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Letter to Editor

Pesticide Residues in Fruit and Vegetables from Southeastern Poland, 2004-05

S. Sadło[1]*, E. Szpyrka[2], A. Jaźwa[1], A. Zawiślak[2]

[1]Department of Biotechnology, University of Rzeszów, 36-100 Kolbuszowa, Poland
[2]Experimental Station, Institute of Plant Protection, ul. Langiewicza 28, 35-101 Rzeszów, Poland

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Abstract

Our paper presents results from surveillance of pesticide residues in fruits and vegetables carried out in 2004-05. 747 samples of 39 different types of fresh fruit and vegetables were analyzed for their pesticide residue contents. The highest resides found were: bupirimate residues (2.19 mg/kg), captan residues (1.82 mg/kg), ethylenebisdithiocarbamate residues (1.6 mg/kg), tolylfluanid residues (1.44 mg/kg), procymidone residues (1.19 mg/kg) and chlorpyrifos residues (1.01 mg/kg). In 27 samples (3.6%) residues exceeded national MRLs. Comparisons of the highest residues to ADI levels indicate that fresh fruit and vegetables from southeastern Poland seem to be quite safe for toddlers and adults.

Keywords: southeastern Poland, fresh fruits and vegetables, pesticide residues, daily intake

Introduction

The Polish national monitoring programme for pesticide residues in food of plant origin, now conducted by five analytical laboratories of the Institute of Plant Protection and Central Laboratory of Toruń, is aimed at ensuring that consumers are not exposed to unacceptable pesticide residue levels. In addition, it is aimed at ensuring that authorised pesticides are correctly applied to food crops. Each year a total of 2200 samples were taken by trained inspectors from the local Inspectorates of Plant Protection Services according to a sampling plan designed at the beginning of each year. Besides the national monitoring programme, the analytical laboratories of the Institute of Plant Protection have run surveillance analyses for pesticide residues in food of plant origin destined for export and for regional consumption.

The purpose of this paper was to present data on pesticide residues in fruit and vegetables from southeastern Poland carried out in 2004-05. Pesticide residue levels were evaluated in relation to their Maximum Residue Levels/Limits (MRLs), Acceptable Daily Intakes (ADIs) and Acute Reference Doses (ARfDs) derived from toxicological studies.

Experimental Procedures

Analytical Programme

Samples were generally analyzed unwashed and unpeeled by the multi-residue method (MRM) consisting of an extraction of residues into an organic solvent followed by a chromatographic separation and selective EC and NP detection [1-4]. Along with the multiresidue method, spectrophotometric and thin layer chromatographic (TLC) determination of ethylenebisdithiocarbamate residues (EBDC) expressed in mg CS_2/kg and benzimidazoles expressed as carbendazim residues were carried out [5, 6].

Quality Assurance Procedures

Recovery studies were carried out regularly by spiking analytical samples with one of the pesticide mixtures consisting of 4-12 compounds. In addition of the in-house quality assurance programme, in 2000-05 the laboratory successfully participated in twelve rounds of proficiency testing schemes organized and run by the Food Analysis Performance Assessment Scheme (FAPAS; Central Science Laboratory in York) and by the European Commission (in the beginning by the University of Uppsala and then by the University of Almeria). This involved analysis of tomatoes, apples, lettuce, oranges, melon, peppers, strawberries, and

Table 1. Pesticide residues in fruit and vegetables analyzed in 2004-05.

Commodity	N	Name	n	Mean	Max	MRL	R>MRL
Gooseberry	14	bupirimate	6	0.48	2.19	0.5	1
		EBDC	5	0.60	1.51	5.0	-
		fenitrothion	4	0.04	0.08	0.5	-
		fenarimol	3	0.01	0.02	1.0	-
		captan	3	0.13	0.21	3.0	-
		diazinon	1	0.01	0.01	0.2	-
Berry	11	tolylfluanid	2	0.04	0.07	no	?
		pyrimethanil	1	0.08	0.08	5.0	-
Pear	2	captan	1	0.03	0.03	3.0	-
Apple	42	captan	15	0.28	1.82	3.0	-
		EBDC	12	0.16	0.46	3.0	-
		tolylfluanid	9	0.10	0.23	5.0	-
		phosalone	2	0.02	0.02	2.0	-
		pirimikarb	1	0.02	0.02	0.5	-
		fenarimol	1	0.03	0.03	0.3	-
Raspberry	29	tolylfluanid	16	0.29	1.02	5.0	-
		procymidone	13	0.28	1.19	10.0	-
		pyrimethanil	8	0.17	0.48	5.0	-
		EBDC	6	0.58	1.6	0.05	6
		bifenthrin	3	0.02	0.03	0.3	-
		cypermethrin	2	0.05	0.07	0.5	-
		phosalone	1	0.02	0.02	2.0	-
		diazinon	1	0.02	0.02	0.02	-
		iprodione	1	0.04	0.04	5.0	-
		folpet	1	0.09	0.09	3.0	-
Black currant	43	EBDC	10	0.16	0.54	5.0	-
		fenitrothion	5	0.02	0.04	0.5	-
		endosulfan	4	0.02	0.02	0.05	-
		procymidone	3	0.09	0.12	0.02	3
		captan	1	0.01	0.01	3.0	-
		tolylfluanid	1	0.06	0.06	2.0	-
		cyhalothrin	1	0.01	0.01	0.1	-
		phosalone	1	0.04	0.04	2.0	-

