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Occurrence of pesticide residues in fruit from Podlasie (Poland) in 2012

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Abstract: Extensive use of pesticides in agriculture can lead to contamination of fruit harvests and an increased risk of toxic effects on humans. A total of 123 fruit samples harvested in 2012 in the north-eastern region of Poland were analysed for pesticide residues as part of the national monitoring programme, and as part of research commissioned by private customers. Pesticide residues were found in 64.2% of the samples. There were pesticide residues below the maximum residue level (MRL) in 63 (51.2%) of the samples, while 16 (13%) exceeded MRLs set by Regulation (EC) 396/2005. The gooseberry, currant, and strawberry samples showed the most contamination. The most frequently detected pesticides were dithiocarbamates (54) followed by difenoconazole (22), boscalid (17), and alpha-cypermethrin (15). More than half of analysed samples had multiple residues (up to 8 residues), with multiple residues most common in gooseberry and currant samples. This study shows cases of non-authorised pesticide use by farmers who are trying to protect certain fruit.

Key words: fruits, monitoring programme, pesticide residues, plant protection, private customers

Introduction

In Poland, fruit production is spread throughout the country. In 2012, there were 3.84 mln tons of fruit harvested. This harvest was around 13% higher than in the previous year, and 23% higher than the average 2004–2011 harvest. The fruit production area, in total, amounted to 431,700 ha (GUS 2013).

Fruit constitutes an important part of the human diet. Fruit contains carbohydrates, proteins, vitamins, and minerals required for human health. Black currants contain high amounts of vitamin C, essential for the immune system. Apples are a valuable source of fibre**.** Fibre acts as an appetite suppressant. Furthermore, apples are a rich source of antioxidants and antioxidants have antiatherogenic potential. Raspberries contain large amounts of tannins and flavonoids (Łozowicka *et al.* 2012), which have diuretic properties.

It is important that the nutritional constituents found in fruit are completely used and are able to perform their functions. For these reasons, within permissible limits, crops must be free from toxic substances and other harmful compounds. However, since fruit is very sensitive to various fungal and bacterial diseases, pests, and even weeds, it has become a widely adopted strategy to use plant protection products (p.p.p.) to protect fruit.

More than 1,000 substances that are active against pests are currently used worldwide (Tomlin 2009). In Poland, there are more than 200 pesticides (active substances) and 1,183 plant protection products registered. Matyjaszczyk (2011) observed a reduction in the general use of pesticides. The amount of active substances decreased from 340 in 2003 to 279 in 2009. According to the GUS (2012), in 2012 the exposure to p.p.p. significantly increased. The sales of p.p.p. in agriculture were approximately 62,000 tons of active substances.

Pesticides are repeatedly applied during the entire period of growth and sometimes even at the fruiting stage (Sharma *et al.* 2010). Pest- and disease control use a variety of plant protection products. For example, there are 270 p.p.p. registered for growing apple trees, 70 for strawberry, 50 for currants, 27 for raspberry, and 22 for gooseberry (www.minrol.gov.pl). The least p.p.p. are registered for raspberry and gooseberry; fruits considered as minor crops.

The use of p.p.p. can endanger human health and the environment because of the toxic potential, high persistence, and bioaccumulation of p.p.p. (Nowacka and Gnusowski 2007; Bempah *et al.* 2011). 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 (Berrada *et al.* 2010). The improper use of pesticides may cause some residues to remain in edible fruits. The diet is the main exposure route to pesticide residues. It is the

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diet that is thought to be five times higher than other exposure routes, such as air, and drinking water (Juraske *et al.* 2009). Fruit contains higher pesticide residue levels compared to other food of plant origin, because fruit is mainly consumed raw or semi-processed (Berrada *et al.* 2010; Chen *et al.* 2011).

Monitoring surveys are of increasing importance to ensure minimal pesticide residue levels in food. Nowadays, monitoring programmes for pesticides in food are carried out worldwide to protect consumer health, improve management of agricultural resources, and to prevent economic losses (Arias *et al.* 2014). Governments and international organisations regulate the use of pesticides by setting the maximum residue level (MRL) of pesticides allowed in food (Lee and Jo 2012). The surveillance focuses on the proper use of pesticides in terms of authorisation and registration and also focuses on compliance with maximum residue limits (Claeys *et al.* 2011).

The objective of this paper is to present and discuss the results obtained by national monitoring and research commissioned for private customers, of pesticide residue in fruit grown in north-eastern Poland. The results can be used when designing future control programmes for this region and taking preventive actions to minimise human health risks.

Materials and Methods

Samples

A total of 123 samples were analysed for pesticide residues in 2012, of which 31 were from the monitoring program and 92 from private customers. The percentages of the types of fruit are shown in figure 1. Currants and strawberries were the most abundant samples analysed – 53.3% (46 and 20 samples, respectively).

