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ASSESSMENT OF THE PESTICIDE RESIDUE OCCURRENCE IN FRUIT FROM THE SOUTH-EASTERN REGION OF POLAND DURING 2010-2011 SEASONS

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A B S T R A C T

During the 2010-2011 seasons, analyses of 171 samples of fresh fruit from the south-eastern region of Poland were performed. The research program included the determination of 137 (in 2010) to 152 (in 2011) active substances, together with their metabolites and decomposition products. The analytical methods used in the research were gas chromatography (GC/ECD/NPD) and spectrophotometry (to determine residues of dithiocarbamates). The results were compared with Poland's allowed maximum residue levels (MRLs).

Residues of active plant protection product substances were detected in 85 samples (50%), while 7 (4%) samples had exceeded the MRLs.

Violations of MRLs were mainly concerned with the following group of insecticides: cypermethrin (in black currant), esfenwalerate (in raspberry), and the fungicides: propiconazole, and difenoconazole (in gooseberries).

Key words: Fruit, pesticide residues, plant protection products

INTRODUCTION

For the protection of consumers' health, both fresh fruit and its processed products should be free of any toxic substances, including pesticides. Risks to consumers related to the use of plant protection products (PPPs) is minimised by stringent requirements for registration of PPPs as well as by subsequent regular monitoring of PPP residues in food.

The issue of residues of PPPs in agricultural products is related not only to reasonable use of the plant protection products, but also to consumer awareness. Currently, the population demands safe and healthy food. Modern technologies allow for less and less toxic PPPs in production, yet a formulation that would be completely harmless to human or animal health has not yet been produced.

The Residue Analyses Laboratory in Rzeszow, Poland is accredited according to PN-EN ISO/IEC 17025. For several years this lab has been conducting routine tests to detect pesticide residues on fruit and vegetables. Those analyses use monitoring tests ordered by the Ministry of Agriculture and Rural Development as well as the Voivodeship Inspectorates of Plant Health and Seed Inspection (WIORiN). The main objective of the tests is to determine possible threats to human health and life, and to ensure that preparations applied by farmers have been used in accordance with information on labels, and therefore with current legislation (Regulation, 2005). The study covers results of research concerning pesticide residues in fruits from 2010 to 2011.

MATERIAL AND METHODS

During the 2010-2011 time period, 171 samples of fruits were tested in the laboratory. The tests covered determinations of active substances; from 137 in 2010 to 152 in 2011, together with their metabolites and products of decomposition (Tab. 1). Pesticides were validated and quality control procedures were used during the testing of the samples according to guidelines described in the SANCO document (Document SANCO, 2009).

In the analytical method, extraction of residues was done with organic solvent, and further purification of the extract was done using column chromatography. Quantification of residues was carried out with gas chromatographs, Agilent 6890 and HP 5890, equipped with ECD and NPD detectors (Luke et al., 1975, 1981; Ambrus et al., 1981; Sadło, 1998).

Dithiocarbamate fungicides, based on their decomposition to CS_2 in an acid environment, were analysed and then transferred to methyl blue. The spectrometer Unicam Helios was then used in the analysis (Chmiel, 1979).

The obtained results were compared with Poland's Maximum Residue Limits (MRL) (Regulation, 2005).

The laboratory confirms reliability of its tests by participating regularly in the international proficiency tests organised by the European Commission, and also in inter-laboratory comparative research, in which it achieves correct results.

RESULTS

Pesticide residues were found in 85 samples (50% of the tested samples).

In the analysed samples of fruit, 26 active substances were found, 15 of them belonged to fungicides and 11 to insecticides.

Table 1. Analyzed active substances

Insecticides	acetamiprid, acrinathrin, aldrin, alpha-cypermethrin, azinophos-ethyl, azinophos-methyl, beta-cyfluthrin, bifenthrin, bromophos-ethyl, bromophos-methyl bromopropylate, buprofezin, carbaryl, carbofuran, chlorfenvinfos, 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, α-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-ethyl, parathion-methyl, permethrin, phosalone, phosmet, piridaben, pirimiphos-ethyl pirimiphos-methyl, pirimicarb, piriproxyfen, profenofos, propoxur, quinalphos, tebufenpyrad, tetrachlorvinphos, tetradifon, triazophos, zeta-cypermethrin
Fungicides	azaconazole, azoxystrobin, benalaxyl, bitertanol, bromuconazole, boscalid, bupirimate, captan, carbendazim, chinoxifen, chlorothalonil, cyprodinil, cyproconazole, dichlofluanid, dicloran, difenoconazole, dimethomorph, dimoxystrobin, diniconazole, diphenylamine, dithiocarbamates, epoxiconazole, fenarimol, fenbuconazole, fenhexamid, fenpropimorph, fluchinconazole, fludioxonil, flusilazole, flutriafol, folpet, imazalil, imibenconazole, iprodione, krezoxim-methyl, mepanipyrim, quintozene, metalaxyl, myclobutanil, oxadiksyl, penconazole, picoxystrobin, pirimethanil, prochloraz, procymidone, propiconazole, tebuconazole, tecnazene, tetraconazole, tolclofos-methyl, tolylfluanid, triadimefon, triadimenol, trifloxystrobin, vinclozolin
Herbicides	acetochlor, atrazin, chlorprofam, lenacil, mertibuzin, metazachlor, napropamide, nitrofen, pendimethalin, profam, promethrin, propachlor, propyzamide, simazin, trifluralin
Growth retardant	paclobutrazol

In the tested samples of apples and raspberries, multiple residues were found. In 4 samples there were residues of 5 compounds, and in 6 samples residues of 4 compounds, while in 11 samples − residues of 3 different compounds were found, 21 samples contained 2 compounds, while in 44 samples, 1 active substance was found.