Table 1. continued

Commodity	N	Name	n	Mean	Max	MRL	R>MRL
Strawberry	188	procymidone	29	0.11	0.28	5.0	-
		tolylfluanid	28	0.09	1.44	3.0	-
		cyprodinil	7	0.06	0.14	3.0	-
		fludioxonil	4	0.10	0.16	3.0	-
		dichlofluanid	3	0.06	0.16	5.0	-
		chlorpyrifos	3	0.03	0.12	0.2	-
		endosulfan	1	0.02	0.02	0.05	-
		iprodione	1	0.13	0.13	10.0	-
		bupirimate	1	0.02	0.02	0.5	-
		EBDC	1	0.10	0.1	2.0	-
		phosalone	1	0.04	0.04	1.0	-
		vinchlozolin	1	0.04	0.04	5.0	-
		pyrimethanil	1	0.10	0.1	5.0	-
Cherry	30	captan	10	0.16	1.05	2.0	-
		EBDC	4	0.11	0.2	1.0	-
		pirimicarb	3	0.04	0.06	0.5	-
		fenarimol	2	0.13	0.25	1.0	-
		cypermethrin	2	0.02	0.02	1.0	-
		phosalone	1	0.05	0.05	2.0	-
		carbendazim	1	0.05	0.05	0.1	-
Blackberry	3	EBDC	1	0.14	0.14	0.05	1
Red currant	14	EBDC	4	0.41	0.9	5.0	-
Rhubarb	9	simazin	1	0.02	0.02	no	?
Cucumber	24	procymidone	4	0.12	0.33	1.0	-
		chlorothalonil	1	0.01	0.01	1.0	-
Greenhouse tomato	72	procymidone	30	0.18	0.95	2.0	-
		chlorothalonil	16	0.20	0.92	2.0	-
		iprodione	9	0.12	0.54	5.0	-
		tolylfluanid	5	0.08	0.2	2.0	-
		azoxystrobin	2	0.07	0.11	2.0	-
		bifenthrin	2	0.04	0.07	0.2	-
		pyrimethanil	1	0.02	0.02	2.0	-
		cyprodinil	1	0.11	0.11	0.5	-
		fludioxonil	1	0.06	0.06	0.5	-
Sweet pepper	5	chlorpyrifos	1	0.03	0.03	0.5	-
		procymidone	1	0.07	0.07	2.0	-
Broad bean	3	endosulfan	2	0.02	0.03	0.05	-
Bean with pods	19	procymidone	2	0.01	0.01	1.0	-
		vinchlozolin	2	0.05	0.08	0.5	-

