerning the use of plant protection products in crop cultivation was ascertained. Pesticide residues were found in 192 samples (61.5 % of tested samples). In six samples (1.9 %), residues exceeded maximum residue limits. Violations concerned the insecticides: indoxacarb, diazinon and fenitrothion. The highest long-term consumer exposure was found in the case of consumption of apples with diazinon residue for both groups, adults and toddlers [4 % acceptable daily intake (ADI), adults; 21 % ADI, toddlers]. The highest values of short-term exposure were obtained in the case of consumption of apples with indoxacarb [5 % acute reference dose (ARfD), adults; 27 % ARfD, toddlers] and fenitrothion (4 % ARfD, adults; 23 % ARfD, toddlers). Although fungicides are the pesticides found most often in apples, the consumption of apples with insecticide residues constitutes the greatest hazard to human health.

Keywords Pesticide residues · Dietary exposure · Intake

E. Szpyrka (✉) · A. Kurdziel · M. Słowik-Borowiec · M. Grzegorzak · A. Matyaszek
Laboratory of Pesticide Residue Analysis,
Regional Experimental Station in Rzeszow,
Institute of Plant Protection – National Research Institute,
ul. Langiewicza 28,
35-101 Rzeszow, Poland
e-mail: e.szpyrka@iorpib.poznan.pl

Introduction

Crops yields are constantly affected by harmful organisms. It is essential to protect plants and plant products against such organisms in order to prevent a reduction in yield or damage to them and to ensure both the quality of the harvested products and high agricultural productivity. One of the most common methods of protecting plants and plant products from 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 the treated products (Regulation EC 2005).

The production of apples in Poland is the largest among the countries of the European Union, and therefore, consumption of these fruits is high in our country. In Poland, over 55 % consumers declared a consumption of more than five apples per week (Konopacka et al. 2010; Eurostat 2011, 2012).

The aim of the study was to determine the presence of pesticide residues in Polish apples and to assess if the residues pose a risk to the health of the consumer. Furthermore, compliance with legal regulations concerning the use of plant protection products in crop cultivation was ascertained.

Materials and methods

Determination of pesticide residues

In 2008–2012, 312 samples of apples from south-eastern Poland were tested in the laboratory. Samples were obtained during an official inspection of pesticide residues conducted in 2008–2012 on behalf of the Ministry of Agriculture and Rural Development, implemented in cooperation with the regional Inspectorates of Plant Health and Seed Inspection. Besides the national inspection programme, the laboratory has conducted monitoring analyses of pesticide residues in food of plant origin destined for export and for regional consumption.

The tests covered the determination of pesticides, from 121 in 2008 to 167 in 2012 (Table 1). Accredited methods were used to determine the presence of pesticide residues (ISO/IEC 17025: 2005; ISO/IEC 2005). The multi-residue analytical method was based on the extraction of residues with an organic solvent and further purification of the extract using column chromatography (Sadło 1998; Valverde-Garcia et al. 1993). Quantification of residues was carried out with Agilent 6890 and Agilent 7890 gas chromatographs equipped with ECD and NPD detectors. Along with the multi-residue method, spectrophotometric determination of dithiocarbamate residues expressed in milligram of CS_2 per kilogram and thin layer chromatographic determination of benzimidazoles expressed as carbendazim