Standards and reagents

All reagents which were used in the procedure have an analytical grade. In 2012, the scope of the monitoring programme was to analyse 168 active substances (Table 1). The results of the analysis were compared against the MRL according to Regulation (EC) No. 396/2005 (Reg. 2005).

Analytical procedure

Sample preparation was done using three techniques (Fig. 2): a multi-residue method (MRM) and two single residue methods (SRM), fully described in our earlier published work (Łozowicka *et al.* 2012; Łozowicka *et al.* 2014; Łozowicka 2015). These methods were validated (SANCO 2011) and accredited in accordance with PN-EN ISO/IEC 17025 (ISO 2005) by the Polish Centre of Accreditation (PCA).

Method 1. *MRM – isolation and determination of 166 pesticide residues using gas chromatography* (*GC*)

A homogenised sample of 2 g was put in a mortar in which the mortar had a 4 g solid support. Depending on the commodity, either silica gel (e.g. strawberries) or florisil (e.g. apples) was used. Everything was manually blended using a pestle to obtain a homogeneous mixture. After homogenisation, the blend was quantitatively transferred with a spatula to a glass macro column packed with anhydrous sodium sulfate (5.0 g) and silica gel (2.5 g). The analytes were eluted using 15 ml hexane/acetone (8 : 2, v/v) and 15 ml hexane/diethyl ether/acetone (1 : 2 : 2, v/v/v). The extract was evaporated to dryness using a rotary vacuum evaporator at a temperature of about 40°C. Then the eluate was re-dissolved using 2 ml of hexane/acetone (9 : 1, v/v). The final solution was transferred into a GC vessel and placed in the rack of the autosampler.

Method 2. *SRM – isolation and determination of carbendazim residues using high performance liquid chromatography* (*HPLC*)

A representative sample of 20 g was homogenised with 150 ml acetone for 5 min. Then 2.5 g of celite was added to the extract and filtered through a Buchner funnel. The final filtrate was evaporated in a rotary evaporator leaving