During tests, the highest amount of pesticide residues was found in raspberries (67% of all raspberry samples), apples (59%), black currants (48%), and in strawberries (36%). Presence of pesticide residues in fruit is shown in Figure 1.

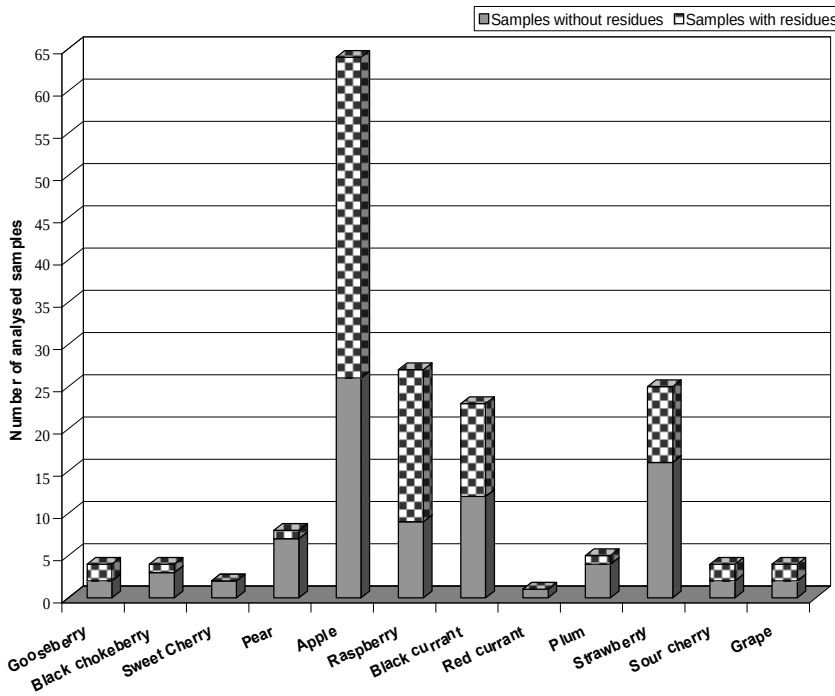

Figure 1. Pesticide residues in fruits (2010-2011)

In 7 samples (4%), those residues exceeded MRL levels. Violations mainly concerned pesticides belonging to the group of pyrethroid insecticides, i.e., cypermethrin (in black currant), esfenvalerate (in raspberry) and the fungicides: propiconazole and difenoconazole (in gooseberry). Detailed data is included in Table 2.

In 4 analysed samples, active substance not recommended for protection of a given crop were found, and those were agents from the fungicide groups: captan present in raspberries, propiconazole in gooseberries, and iprodione in black currant. The results of the analyses are listed in Table 2, which also includes the maximum residue limits for residues found in fruit.

The analyses of samples also disclosed the presence of plant protection substances whose use was banned by the decision of the Minister of Health (Regulation, 2008). There were 3 cases of such substances found in apples, i.e.: fenitrothion, procymidone, and fenarimol.

In the case of residues exceeding MRL and residues of banned formulations, informative notifications were sent under the Rapid Alert System for Food and Feed (RASFF).

