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PESTICIDE RESIDUES IN BERRIES HARVESTED FROM SOUTH-EASTERN POLAND (2009–2011)

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ABSTRACT

Background. Poland is a leading grower/producer of berries in Europe that are either eaten raw or processed. As well as berries this includes fruit such as grapes, strawberries and other small fruits. Testing for the presence of active substances in Plant Protection Products, (PPP), in such fruit is however important, as part of measures taken to minimise human intake.
Objective. To determine the incidence of pesticide residues in berries harvested from South-Eastern Poland in 2009-2011.
Material and methods. Chromatographic separation followed by analytical detection was performed on 250 samples of various test fruits using an accredited methodology: GC/ECD/NPD, together with spectrophotometric detection wherever necessary, according to PN-EN ISO/IEC 17025. As part of previous monitoring, 126 active substances were identified in 2009, 132 in 2010 and 153 in 2011; levels were compared to Maximum Residue Limits (MRLs).
Results. Analyses showed that 46.4% of samples contained PPPs of which 4% exceeded the MRL. The most were found in raspberries, (58.8% of all tested), followed by 58.3% redcurrants, and gooseberries as well as 50% grapes. The most frequently found active substances of PPPs were pyrimethanil (15.6%), dithiocarbamates (12.4%), procymidone (8%), cyprodinil (5.6%) and difenoconazole (5.2%). The highest MRL exceedances were found in blackcurrants. Testing also revealed many examples of pesticides not recommended for the protection of specific crops: propiconazole in gooseberries, cyprodinil, flusilazole, iprodione, pyrimethanil in blackcurrants and folpet and captan in raspberries. Furthermore, active substances whose use in PPPs have been forbidden since 2008 were also detected, ie. endosulfan in blackcurrants and strawberries, fenitrothion in black and red currants as well as procymidone in raspberries, blackcurrants and strawberries. These data are consistent to those obtained from the whole of Poland and the European Union (EU).
Conclusions. Most pesticides were present in raspberries, redcurrants, gooseberries and grapes of which fungicides were the most frequently detected. These results are in keeping with other similar studies.

Key words: *residues, pesticides, berries*

STRESZCZENIE

Wprowadzenie. Polska jest liderem w produkcji owoców jagodowych w Europie, które są spożywane w postaci surowej i przetwarzanej. Do grupy tych owoców należą: winogrona, truskawki, owoce leśne i inne drobne owoce i jagody. Badania na obecność substancji aktywnych środków ochrony roślin (ś.o.r.) są bardzo ważne aby zminimalizować ich spożycie przez ludzi.
Cel badań. Celem pracy było przedstawienie występowania pozostałości pestycydów w owocach jagodowych pochodzących z rejonu południowo-wschodniej Polski w latach 2009–2011.
Materiał i metoda. Przebadano 250 próbek stosując akredytowane, wg PN-EN ISO/IEC 17025, metody badawcze: chromatograficzną (GC/ECD/NPD) oraz spektrofotometryczną. Program kontroli obejmował oznaczenie 126 substancji aktywnych w 2009 roku, 132 substancji aktywnych w 2010 roku i 153 substancji aktywnych ś.o.r. w 2011 roku. Uzyskane wyniki porównywano z najwyższymi dopuszczalnymi poziomami pozostałości (NDP).
Wyniki. 46,4% przebadanych próbek zawierało pozostałości pestycydów, a przekroczenia NDP zanotowano w 4% próbek. Najwięcej pozostałości stwierdzano w malinach – 58,8% (wszystkich próbek malin), następnie w czerwonych porzeczkach – 58,3%, agreście i winogronie – 50%. Najczęściej wykrywano pozostałości fungicydów m.in. pirymetanilu (15,6% próbek), ditiokarbaminianów (12,4%), procymidonu (8%), cyprodynilu (5,6%) i difenokonazolu (5,2%). Największą liczbę przekroczeń NDP stwierdzono w czarnych porzeczkach. Badania wskazały na obecność pestycydów nie zalecanych do ochrony określonych upraw. Wykryto np. propikonazol w agreście, cyprodynil, flusilazol, iprodion, pirymetanil w porzeczkach czarnych, a także folpet i kaptan w malinach. Wykryto także substancje aktywne, których stosowanie w ś.o.r. jest zabronione od 2008 roku, tj. endosulfan w czarnych porzeczkach i truskawkach, fenitrotion w czarnych i czerwonych

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porzeczkach, procymidon w malinach, czarnych porzeczkach i truskawkach. Uzyskane wyniki badań korelują z danymi otrzymanymi z obszaru całej Polski oraz z Unii Europejskiej.
Wnioski. Najwięcej pestycydów było obecnych w owocach malin, porzeczek czerwonych, agrestu i winogron. Najczęściej wykrywaną grupą pestycydów były fungicydy. Oznaczone ilości i rodzaje pestycydów w badanym materiale były porównywalne z wynikami badań podawanymi przez innych autorów.