Table 1 Scope of analysis

Group	Active substance
Insecticides	Acetamiprid (0.05), acrinathrin (0.01), aldrin (0.01), alpha-cypermethrin (0.01), azinophos-ethyl (0.01), azinophos-methyl (0.05), beta-cyfluthrin (0.01), bifenthrin (0.01), bromophos-ethyl (0.01), bromophos-methyl (0.01), bromopropylate (0.01), buprofezin (0.01), cadusafos (0.01), carbaryl (0.02), carbofuran (0.02), chlorfenvinphos (0.01), chlorpyrifos (0.01), chlorpyrifos-methyl (0.01), cyfluthrin (0.01), cypermethrin (0.01), p,p′-DDD (0.01), p,p′-DDE (0.01), o,p′-DDT (0.01), p,p′-DDT (0.01), deltamethrin (0.02), diazinon (0.01), dichlorvos (0.01), dicofol (0.01), dieldrin (0.006), dimethoate (0.02), endosulfan alfa (0.01), endosulfan beta (0.01), endosulfan SO_2 (0.01), endrin (0.01), esfenvalerate (0.01), ethion (0.01), ethoprophos (0.01), fenazaquin (0.01), fenchlorphos (0.01), fenitrothion (0.01), fenpropathrin (0.01), fenthion (0.01), fenvalerate (0.01), fipronil (0.005), formothion (0.01), HCB (0.01), α-HCH (0.01), β-HCH (0.01), γ-HCH (lindane) (0.01), heptachlor (0.01), heptachlor-endo-epoxide (0.003), heptachlor-exo-epoxide (0.001), heptenophos (0.01), hexythiazox (0.01), indoxacarb (0.02), isofenphos (0.01), isofenphos-methyl (0.01), lambda-cyhalothrin (0.01), malathion (0.01), mecarbam (0.01), methacrifos (0.01), methidathion (0.01), methoxychlor (0.01), parathion-ethyl (0.01), parathion-methyl (0.01), permethrin (0.02), phosalone (0.01), phosmet (0.01), pirimicarb (0.01), pirimiphos-ethyl (0.01) pirimiphos-methyl (0.01), profenofos (0.01), propoxur (0.05), pyridaben (0.02), pyriproxyfen (0.02), quinalphos (0.01), tebufenpyrad (0.01), teflubenzuron (0.01), tetrachlorvinphos (0.01), tetradifon (0.01), triazophos (0.01), zeta-cypermethrin (0.01)
Fungicides	Azaconazole (0.01), azoxystrobin (0.01), benalaxyl (0.05), bitertanol (0.05), boscalid (0.01), bromuconazole (0.01), bupirimate (0.01), captan (0.02), carbendazim (0.05), chlorothalonil (0.01), cyproconazole (0.01), cyprodinil (0.02), dichlofluanid (0.01), dicloran (0.01), difenoconazole (0.01), dimethomorph (0.01), dimoxystrobin (0.01), diniconazole (0.01), diphenylamine (0.05), dithiocarbamates (mancozeb, maneb metiram propineb, thiram, zineb, ziram) (0.05), epoxiconazole (0.01), fenarimol (0.01), fenbuconazole (0.02), fenhexamid (0.05), fenpropimorph (0.02), fludioxonil (0.01), fluquinconazole (0.01), flusilazole (0.01), flutriafol (0.02), folpet (0.01), hexaconazole (0.01), imazalil (0.02), imibenconazole (0.01), iprodione (0.02), krezoxim-methyl (0.01), mepanipyrim (0.01), metalaxyl (0.01), metconazole (0.02), myclobutanil (0.01), oxadixyl (0.01), penconazole (0.01), pencycuron (0.05), picoxystrobin (0.01), prochloraz (0.01), procymidone (0.01), propiconazole (0.01), pyrazophos (0.01), pyrimethanil (0.01), quinoxyfen (0.01), quintozene (0.01), tebuconazole (0.02), tecnazene (0.01), tetraconazole (0.01), tolclofos-methyl (0.01), tolylfluanid (0.01), triadimefon (0.01), triadimenol (0.01), trifloxystrobin (0.01), vinclozolin (0.01), zoxamide (0.01)
Herbicides	Acetochlor (0.01), atrazine (0.01), bromacil (0.01), chlorpropham (0.01), cyanazine (0.01), cyprazine (0.01), diflufenican (0.01), flurochloridone (0.01), lenacil (0.05), linuron (0.05), metribuzin (0.01), metazachlor (0.01), napropamide (0.05), nitrofen (0.01), oxyfluorfen (0.01), pendimethalin (0.02), prometryn (0.01), propachlor (0.01), propaquizafop (0.05), propazine (0.01), propham (0.02), propyzamide (0.01), simazine (0.01), trifluralin (0.01)
Growth retardant	Paclobutrazol (0.01)

residues were carried out (Chmiel 1979; Murawska 1980). Test results were confirmed in accordance with European Commission guidelines (Document SANCO 2011). The obtained results were compared with the maximum residue limits (MRL) in force in Poland (Regulation EC 2005).