Table 1. continued

Commodity	N	Name	n	Mean	Max	MRL	R>MRL
Carrot	38	chlorpyrifos	13	0.08	0.2	0.1	3
		linuron	6	0.02	0.06	0.2	-
		prometryne	3	0.04	0.08	0.5	-
		diazinon	2	0.02	0.03	0.2	-
		trifluralin	2	0.04	0.06	0.5	-
Leek	5	azoxystrobin	1	0.38	0.38	0.1	1
		chlorpyrifos	1	0.02	0.02	0.05	-
		cypermethrin	1	0.03	0.03	0.5	-
Kale	9	cypermethrin	8	0.06	0.11	2.0	-
		chlorpyrifos	7	0.24	0.41	0.05	7
		EBDC	6	0.12	0.16	2.0	-
		cyhalothrin	6	0.15	0.22	1.0	-
		azoxystrobin	5	0.11	0.21	5.0	-
		fenitrothion	1	0.13	0.13	0.5	-
Courgette	5	chlorothalonil	1	0.11	0.11	2.0	-
		procymidone	1	0.01	0.01	0.02	-
Brussels sprout	24	chlorpyrifos	2	0.02	0.03	0.05	-
Cauliflower	40	chlorpyrifos	1	1.01	1.01	0.05	1
		pyrimethanil	1	0.11	0.11	no	?
Broccoli	23	chlorpyrifos	10	0.12	0.75	0.05	3
		cypermethrin	1	0.03	0.03	2.0	-
		pyrimethanil	1	0.08	0.08	no	?
Spinach	1	EBDC	1	0.28	0.27	0.05	1
Chives	3	chlorpyrifos	2	0.03	0.04	0.05	-
Mushroom	6	carbendazim	1	0.02	0.02	1.0	-
Cabbage	22	-	0	-	-		-
Beetroot	17	-	0	-	-	-	-
Onion	10	-	0	-	-	-	-
Potato	10	-	0	-	-	-	-
Lettuce	8	-	0	-	-	-	-
Green peas	4	-	0	-	-	-	-
Plum	4	-	0	-	-	-	-
Black choke-berry	3	-	0	-	-	-	-
Asparagus	2	-	0	-	-	-	-
Parsley	2	-	0	-	-	-	-
Sweet cherry	1	-	0	-	-	-	-
Blueberry	1	-	0	-	-	-	-
Celeriac	1	-	0	-	-	-	-
In total	**747**		**418**				**27**

grapes – all of which contained incurred and spiked residues. The results obtained by the Rzeszów Laboratory of the Institute of Plant Protection in all cases were acceptable.

Chemicals

Acetone, dichloromethane and petroleum ether were of analytical grade. Pesticide standards were purchased from Ehrenstorfer (Germany) and their stock solutions (10 µg/ml) were prepared in acetone and stored at 4°C. Working standard solutions (0.2 µg/ml) were obtained by diluting the stock solution with petroleum ether.

Results and Discussion

Evaluation of Pesticide Residue Levels in Comparison to MRLs

Maximum residue levels/limits (MRLs) are defined as the highest concentrations of pesticide residues (expressed in milligrams of a substance per kilogram of commodity) likely to occur in or on food commodities after the use of plant protection products according to Good Agricultural Practice (GAP). MRLs are intended primarily as a check that GAP is being followed and to assist international trade in produce treated with pesticides. MRLs are not safety limits, and exposure to residues in excess of an MRL does not automatically imply a hazard to health.

In 2004-05, 747 samples of 39 different types of fresh fruit and vegetables were analyzed for their pesticide residue contents and samples of 13 commodities were free of measured (above Limits of Determinations; LODs) residues. Samples were analyzed for residues of 98 pesticides and metabolites. 268 (35.8%) samples were found to contain pesticide residues above their LODs of the methods applied. The average residue value reached the level of 0.08 mg/kg. Details of the residues detected are provided in Table 1.

In total, 418 detections of 29 different pesticides were stated. Procymidone (11.3% of samples), tolylfluanid (8.2%), EBDC (7.6%), chlorpyrifos (5.4%), captan (4.0%), chlorothalonil (2.4%), cypermethrin (2%), pyrimethanil (1.9%), iprodione (1.5%), fenitrothion (1.3%), endosulfan, cyprodinil and azoxystrobin (1.1%) were the most frequently detected. The other pesticides were detected in less than 1% of the samples analyzed.

In total, 56 samples (7.5%) contained residues of two pesticides, 16 samples (2%) contained residues of three pesticides, 11 samples (1.5%) four pesticides, 6 (0.8%) five pesticides and 1 (0.1%) six pesticides (Table 2).

The highest resides found were: bupirimate residues (2.19 mg/kg), captan residues (1.82 mg/kg), EBDC residues (1.6 mg/kg), tolylfluanid residues (1.44 mg/kg), procymidone residues (1.19 mg/kg) and chlorpyrifos residues (1.01 mg/kg). With the exception of chlorpyrifos there were fungicide residues. In most cases pesticide residues occurred on levels well below the national MRLs.

Table 2. Occurrence of multiple residues in fruit and vegetables in 2004-05.

Commodity	Number of pesticides detected				
	2	3	4	5	6
Strawberry	15	1	0	0	0
Tomato	11	3	2	0	0
Apple	7	4	0	0	0
Carrot	5	2	0	0	0
Raspberry	5	2	2	2	1
Cherry	4	1	0	0	0
Black currant	3	0	2	0	0
Gooseberry	1	1	2	1	0
Broccoli	1	0	0	0	0
Courgette	1	0	0	0	0
Bean with pods	1	0	0	0	0
Leek	1	0	0	0	0
Chives	1	0	0	0	0
Kale	0	2	3	3	0
In total	**56**	**16**	**11**	**6**	**1**