Słowa kluczowe: *pozostałości, pestycydy, owoce jagodowe*

INTRODUCTION

Cultivating berries in Poland forms an important and dynamic part of fruit farming industry. Amongst the many small plantations that are thriving in this country, there are many multi-hectare ones growing black/redcurrants, strawberries, raspberries, forest fruits and cranberries. In order to secure successful crop harvests it is necessary to have healthy seedlings and that the land is fit for its intended use. Profitability of harvests mainly depend on plantation size and fruit yield which may be significantly reduced by pests or plant disease [4]. Fruit belonging to plants that bear berries include: grapes for winemaking, strawberries, forest fruits (e.g. blackberries, raspberries) and other small fruit (e.g. American bilberries, cranberries, cowberries, black/red/white currants, gooseberries, wild rose fruit, mulberries, hawthorns, elderberries and chokeberries) [8].

As previously alluded, Poland is the main commercial grower of berries in Europe [2] which in 2011 yielded around 0.5 million tons of crops. Average domestic consumption of such berries per person, per month, living in farms is 0.42 kg [1]. It is thereby evident that a large scale cultivation of berries occurs in Poland which are consumed in either raw or processed forms. For this reason that these fruit are tested for the presence of active substances in PPPs, so that if necessary, human intakes are minimised. The present study therefore aims to demonstrate the levels of pesticides found in fruit berries from South-Eastern Poland in 2009-2011, being an important berry growing region.

MATERIAL AND METHODS

Some 250 samples of fruit berries were analysed in 2009-2011 by the National Research Institute of Plant Protection Products in Rzeszow for laboratory analysis. This was in accordance with official monitoring conducted by inspectors from the Ministry of Agriculture and Rural Development and the Chief Inspectorate of Plant Health and Seeds as well as relevant commercial concerns involved in this region of Poland. Sample frequencies consisted of; gooseberries (10), chokeberries (5), raspberries (68), blackcurrants (85), redcurrants (12), strawberries (66) and grapes (4). As part of previous monitoring, 126 active substances were identified in 2009, 132 in 2010 and 153 in 2011(Table 1). Methods used to analyse pesticide residues PPPs were performed according to PN-EN ISO/IEC 17025 accreditation [7]. Analyses were performed by GC/ECD/NPD which allowed the simultaneous detection of structurally diverse

Table 1. Analysed active substances

Insecticides	acetamiprid, acrinathrin, aldrin, alpha-cypermethrin, azinphos-ethyl, azinphos-methyl, beta-cyfluthrin, bifenthrin, bromophos-ethyl, bromophos-methyl, bromopropylate, buprofezin, carbaryl, carbofuran, chlorfenvinphos, chlorpyrifos, 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 sum (α, β, sulphate), endrin, esfenvalerate, ethion, ethoprophos, fenazaquin, fenchlorphos, fenitrothion, fenpropathrin, fenthion, fenvalerate, fipronil, formothion, -HCH, β-HCH, HCB, heptachlor, heptachlor exo-epoxide, heptachlor endo-epoxide, heptenophos, hexythiazox, indoxacarb, isofenphos, isofenphos-methyl, lambda-cyhalothrin, lindane (γ-HCH), malathion, mecarbam, methacrifos, methoxychlor, methidathion, parathion, parathion-methyl, permethrin, phosalone, phosmet, pirimicarb, pirimiphos-ethyl, pirimiphos-methyl, profenofos, propoxur, pyridaben, pyriproxyfen, quinalphos, tebufenpyrad, tetrachlorvinphos, tetradifon, triazophos, zeta-cypermethrin,
Fungicides	azaconazole, azoxystrobin, benalaxyl, bitertanol, bromuconazole, boscalid, bupirimate, captan, carbendazim, chlorothalonil, cyproconazole, cyprodinil, dichlofluanid, dicloran, difenoconazole, dimethomorph, dimoxystrobin, diniconazole, diphenylamine, dithiocarbamates, epoxiconazole, fenarimol, fenbuconazole, fenhexamid, fenpropimorph, fluquinconazole, fludioxonil, flusilazole, flutriafol, folpet, imazalil, imibenconazole, iprodione, kresoxim-methyl, mepanipyrim, quintozene, metalaxyl, myclobutanil, oxadixyl, penconazole, picoxystrobin, prochloraz, procymidone, propiconazole, pyrimethanil, quinoxyfen, tebuconazole, tecnazene, tetraconazole, tolclofos-methyl, tolylfluanid, triadimefon, triadimenol, trifloxystrobin, vinclozolin,
Herbicides	acetochlor, atrazine, chlorpropham, lenacil, mertibuzin, metazachlor, napropamide, nitrofen, pendimethalin, propham, prometryne, propachlor, propyzamide, simazine, trifluralin,
Growth retardants	paclobutrazol