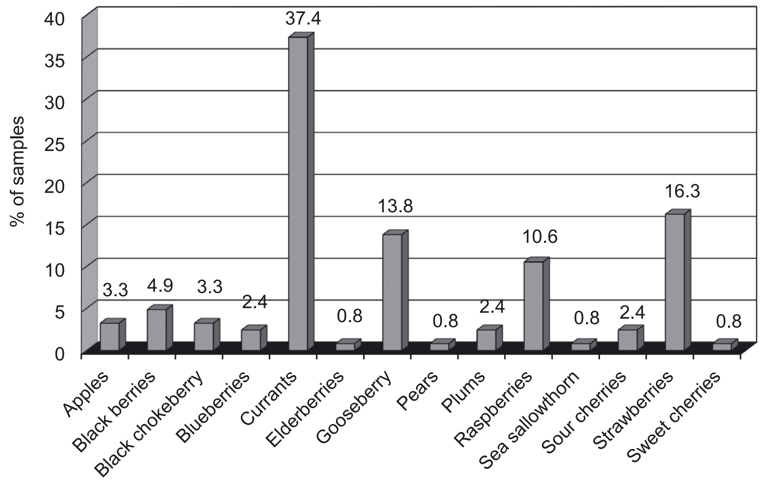

Fig. 1. Fruits analysed in 2012

Table 1. Analysed active substances and their limits of detection

Pesticides	Active substances
Insecticides and acaricides (82)	acetamiprid (0.01); acrinathrin (0.02); aldrin (0.005); alpha-cypermethrin (0.03); alpha-HCH (0.005); azinphos-ethyl (0.02); azinphos-methyl (0.02); beta-cyfluthrin (0.02); beta-HCH (0.01); bifenthrin (0.01); bromopropylate (0.01); bromophos-ethyl (0.02); bromophos-methyl (0.01); buprofezin (0.02); cadusafos (0.01); carbaryl (0.05); carbofuran (0.02); chlorfenvinphos (0.01); chlorpyrifos (0.01); chlorpyrifos-methyl (0.01); cyfluthrin (0.01); cypermethrin (0.03); deltamethrin (0.05); diazinon (0.01); dichlorvos (0.01); dicofol (0.02); dieldrin (0.005); dimethoate (0.01); endosulfan sum of alpha-endosulfan, beta-endosulfan, endosulfan-sulfate (0.03); endrin (0.005); esfenvalerate (0.02); ethion (0.01); ethoprophos (0.02); fenazaquin (0.02); fenthion (0.01); fenitrothion (0.01); fenpropathrin (0.01); fenvalerate (0.02); fipronil (0.005); formothion (0.01); gamma-HCH (lindane) (0.005); HCB (0.005); heptachlor (0.005); heptachlor-epoxide (0.005); heptenophos (0.01); hexythiazox (0.05); indoxacarb (0.02); isofenphos (0.01); isofenphos-methyl (0.01); lambda-cyhalothrin (0.01); malathion (0.02); mecarbam (0.02); methacrifos (0.05); mevinphos (0.01); methidathion (0.01); methoxychlor (DMDT) (0.01); DDT sum of o,p′-DDT, p,p′-DDD, p,p′-DDE, p,p′-DDT (0.03); parathion-ethyl (0.01); parathion-methyl (0.01); permethrin (0.04); phenthoate (0.01); phosalone (0.01); phosmet (0.01); pirimicarb (0.02); pirimiphos (0.01); pirimiphos-methyl (0.01); profenofos (0.01); propoxur (0.01); pyridaben (0.02); pyriproxyfen (0.05); quinalphos (0.01); tebufenpyrad (0.01); teflubenzuron (0.03); tetrachlorvinphos (0.01); tetradifon (0.01); triazophos (0.01); zeta-cypermethrin (0.02)
Fungicides (62)	azaconazole (0.01); azoxystrobin (0.02); benalaxyl (0.03); bitertanol (0.013); boscalid (0.01); bromuconazole (0.01); bupirimate (0.01); captan (0.01); carbendazim (0.02); chlorothalonil (0.01); cyproconazole (0.01); cyprodinil (0.01); dichlofluanid (0.01); dicloran (0.01); difenoconazole (0.05); dimethomorph (0.05); dimoxystrobin (0.01); diniconazole (0.01); diphenylamine (0.01); dithiocarbamates* (0.05); epoxiconazole (0.01); fenarimol (0.01); fenbuconazole (0.01); fenchlorphos (0.01); fenhexamid (0.01); fenpropimorph (0.02); fludioxonil (0.01); fluquinconazole (0.01); flusilazole (0.01); flutriafol (0.01); folpet (0.01); hexaconazole (0.01); imazalil (0.01); imibenconazole (0.01); iprodione (0.02); kresoxim-methyl (0.01); mepanipyrim (0.01); metalaxyl (0.01); metconazole (0.01); myclobutanil (0.01); oxadixyl (0.03); paclobutrazol (0.02); penconazole (0.02); pencycuron (0.03); 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 (0.01); tecnazene (0.02); tetraconazole (0.01); tolclofos-methyl (0.01); tolylfluanid (0.02); triadimefon (0.02); triadimenol (0.05); trifloxystrobin (0.01); qvinclozolin (0.01); zoxamide (0.02)
Herbicides and growth regulators (24)	acetochlor (0.02); atrazine (0.01); bromacil (0.01); chlorpropham (0.01); cyanazine (0.01); cyprazine (0.01); diflufenican (DFF) (0.01); flurochloridone (0.01); lenacil (0.02); metazachlor (0.01); metholachlor (0.02); metribuzin (0.02); napropamide (0.02); nitrofen (0.01); oxyfluorfen (0.01); pendimethalin (0.02); prometryn (0.01); propachlor (0.02); propaquizafop (0.03); propazine (0.01); propham (0.02); propyzamide (0.02); simazine (0.01); trifluralin (0.01)

*determined as CS_2 residues

The limits of detection were given in brackets in mg · kg^{-1}

about 20 ml. Then, this solution was applied to a ChemElut cartridge containing diatomaceous earth. After 25 min of equilibration, the pesticides were eluted with dichloromethane. The organic solvent was evaporated to dryness using a rotary vacuum evaporator at 40°C and dissolved in a 2 ml volume of a mixture of acetonitrile/water (2 : 8 v/v). The final solution was put into a HPLC (Łozowicka and Kaczyński 2009a) vessel and placed in the rack of the autosampler.

Method 3. *SRM – isolation and determination of dithiocarbamates using spectrophotometry*

Dithiocarbamate residues were determined by a modified colorimetric method (Chmiel 1979). This method allows determination of dithiocarbamate fungicides as a group (mancozeb, maneb, methiram, propineb, thiram, ziram), expressed as carbon disulphide. A fifty g sample was heated for 45 min (temperature about 80°C) with 60 ml of hydrochloric acid and tin (II) chloride to release carbon disulphide from the dithiocarbamates in an alkaline pH. The ditiocarbamates decomposed with the emission of carbon disulphide. Carbon disulphide was separated and collected in a methanolic solution of potassium hydroxide. Under these conditions, carbon disulphide formed potassium xantogenate which was next heated with zinc acetate to obtain zinc sulfide. This compound in an acidic medium released hydrogen sulfide which formed with N, N-dimethyl-1,4-phenylenediammonium dichloride and in presence of iron ions Fe(III) (from ferrous ammonium sulfate solution) methylene blue. Finally, the quantity of the formed complex (final volume 25 ml) was estimated by measuring the absorbance at a wavelength of 662 nm on a spectrophotometer (Helios Delta VIS) (Łozowicka and Kaczyński 2009b). The concentration was calculated from the absorbance of the complex, and the results were expressed in mg CS_2 · kg^{-1}.