Estimation of dietary exposure

According to Directive 396/2005, the lifetime exposure, and where appropriate, the acute exposure of consumers to pesticide residues in food products should be evaluated in accordance with community procedures and practices, with consideration of the guidelines published by the World Health Organisation (Regulation EC 2005).

Dietary exposure assessments combine food consumption data with data on concentrations of chemicals in food. The resultant dietary exposure estimate is then compared with the relevant toxicological or nutritional reference values for the food chemical of interest. Acute or chronic exposure may be assessed,

Table 2 Pesticide residues found in samples

Active substance	Samples with residues		Range of found residues		MRL (mg/kg)
	Number	Percent (%)	Min(mg/kg)	Max (mg/kg)	
Boscalid (F)	28	9.0	0.01	0.21	2
Chlorpyrifos (I)	17	5.4	0.01	0.10	0.5
Chlorpyrifos-methyl (I)	4	1.3	0.01	0.06	0.5
Captan (F)	129	41.3	0.01	0.72	3
Cypermethrin (I)	11	3.5	0.01	0.07	1
Cyprodinil (F)	14	4.5	0.01	0.11	1
Diazinon[a, b] (I)	4	1.3	0.01	0.02	0.01
Difenoconazole (F)	10	3.2	0.01	0.09	0.5
Dithiocarbamates (dithiocarbamates expressed as CS_2, including maneb, mancozeb, metiram, propineb, thiram and ziram) (F)	21	6.7	0.01	0.87	5
Dimethoate (I)	1	0.3	0.02	–	0.05
Fenarimol[a] (F)	1	0.3	0.03	–	0.3
Fenazaquin (I)	10	3.2	0.01	0.10	0.1
Fenitrothion[a, b] (I)	5	1.6	0.01	0.05	0.01
Flusilazole (F)	4	1.3	0.01	0.02	0.02
Folpet (F)	14	4.5	0.01	0.19	3
Indoxacarb[b] (I)	9	2.9	0.02	0.55	0.5
Iprodione[c] (F)	1	0.3	0.14	–	5
Kresoxim-methyl (F)	2	0.6	0.01	0.03	0.2
Myclobutanil (F)	6	1.9	0.01	0.02	0.5
Pyrimethanil (F)	20	6.4	0.01	0.59	5
Pirimicarb (I)	18	5.8	0.01	0.05	2
Procymidone[a] (F)	1	0.3	0.01	–	0.02
Propiconazole (F)	2	0.6	0.01	0.03	0.15
Tolylfluanid[a] (F)	1	0.3	0.08	–	3
Trifloxystrobin (F)	17	5.4	0.01	0.11	0.5

F fungicide, *I* insecticide, *MRL* maximum residues limit

[a] Application of the substance was forbidden

[b] The substance of which residue level exceeded MRL

[c] Application of the substance was not recommended for that crop

where short-term exposure covers a period of 24 h, and long-term exposure covers average daily exposure over the entire lifetime (WHO 2008).

WHO templates were used for dietary exposure assessments (WHO 2011a, b).

International Estimated Daily Intakes (IEDI) were calculated according to Eq. 1 and were then compared to acceptable daily intakes (ADIs).

$$\mathrm{IEDI} = \sum \frac{\text{Food chemical concetration} \times \text{Food consumption}}{\text{Body weight}} \quad (1)$$

Food consumption was accepted according to data from the WHO database at the level of 0.0406 kg/person/day.

International Estimated Short-Term Intakes (IESTI) were calculated according to Eq. 2 and were then compared with acute reference doses (ARfDs).