Table 2. Occurrence of pesticide residues in fruits

Crop	Number of analyzed samples	Active substances	Samples with residues		Range of found residues		MRL* [mg/kg]
			number	[%]	min [mg/kg]	max [mg/kg]	
Gooseberry	4	bupirymate	2	50	0.02	0.04	5
		difenoconazole[3]	1	25	0.31	–	0.1
		ditiocarbamates	1	25	1.14	–	5
		fenarimol	1	25	0.02	–	1
		propiconazole[2,3]	1	25	0.08	–	0.05
Black chokeberry	4	ditiocarbamates	1	25	0.05	–	0.05
Pear	8	ditiocarbamates	1	12.5	0,02	–	5
Apple	64	chlorpyrifos	2	3.1	0,03	0.08	0.5
		chlorpyrifos-methyl	1	1.6	0,01	–	0.5
		cypermethrin	4	6.2	0.01	0.07	1
		difenoconazole	7	10.9	0.01	0.09	0.5
		ditiocarbamates	12	18.8	0.01	0.29	5
		fenarimol[1]	1	1.6	0.03	–	0.3
		fenazaquin	2	3.1	0.04	0.05	0.1
		fenitrothion[1,3]	1	1.6	0.02	–	0.01
		indoxacarb	3	4.7	0.02	–	0.5
		captan	28	43.8	0.01	0.69	3
		myclobutanil	2	3.1	0.01	–	0.5
		pyrimethanil	4	6.2	0.01	0.17	5
		pirimicarb	9	14.1	0.01	0.05	2
		procymidone[1]	1	1.6	0.01	–	0.02
		propiconazole	1	1.6	0.03	–	0.05
		trifloxystrobin	2	3.1	0.01	0.06	0.5
Raspberry	38	boscalid	1	2.6	0.63	–	10
		captan[2]	1	2.6	0.02	–	3
		lambda-cyhalothrin	1	2.6	0.01	–	0.2
		cypermethrin	3	7.9	0.03	0.08	0.5
		cyprodinil	7	18.4	0.03	0.36	10
		esfenwalerate[3]	1	2.6	0.04	–	0.02
		fenhexamid	1	2.6	0.18	–	10
		fludioxonil	6	15.8	0.03	0.15	5
		iprodione	6	15.8	0.08	0.75	10
		pyrimethanil	11	28.9	0.03	0.85	10
Black currant	23	bifenthrin	1	4.3	0.05	–	0.5
		chlorpyrifos-methyl	2	8.7	0.01	0.09	0.05
		lambda-cyhalothrin	1	4.3	0.02	–	0.1
		cypermethrin[3]	3	13.0	0.1	0.3	0.05
		difenoconazole	3	13.0	0.05	0.11	0.2
		ditiocarbamates	9	39.1	0.02	3.24	5
		iprodione[2]	1	4.3	0.44	–	10
Plum	5	ditiocarbamates	1	20	0,01	–	2
Strawberry	25	boscalid	2	8	0.03	0.08	10
		cyprodinil	1	4	0.01	–	5
		ditiocarbamates	2	8	0.01	0.06	10
		pyrimethanil	6	24	0.02	0.10	5
Grapes	4	ditiocarbamates	2	50	0.03	0.08	5
		folpet	1	25	0.01	–	0.01
Sour cherry	4	captan	2	50	0.07	0.16	5
		cypermethrin	1	25	0.02	–	1

MRL* – maximum residue levels
1 – application of the substance was forbidden
2 – application of the substance was not recommended for that crop
3 – a substance in which the residue level exceeded maximum residue levels (MRL)

DISCUSSION

The analysis of the results of official monitoring tests conducted in 2010-2011 shows that in half of the tested samples, pesticide residues were found. Residues of fungicides, such as captan, pyrimethanil or dithiocarbamates were found most often. The results of these findings were related to the protection of fruit against burdensome diseases, particularly fungal diseases, with which the farmers struggle against. The most common diseases are apple scab (*Venturia inaequalis*), bitter rot (*Pezicula* spp.), and grey mould (*Botrytis cinerea* Pers.). Due to large amounts of rain, especially during the summer, 2010 was a particularly favourable year for those diseases.

Only in 5% of the cases did the found residues exceed the acceptable level, and this confirms an increased awareness of the produces as well as effective supervision by WIORiN. The cases where formulations were found which were not recommended for a given crop or withdrawn from the market, may be treated as incidental.

Our research results correlated with the results obtained by Nowacka in the official testing conducted throughout the country in the 2009 and 2010 time period. The same pesticides in the same crops were found (Nowacka et al., 2010, 2011).

Currently, there is a wide range of plant protection products available in the market, it is therefore important to use correctly available formulations, skills, and knowledge to avoid problems related to products' excessive levels of residues.

When selecting formulations, particular attention must be paid to durability and effectiveness at low doses. Finally, it is also essential to note, that ecological aspects have become an important factor, especially in recent years.

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OCENA WSTĘPOWANIA POZOSTAŁOŚCI PESTYCYDÓW W OWOCACH Z TERENU POŁUDNIOWO-WSCHODNIEJ POLSKI W LATACH 2010-2011

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S T R E S Z C Z E N I E

W latach 2010-2011 wykonano analizy 171 próbek owoców pochodzących z terenu południowo-wschodniej Polski w ramach urzędowej kontroli. Program badań obejmował oznaczenie od 137 (w 2010 roku) do 152 (w 2011 roku) substancji aktywnych wraz z metabolitami i produktami ich rozkładu. W badaniach stosowano metody

badawcze: chromatografii gazowej (GC/ECD/NPD), oraz spektrofotometryczne (w celu oznaczenia pozostałości ditiokarbaminianów).

Uzyskane wyniki porównywano z najwyższymi dopuszczalnymi poziomami pozostałości (NDP) obowiązującymi w Polsce.

Pozostałości substancji aktywnych wykryto w 85 próbkach, co stanowiło 50% wszystkich przebadanych próbek, w 7 próbkach (4%) pozostałości te przekroczyły poziom NDP. Przekroczenia dotyczyły przede wszystkim pestycydów z grupy insektycydów pyretroidowych, tj. cypermetryny (w czarnej porzeczce) i esfenwaleratu (w malinie) oraz fungicydów − propikonazolu oraz difenokonazolu (w agreście).

Słowa kluczowe: pozostałości pestycydów, środki ochrony roślin, owoce