Table 2. Occurrence of pesticide residues in berries in 2009–2011

Crop	Number of analysed samples	Active substance	Samples with residues		Range of found residues	NDP* [mg/kg]
			number	[%]	min- max [mg/kg]	
Gooseberry	10	bupirimate	5	50.0	0.01–0.12	5
		difenoconazole [3]	1	10.0	0.31	0.1
		dithiocarbamates	2	20.0	0.66–1.14	5
		fenarimol [2]	1	10.0	0.02	1
		propiconazole [2, 3]	1	10.0	0.08	0.05
Black chokeberry	5	dithiocarbamates	1	20.0	0.05	0.05
Raspberry	68	boscalid	1	1.5	0.63	10
		captan [2]	1	1.5	0.02	3
		chlorpyrifos	3	4.4	0.01–0.11	0.5
		lambda-cyhalothrin	1	1.5	0.01	0.2
		cypermethrin	3	4.4	0.03–0.08	0.5
		cyprodinil	11	16.2	0.01–0.36	10
		esfenvalerate [3]	1	1.5	0.04	0.02
		fenhexamid	1	1.5	0.18	10
		fludioxonil	8	11.8	0.03–0.15	5
		folpet [2]	1	1.5	0.04	3
		iprodione	9	13.2	0.05–0.75	10
		pyrimethanil	27	39.7	0.02–0.85	10
		pirimicarb	2	2.9	0.06–0.09	2
		procymidone [1,3]	16	23.5	0.01–1.68	0.02
Black currant	85	bifenthrin	2	2.4	0.05–0.19	0.5
		boscalid	2	2.4	0.13–0.22	10
		bupirimate	1	1.2	0.14	5
		chlorpyrifos	2	2.4	0.01–0.14	1
		chlorpyrifos-methyl	3	3.5	0.01–0.09	0.05
		lambda-cyhalothrin	4	4.7	0.01–0.02	0.2
		cypermethrin [3]	11	12.9	0.04–0.3	0.05
		cyprodinil [2]	2	2.4	0.03–0.09	5
		difenoconazole	12	14.1	0.02–0.11	0.2
		dithiocarbamates	19	22.4	0.01–3.24	5
		endosulfan [1, 3]	1	1.2	0.13	0.05
		fenitrothion [1]	2	2.4	0.01	0.01
		flusilazole [2, 3]	4	4.7	0.01–0.06	0.02
		iprodione [2]	1	1.2	0.44	10
		pyrimethanil [2]	4	4.7	0.01–0.02	5
		pirimicarb	2	2.4	0.04–0.08	1
		procymidone [1,3]	1	1.2	0.03	0.02
Red currant	12	chlorpyrifos	1	8.3	0.01	1
		lambda-cyhalothrin	1	8.3	0.01	0.2
		cypermethrin	1	8.3	0.05	0.05
		dithiocarbamates	4	33.3	0.04–0.22	5
		fenitrothion [1]	1	8.3	0.01	0.01
		flusilazole	1	8.3	0.01	0.02
Strawberry	66	boscalid	4	6.1	0.03–0.08	10
		bupirimate	1	1.5	0.01	1
		chlorpyrifos	1	1.5	0.16	0.2
		cyprodinil	1	1.5	0.01	5
		dithiocarbamates	3	4.6	0.01–0.06	10
		endosulfan [1]	1	1.5	0.03	0.05
		folpet	1	1.5	0.07	3
		iprodione	1	1.5	0.02	15
		pyrimethanil	8	12.1	0.02–0.10	5
		procymidone [1, 3]	3	4.6	0.02–0.14	0.02
Grapes	4	dithiocarbamates	2	50.0	0.03–0.08	5
		folpet	1	25.0	0.01	0.01

* MRLs – maximum residues limits

[1] – application of the substance was forbidden

[2] – application of the substance was not recommended for that crop

[3] – the substance of which residue level exceeded Maximum Residue Limit (MRL)

chemical substances. Whenever required, spectrophotometric detection was used to identify dithiocarbamines. Results were compared with mandatory standards set to levels of MRLs as defined by the EU.

RESULTS AND DISCUSSION

Analyses of the 250 samples demonstrated that 46.4% (116) contained pesticide residues, of which those not exceeding the MRL were 42.4%, (106 samples) (Figure 1). MRL levels were exceeded in 4% of the samples taken which was due to cypermethrine in blackcurrants. The highest PPP levels were however found in raspberries (58.8%) which was similar to those detected in 2000-2005, where 63% exceeded the accepted limits [11]. Lower but still closely similar exceedance levels of PPPs were also found in samples of gooseberries 58.35 and grapes 50% (Figure 2).