Method of validation

In this study, four matrices were selected as a commodity for the validation of these methods used to determine pesticide residue (SANCO 2011). Calibration curves were obtained from matrix–matching calibration solutions. The lowest concentration level in the calibration curve was established as a limit of detection. Calibration standards were prepared by adding appropriate spiking solutions to a blank matrix. Recovery data was obtained at the three spiking levels of the pesticides in the matrix, each day, using blank samples in accordance with European Commission (EC) guidelines (SANCO 2011). The method accuracy and precision were evaluated by performing recovery studies. The precision was expressed as the relative standard deviation (RSD). Accuracy can be

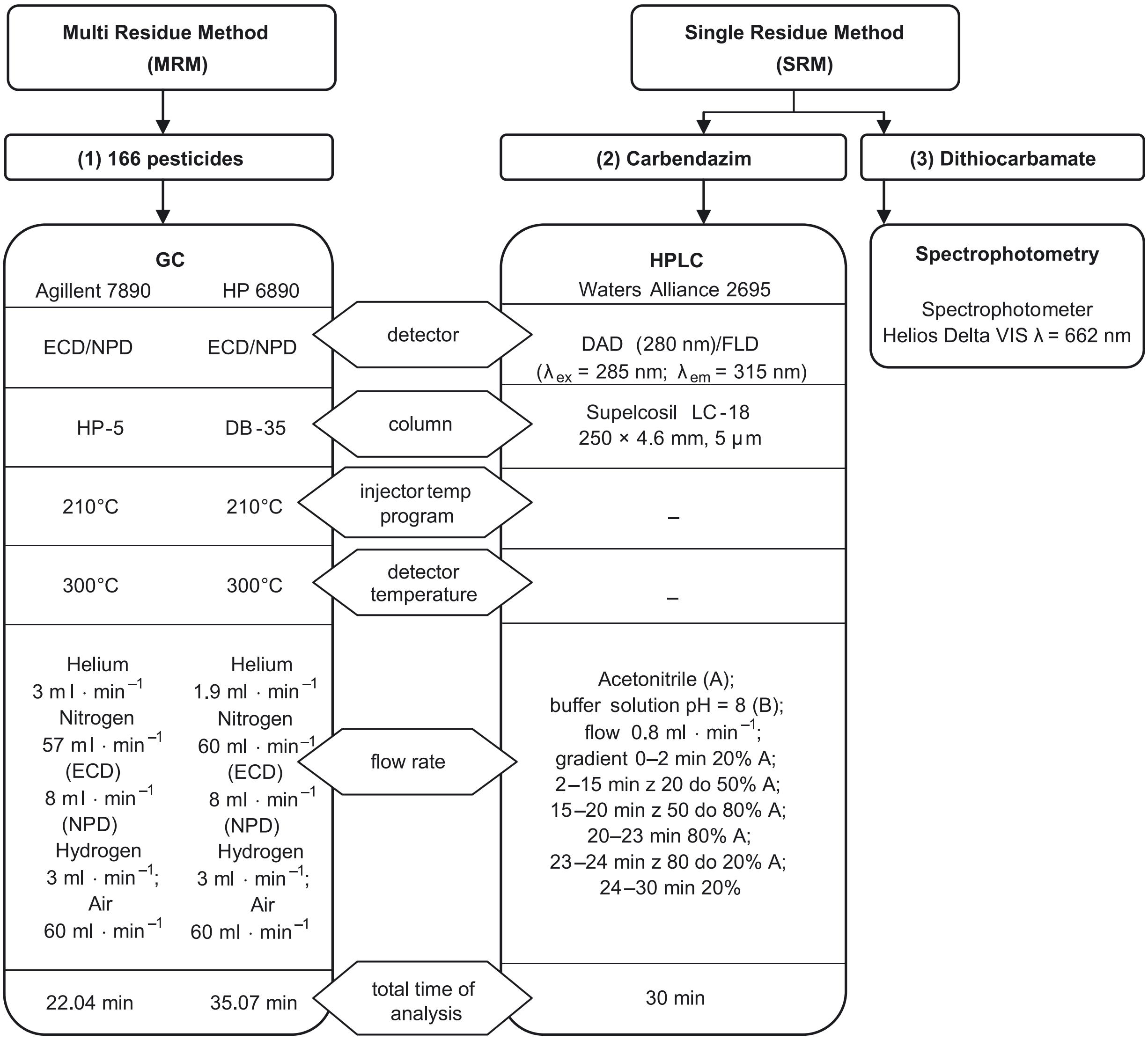

Fig. 2. Scheme of sample preparation procedures. GC – gas chromatography, HPLC – high performance liquid chromatography, ECD – electron capture detector, NPD – nitrogen phosphorus detector, DAD – diode array detector, FLD – fluorescence detector