For some pesticides MRLs were not established in Poland. However, those four cases concerned commonly used fungicides: tolylfluanid (berries), pyrimethanil (cauliflower and broccoli), and a sample of rhubarb with simazine (herbicide), but their residues were found to be at low levels. In 27 samples (3.6%) residues exceeded national MRLs [10-13]. Those compounds were: bupirimate residues (in 1 sample of gooseberry), EBDC residues (in 6 samples of raspberries, 1 sample of blackberry and 1 sample of spinach), procymidone residues (in 3 samples of black currant), pirimicarb residues (in 1 sample of cherry), chlorpyrifos residues (in 3 samples of carrot, in 7 samples of kale, in 1 sample of cauliflower and in 3 samples of broccoli) and azoxystrobin residues (in 1 sample of leek).

Evaluation of Pesticide Residue Levels in Comparison to ARfD

Estimates of pesticide intake need to be made in order to compare potential consumer dietary exposure with Acceptable Daily Intakes (ADIs) and Acute Reference Doses (ARfDs), both derived from similar toxicological studies. Short-term dietary intake estimates in relation to ARfD may be carried out using the following equation:

$$Intake = \frac{C \times R_{max}}{b.w.} [\text{mg/kg b.w.}]$$

where:
C – consumption [in kg],
R_{max}- the highest residue found in a given commodity [in mg/kg],
b.w. – bodyweight [for a toddler 14.5 kg, for an adult 70.1 kg].

If estimates of short-term intake are less than the ARfD (Intake/ARfD<1), then the risks to the consumer may be regarded as acceptable [7]. At present, ARfD have been fixed only for certain pesticides. Therefore, in some cases short-term dietary intakes have been estimated in relation to the ADIs taken from the "Pesticide Manual" [8]. The results obtained can be easily recalculated using actual ARfD values.

Short-term exposure may be estimated using the critical crop pesticide concentration (CCPC), defined by the formula below:

$$CCPC = \frac{(ARfD \times b.w.)}{C} [\text{mg/kg}]$$

where: C – consumption of a given commodity; in paper assumed 0.5 kg

CCPC enables fast and easy risk assessment under assumed consumption. MRLs should be lower than the CCPC [9].

Because of the lack of consumption data it is possible to estimate acceptable daily consumption (ADC) of any food using formula derived from CCPC:

$$ADC = \frac{(ARfD \times b.w.)}{R_{max}} [\text{kg}]$$

Table 3. CCPC, ADC and Daily Intake in comparison to ARfD (or ADI) estimated for the highest residues (R_{max}) and for toddlers (b.w.=14.5 kg).

Commodity	Name	R_{max}	ADI	ARfD	CCPC	ADC	Intake
Gooseberry	bupirimate	2.19	0.20	no	5.80	1.32	0.38
	EBDC	1.51	0.03	no	0.87*	0.29	1.74
Broccoli	chlorpyrifos	0.75	0.01	0.10	2.90	1.93	0.26
Apple	captan	1.82	0.10	no	2.90	0.80	0.63
Kale	chlorpyrifos	0.41	0.10	no	2.90	3.54	0.14
Cauliflower	chlorpyrifos	1.01	0.01	0.10	2.90	1.44	0.35
Raspberry	tolylfluanid	1.02	0.08	0.50	14.50	7.11	0.07
	procymidone	1.19	0.03	0.10	2.90	1.22	0.41
	EBDC	1.60	0.03	no	0.87*	0.27	1.84
Greenhouse tomato	procymidone	0.95	0.03	0.10	2.90	1.53	0.33
	chlorothalonil	0.92	0.03	no	0.78*	0.43	1.17
	iprodione	0.54	0.06	0.20	5.80	5.37	0.09
Strawberry	tolylfluanid	1.44	0.08	0.50	14.50	5.03	0.10
Cherry	captan	1.05	0.10	no	2.90	1.38	0.36

*R_{max}>CCPC level

ADC enables fast and easy risk assessment based on real consumption data. The real consumption of a given commodity should not exceed the ADC level.

Results of the surveys presented in this paper indicate that only in the cases of raspberries, gooseberries and greenhouse tomato did the highest residues occur above CCPC levels. It means that the intake of EBDC and chlorothalonil residues by toddlers could exceed ADI levels. ADCs (0.29, 0.27, and 0.43 kg) estimated for the commodities mentioned above could be quite easily exceeded. However, the three cases of possible excessive intake of the pesticides were calculated in comparison to ADIs, usually c.a. 5 times lower than ARfD. Therefore the results of surveys carried out in 2004-05 indicate that fresh fruit and vegetables coming from southeastern Poland seem to be quite safe for toddlers and, therefore, also for adults.

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