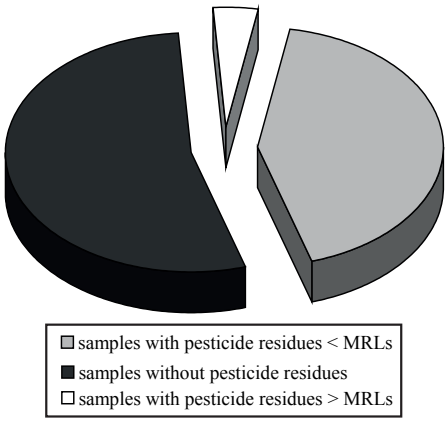

Figure 1. Pesticide residues found in berries 2009-2011

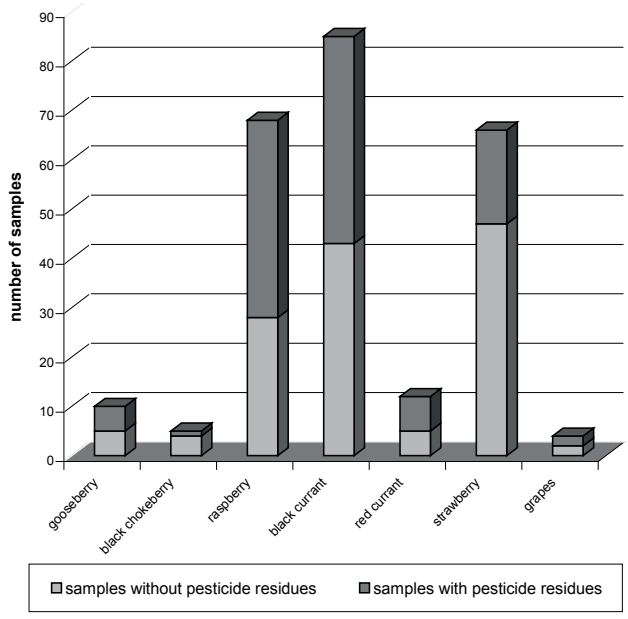

Figure 2. The incidence of pesticide residues in berries in 2009-2011

Fungicides were the most commonly found substances that included: pyrimethanil (15.6%), dithiocarbamates (12.4%), procymidone (8%), cyprodinil (5.6%) and difenoconazole (5.2%). The most often found insecticide was cypermetrine (6%). Table 2 shows all the results in detail. The current study however also revealed pesticides that were inappropriate for protecting certain fruit cultivation: propiconazole in gooseberries, cyprodinil, flusilazole, iprodione, pyrimethanil in blackcurrants and folpet and captan in raspberries. Some additional substances were detected which had been banned in 2008 such as endosulfan in blackcurrants and strawberries, fenitrothion in black and red currants as well as procymidone in raspberries, blackcurrants and strawberries; these substances having been detected both alone or in various combinations (Figure 3).

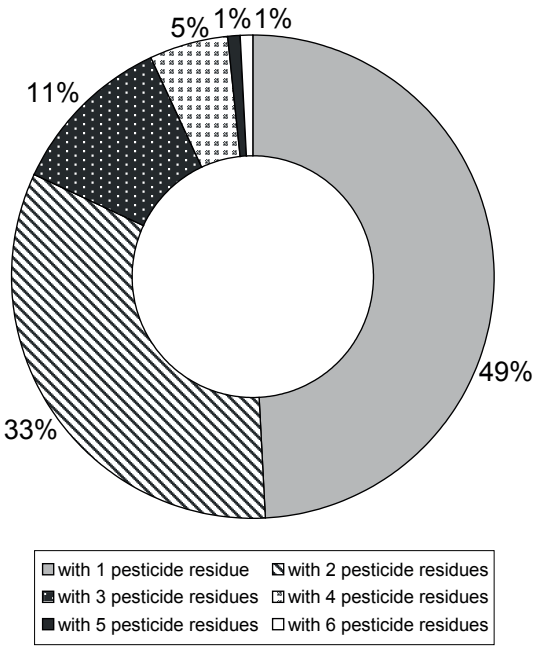

Figure 3. Distribution of pesticide residues found in samples taken from 2009-2011

The PPP results of the presented study found in berry fruit were in fact consistent with those in other areas of Poland and indeed the EU; the most frequent types detected were fungicide residues and the greatest exceedances of MRLs were observed in currants [3, 5, 6].

CONCLUSIONS

1. Pesticide residues were detected in 46% of samples berries; the most common being fungicides.
2. The MRLs were exceeded in 4% cases; most often by cypermethrine in blackcurrants.
3. Raspberries, redcurrants, gooseberries and grapes had the most pesticide residues.
4. The current study showed that the pesticide types

and amounts detected were comparable to those generally found in the scientific literature.

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