measured by analysing samples with known concentrations and comparing the measured values with the true values. The limit of quantification (LOQ) was defined as the lowest concentration of the analyte that could be quantified with acceptable precision and accuracy. The limit of detection (LOD) was defined as the lowest concentration of the analyte in a sample, which could be detected but not necessarily quantified. The limit of quantification and the limit of detection were evaluated as the signal-to-noise ratios (S/N) of 10 : 1 and 3 : 1 for the pesticide, respectively.

To be sure about the quality of the results, the laboratory regularly takes part in proficiency testing schemes organised 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 laboratories undertaking the analysis of these commodities for official control of pesticide residues.

Results and Discussion

Method of validation

The parameters used to validate the methods were: linearity, precision and accuracy, recovery, sensibility (limits of detection and quantification), and repeatability. All the analyses were carried out using pesticide-free apples, raspberries, currants, and sweet cherries. Linearity was evaluated by the calculation of a five-point linear plot with three replicates, based on linear regression and squared correlation coefficient (R^2). All pesticides showed linearity in the concentration range of 0.002–5.0 mg · kg^{-1} (Method 1), 0.02–2.0 mg · kg^{-1} (Method 2) and 0.03–5.0 mg · kg^{-1} (Method 3) with correlation coefficients higher than 0.99553 up to 1. The accuracy and precision of the method via recovery experiments with fortified samples, was tested. In this study, recovery experiments for 166 pesticides at three spiking levels (0.002 to 0.05 mg · kg^{-1}, 0.05–0.5 mg · kg^{-1} and 0.5–5.0 mg · · kg^{-1}), for carbendazim (0.02 mg · kg^{-1}, 0.5 mg · kg^{-1}, 2.0 mg · kg^{-1}), and for dithiocarbamates (0.03 mg · kg^{-1}, 0.1 mg · kg^{-1} and 5.0 mg · kg^{-1}) with a sum expressed as CS_2, for a period of five days, were performed.

Mean recoveries for samples spiked at three fortification levels ranged from 71.07 to 119.90% with the exception of buprofezin, cypermethrin, and phosalone (40–70%) and beta-endosulfan, heptachlor and tetraconazole (120–124%). However, a range of 60–140% may be used in routine multiresidue analysis (SANCO 2011). Relative standard deviations ranged from 0.10 to 12.8%, showing good repeatability. For most compounds the values obtained were lower than their respective MRL. The LOQs ranged from 0.001 to 0.009 mg · kg^{-1} (Method 1), 0.01 to 0.04 mg · · kg^{-1} (Method 2), and 0.02 to 0.05 mg · kg^{-1} (Method 3). These results indicated that the validation parameters were good and consequently the pesticides were satisfactorily determined using these methods.

Pesticide residues in fruits

Pesticide residues were found in 64.2% of the samples. There were pesticide residues below the MRL in 51.2% (63) samples, while 13% (16) of tested sample exceeding MRL. Pesticide residues were not detected in 35.8% of the fruit samples (Table 2).

In the analysed samples, 34 different pesticides were found: 12 insecticides and/or acaricides, 18 fungicides, and four herbicides. Dithiocarbamates (ranging from 0.05 to 2.08 mg · kg^{-1}) were the pesticides most frequently detected (41.5%, 51 samples), mainly in gooseberry, strawberry, and currant samples (Fig. 3). The contents of dithiocarbamates detected in this study, in fruit from north-eastern Poland, were similar to the distribution across Poland (Nowacka *et al.* 2012). In Brazil, dithiocarbamates

Table 2. Samples analysed by the monitoring programs and for private customers in 2012

Crop	Number of samples	n.d.* [%]	< MRL** [%]	> MRL [%]
Apples	4	0.8	2.4	0
Black berries	6	2.4	2.4	0
Black chokeberries	4	3.3	0	0
Blueberries	3	0.8	1.6	0
Currants	46	8.9	17.9	10.6
Elderberries	1	0.8	0	0
Gooseberries	17	0	12.2	1.6
Pears	1	0.8	0	0
Plums	3	2.4	0	0
Raspberries	13	6.5	4.1	0
Sea sallowthorns	1	0.8	0	0
Sour cherries	3	2.4	0	0
Strawberries	20	4.9	10.6	0.8
Sweet cherries	1	0.8	0	0
Total	123	35.8	51.2	13.0