A meal-sized portion, such as a single fruit or vegetable, may have higher residue content than a composite sample if the unit weight of a whole fruit or vegetable is greater than 25 g. The variability factors, *v*, shown below are applied in the equations. When sufficient data on residues in single units is available and makes it

Table 3 Estimation of chronic dietary exposure to pesticide residues for apples in years 2008–2012

Active substance	Average residue level (mg/kg)	Consumption (kg/person/day)	Intake (mg/peson/day)	ADI (mg/kg body weight)	Intake			
					Adult		Toddler	
					(mg/kg body weight/day)	%ADI	(mg/kg body weight/day)	%ADI
Boscalid (F)	0.082	0.0406	0.00332	0.04	0.00004	0.109	0.00023	0.573
Chlorpyrifos (I)	0.032		0.00129	0.01	0.00002	0.170	0.00009	0.889
Chlorpyrifos-methyl (I)	0.025		0.00102	0.01	0.00001	0.134	0.00007	0.700
Captan (F)	0.140		0.00568	0.1	0.00007	0.075	0.00039	0.392
Cypermethrin (I)	0.024		0.00096	0.05	0.00001	0.025	0.00007	0.132
Cyprodinil (F)	0.042		0.00171	0.03	0.00002	0.075	0.00012	0.393
Diazinon[a] (I)	0.015		0.00061	0.0002	0.00001	4.007	0.00004	21.000
Difenoconazole (F)	0.023		0.00093	0.01	0.00001	0.123	0.00006	0.644
Dithiocarbamates (F)	0.148		0.00599	0.05	0.00008	0.158	0.00041	0.827
Dimethoate (I)	0.020		0.00081	0.001	0.00001	1.068	0.00006	5.600
Fenarimol (F)	0.030		0.00122	0.010	0.00002	0.160	0.00008	0.840
Fenazaquin (I)	0.031		0.00126	0.005	0.00002	0.331	0.00009	1.736
Fenitrothion (I)	0.024		0.00097	0.005	0.00001	0.256	0.00007	1.344
Flusilazole (F)	0.013		0.00051	0.002	0.00001	0.334	0.00004	1.750
Folpet (F)	0.099		0.00402	0.1	0.00005	0.053	0.00028	0.277
Indoxacarb (I)	0.098		0.00397	0.006	0.00005	0.871	0.00027	4.563
Iprodione (F)	0.140		0.00568	0.06	0.00007	0.125	0.00039	0.653
Kresoxim-methyl (F)	0.020		0.00081	0.4	0.00001	0.003	0.00006	0.014
Myclobutanil (F)	0.012		0.00047	0.025	0.00001	0.025	0.00003	0.131
Pyrimethanil (F)	0.097		0.00394	0.17	0.00005	0.030	0.00027	0.160
Pirimicarb (I)	0.025		0.00102	0.035	0.00001	0.038	0.00007	0.200
Procymidone (F)	0.010		0.00041	0.0028	0.00001	0.191	0.00003	1.000
Propiconazole (F)	0.020		0.00081	0.04	0.00001	0.027	0.00006	0.140
Tolylfluanid (F)	0.080		0.00325	0.1	0.00004	0.043	0.00022	0.224
Trifloxystrobin (F)	0.025		0.00100	0.1	0.00001	0.013	0.00007	0.069

F fungicide, *I* insecticide, *ADI* acceptable daily intake

[a] The substance of which residue level exceeded MRL

possible to calculate a more realistic variability factor for a commodity, the calculated value should replace the default value of 3 for all commodities (WHO 2008).

$$\text{IESTI} = \frac{U \times \text{HR} \times v + (\text{LP} - U) \times \text{HR}}{\text{Body weight}} \qquad (2)$$

LP Greatest large portion expressed (97.5th percentile of eaters), in kilogram of food per day (for apples 0.6245 kg)
HR Highest residue in composite sample of an edible portion, in milligram per kilogram
U Unit weight, in kilogram (for apples 0.127 kg)
v Variability factor representing the ratio of residue in the 97.5th percentile to the mean residue in single units. This factor has a value of three for apples.

IEDI and IESTI were calculated for two population groups: adults, consumers aged 19 to 64, both male and female, with a mean body weight of 76.0 kg; toddlers, consumers aged 18 months to 4 years, both male and female, with a mean body weight of 14.5 kg.