*n.d. – not detected
**MRL – maximum residue level

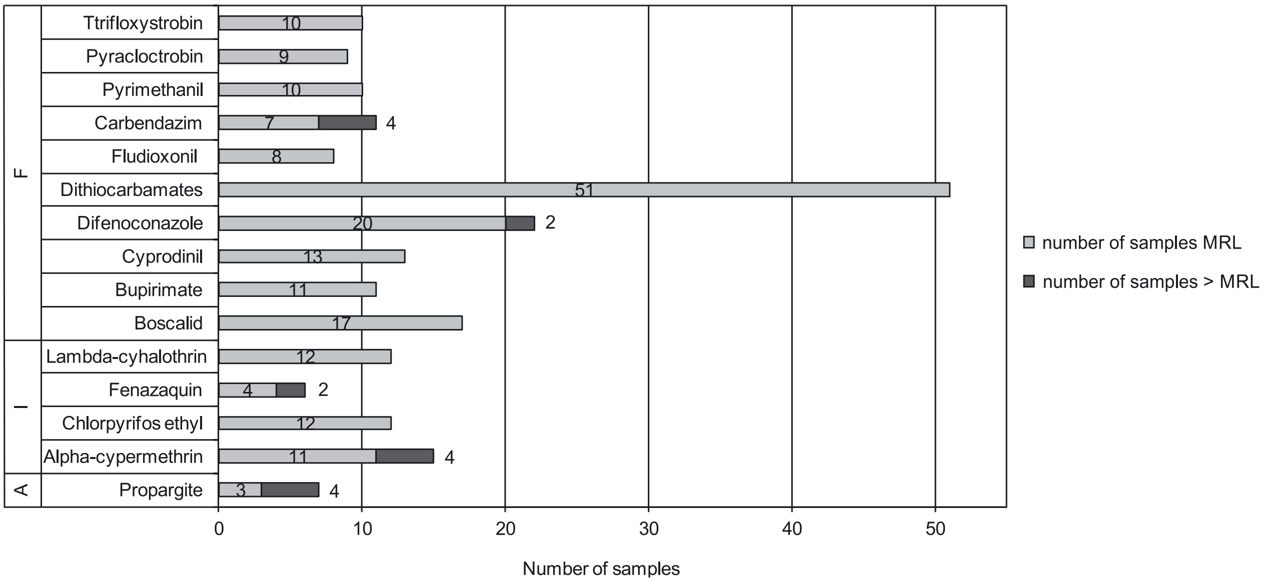

Fig. 3. Type of pesticide detected and frequency of detection (more than 5 tested samples): A – acaricides; I – insecticides; F – fungicides; MRL – maximum residue level

were found in 41.6% of the samples analysed in the monitoring programmes (Jardim *et al.* 2012).

Fungicides frequently found in the analysed samples were difenoconazole (ranging 0.01 to 0.12 mg · kg^{-1}), boscalid (0.04 to 1.13 mg · kg^{-1}), and cyprodinil (0.01 to 0.08 mg · kg^{-1}). The insecticides most frequently found in the analysed samples were alpha-cypermethrin (ranging from 0.01 to 0.07 mg · kg^{-1}), chlorpyrifos ethyl (from 0.004 to 0.02 mg · kg^{-1}), and lambda-cyhalothrin (from 0.01 to 0.07 mg · kg^{-1}).

Other authors have reported contamination with multiple pesticides. Nougadère *et al.* (2012) determined residues of 36 different insecticides and/or acaricides, 32 fungicides, and one herbicide in food purchased from food stores in France. In vegetables from four large supermarkets located in the Al-Qassim region of Saudi Arabia, 15 insecticides and/or acaricides, three fungicides, and three herbicides were detected by Osman *et al.* (2010). The presence of multiple residues may suggest non-compliance with the principles of good agriculture practice (EFSA 2010).

Of the 79 samples, in which one or more residues were detected, 17.9% contained only one substance, 40.1% contained between two to six substances, 5.7% between seven to eight substances. Fruit with multiple residues (up to eight different active substances), representing 46.3% of all samples, are shown in figure 4.

Currants had the highest number of samples with multiple residues (42.1% of positive currant samples), followed by gooseberries (26.3%), and then strawberries (17.5%). With the exception of blueberries, most of the fruit samples shown in figure 4 had two residues. Two currant samples had eight residues, one had seven residues, and one gooseberry sample also had eight different residues.

Chokeberry, elderberry, sweet cherry, pear, sea sallowthorn, plum, and sour cherry samples were free from residues. For gooseberry, 88.2% of the samples had residues below MRL, and 11.76% above MRL. The most frequently detected pesticides in the gooseberry samples were: dithiocarbamates from 0.05 to 1.64 mg · kg^{-1}, and difenoconazole from 0.02 to 0.12 mg · kg^{-1} (Table 3). For currants, 76.1% of the samples had residues, including 28.26% above MRL. The most frequently detected pesticides in the currant samples included: dithiocarbamates which ranged from 0.08 to 2.08 mg · kg^{-1}, and alpha-cypermethrin from 0.01 to 0.07 mg · kg^{-1}. The highest residues found in currants and gooseberries were 2.08 and 1.64 mg · kg^{-1}, respectively. The results of other authors confirm that soft fruits (berries) are the group of crops where the producers most frequently use chemical plant protection products. Recent works by Matyaszek *et al.* 2013 and Walorczyk (2014) also revealed that berries (e.g. currants) more frequently contained pesticide residues than other agricultural crops.

Research has shown two types of infringements relating to the use of plant protection products (Table 3). The prevailing offense was that producers have used p.p.p. which were not recommended for the protection of the crop (45 of samples analysed). In gooseberries, the detected fungicides were trifloxystrobin (10), propiconazole (3), chlorothalonil (2), cyprodinil (2), fenhexamid (1), and tebuconazole (1), in currants – tetraconazole (1), in gooseberries and currants pirimethanil (4). The insecticide detected in gooseberries was chlorpyrifos ethyl (4), and fenazaquin was detected in raspberries and currants (6).

The maximum levels for residues were exceeded by 13% in the gooseberry, strawberry, and currant samples. In many cases, the causes of the detected pesticide residues were found to be the result of farmers using inappropriately measured amounts other than those approved for use in these crops, and the use of available preparations that are registered for other crops. These results confirm problems with the chemical protection of minor crops (Adamczewski *et al.* 2006).

Farmers generally use many types of pesticides to control harmful insects to minimise crop losses, nonetheless, many farmers use pesticides indiscriminately. Excessive and irrational use of pesticides on crops is common, with applications often carried out throughout the growing season (Bempah *et al.* 2012) and also in postharvest storage. Therefore, educating farmers on the safe use of pesticides is important. Increased awareness may help decrease the unsafe levels of pesticide residues (Chowdhury *et al.* 2013).