ADI and ARfD values are given by the European Commission, the European Food Safety Authority, and the Standing Committee on the Food Chain and Animal Health, and these values are derived from the pesticide database (http://ec.europa.eu/sanco_pesticides/public/index.cfm).

Evaluated consumer exposure values that did not exceed 100 % of the ADI or ARfD value were considered to be acceptable and not constituting a threat to health.

Results and discussion

Pesticide residues were found in 192 samples (61.5 % of tested samples). Twenty-five active substances were found in the analysed fruit samples, and 16 of them were fungicides, and 9 were insecticides. In six samples (1.9 %), these residues exceeded MRL levels. Violations concerned the insecticides: indoxacarb, diazinon and fenitrothion.

Analyses of samples also showed the presence of substances banned for use in pesticides (Regulation EC 2009). There were 12 cases where such substances were found in apples, i.e. diazinon, fenitrothion, procymidone, fenarimol and tolylfluanid. Iprodione was found in one analysed sample—an active substance not recommended for protection of apples.

Multiple residues were found in the tested samples, with residues of six compounds being found in one sample, residues of five compounds found in five samples, residues of four compounds found in 14 samples, residues of three compounds found in 23 samples, residues of two compounds found in 45 samples, and one active substance found in 104 samples.

The following fungicides were found the most often: captan (41.3 % of analysed samples), boscalid (9.0 %) and dithiocarbamates (6.7 %), while the most often found insecticides were: pirimicarb (5.8 %),

Table 4 Estimation of short-term dietary exposure to pesticide residues for apples in years 2008–2012

Active substance	The highest residue level (HR) (mg/kg)	Intake (mg/peson/day)	ARfD (mg/kg body weigt)	Intake			
				Adults		Toddler	
				(mg/kg body weight /day)	% ARfD	(mg/kg body weight /day)	% ARfD
Diazinon (I)	0.02	0.01757	0.025	0.00023	0.925	0.00121	4.847
Fenarimol (F)	0.03	0.02636	0.02	0.00035	1.734	0.00182	9.088
Fenitrothion (I)	0.05	0.04393	0.013	0.00058	4.446	0.00303	23.302
Indoxacarb (I)	0.55	0.48318	0.125	0.00636	5.086	0.03332	26.658
Iprodione (F)	0.14	0.12299	1.125	0.00162	0.144	0.00848	0.754
Procymidone (F)	0.01	0.00879	0.012	0.00012	0.963	0.00061	5.049
Tolylfluanid (F)	0.08	0.07028	0.25	0.00092	0.370	0.00485	1.939

F fungicide, *I* insecticide, *ARfD* acute reference dose chlorpyrifos (5.4 %) and cypermethrin (3.5 %). Table 2 contains detailed data.

Table 3 shows evaluated long-term human exposure following the consumption of all determined pesticides. The highest long-term consumer exposure was found in the case of consumption of apples with diazinon residue for both groups, adults and toddlers (4 % ADI, adults; 21 % ADI, toddlers).

Short-term exposure is shown in Table 4. It was calculated for pesticides exceeding MRLs and for banned and unrecommended pesticides. The highest values of short-term exposure were obtained in the case of consumption of apples with indoxacarb (5 % ARfD, adults; 27 % ARfD, toddlers) and fenitrothion (4 % ARfD, adults; 23 % ARfD, toddlers).

Conclusions

- Although fungicides are the pesticides found most often in apples, the consumption of apples with insecticide residues constitutes the greatest hazard to human health.
- The highest long-term consumer exposure was found in the case of consumption of apples with diazinon residue for both groups, adults and toddlers (4 % ADI, adults; 21 % ADI, toddlers).
- The highest values of short-term exposure were obtained in the case of consumption of apples with indoxacarb (5 % ARfD, adults; 27 % ARfD, toddler) and fenitrothion (4 % ARfD, adults; 23 % ARfD, toddler).
- The intake of pesticide residues in Polish apples did not pose a danger to the health of consumers (Nowacka and Gnusowski 2007; Łozowicka and Kaczyński 2011), but consumers may be exposed to many of the same pesticides from a variety of foods, and the diet in general must be taken into consideration to determine the true risk associated with pesticide residue exposure.

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