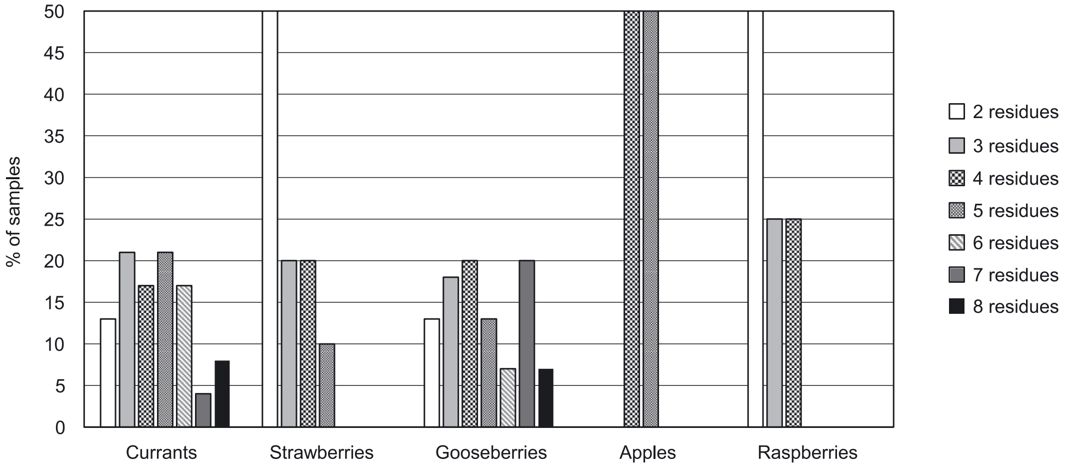

Fig. 4. Fruit with multiple pesticide residues

Table 3. Pesticide residues detected in fruit

Product	Number of samples	Active substance	Samples with residues		Range of detected residues [mg · kg^{-1}]		MRL* [mg · kg^{-1}]
			number	[%]	min.	max.	
1	2	3	4	5	6	7	8
Gooseberries	17	alpha-cypermethrin (I)	2	11.8	0.01	0.02	0.05
		azoxystrobin (F)	2	11.8	0.02	–	5.00
		bupirimate (F)	11	64.7	0.02	0.95	5.00
		chlorpyrifos ethyl (I)	4	23.5	0.005	0.01	1.00
		chlorothalonil (F)	2	11.8	0.05	0.08	10.00
		cyprodinil (F)	2	11.8	0.01	0.02	0.05
		dithiocarbamates (F)	16	94.1	0.05	1.64	5.00
		difenoconazole (F)	14	82.4	0.02	**0.12**	0.10
		fenhexamid (F)	1	5.9	0.05	–	5.00
		pendimethalin (H)	1	5.9	0.02	–	0.05
		pyrimethanil (F)	3	17.6	0.11	0.18	5.00
		propiconazole (F)	3	17.6	0.02	0.05	0.05
		tebuconazole (F)	1	5.9	0.06	–	2.00
		trifloxystrobin (F)	10	58.8	0.01	0.13	1.00
Blueberries	3	boscalid (F)	2	66.7	0.17	–	10.00
		cyprodinil (F)	2	66.7	0.03	0.07	5.00
		fludioxonil (F)	2	66.7	0.02	–	3.00
Blackberries	6	*DEET* (I)	3	50.0	0.005	0.006	0.01
Apples	4	cyprodinil (F)	2	50.0	0.01	–	1.00
		diazinon (I)	1	25.0	0.01	–	0.01
		dithiocarbamates (F)	1	25.0	0.06	–	5.00
		captan (F)	2	50.0	0.03	–	3.00
		pyrimethanil (F)	1	25.0	0.03	–	0.05
		propargite (A)	3	75.0	0.03	0.15	3.00
Raspberries	13	boscalid (F)	2	15.4	0.04	0.12	10.00
		chlorpyrifos ethyl (I)	1	7.7	0.02	–	0.50
		cyprodinil (F)	1	7.7	0.06	–	10.00
		fenazaquin (I)	1	7.7	0.10	–	0.01
		fenhexamid (F)	1	7.7	0.14	–	10.00
		fludioxonil (F)	1	7.7	0.02	–	5.00
		pyrimethanil (F)	3	23.1	0.05	0.29	10.00
		pyraclotrobin (F)	2	15.4	0.02	0.03	2.00
Strawberries	20	boscalid (F)	4	20.0	0.04	–	10.00
		cyprodinil (F)	6	30.0	0.01	0.08	5.00
		dithiocarbamates (F)	9	45.0	0.09	0.40	10.00
		fenhexamid (F)	2	10.0	0.07	0.50	5.00
		fludioxonil (F)	5	25.0	0.01	0.05	3.00
		folpet (F)	2	10.0	0.04	0.07	3.00
		glyphosate (H)	2	5.0	0.10	0.12	–
		pyrimethanil (F)	2	10.0	0.03	0.07	5.00
		propargite (A)	1	5.0	**0.02**	–	0.01

Table 3. Pesticide residues detected in fruit – *continuation*

1	2	3	4	5	6	7	8
Currants	46	acetamiprid (I)	2	4.3	**0.03**	**0.04**	0.01
		alpha-cypermethrin (I)	15	32.6	0.01	**0.07**	0.05
		bifenthrin (I)	1	2.2	0.10	–	0.50
		boscalid (F)	9	19.6	0.100	1.130	10.00
		chlorpyrifos ethyl (I)	7	15.2	0.004	0.012	1.00
		cypermethrin (I)	2	4.3	0.03	0.04	0.05
		difenoconazole (F)	8	17.4	0.01	0.07	0.20
		dithiocarbamates (F)	25	54.3	0.08	2.08	5.00
		esfenvalerate (I)	1	2.2	0.02	–	0.02
		fenazaquin (I)	5	10.9	0.01	**0.12**	0.01
		hexythiazox (A)	5	10.9	0.05	0.06	0.50
		carbendazim (F)	11	23.9	0.02	**0.12**	0.10
		lambda-cyhalothrin (I)	12	26.1	0.01	0.07	0.20
		pyrimethanil (F)	1	2.2	0.07	–	5.00
		propargite (A)	3	6.5	0.02	0.260	0.01
		pyracloctrobin (F)	7	15.2	0.07	0.290	3.00
		tetraconazole (F)	1	2.2	0.03	–	0.20
		thiacloprid (I)	5	10.9	0.01	0.320	1.00

*MRL – maximum residue level
A – acaricides, I – insecticides, F – fungicides, H – herbicides
In bold – samples with residues > MRL
Italics – samples with the detected active substance of plant protection products not-allowed for applying in the given crop

Conclusions

The results of this work highlight the pesticide-residue contamination of fruit harvested in north-eastern Poland during the 2012 season. Pesticide residues were found in 64.2% of the samples. Pesticide residues most often were determined in currant (44.3%), gooseberry (21.5%) and strawberry (17.7%) samples. Analyses of the samples indicate that farmers have problems protecting minor crops. During cultivation, available formulations were used which were registered in other crops. The pesticide-residue monitoring programme data can be useful in assessing whether the product has been applied to the crop according to the instructions on the approved labels. The programme can also predict the risk to consumers from exposure to pesticides through the diet.

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