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POTENTIAL RISK TO CONSUMERS RELATED WITH OCCURRENCE OF PESTICIDE RESIDUES IN EARLY VEGETABLES

POZOSTAŁOŚCI ŚRODKÓW OCHRONY ROŚLIN W NOWALIKACH JAKO POTENCJALNE RYZYKO NARAŻENIA KONSUMENTÓW

Abstract: In years 2009–2011 Laboratory of Pesticide Residue Analysis from March to June carried out research on 96 samples of early vegetables. In 35 tested samples were detected pesticide residues. The aim of the study was to estimate long-term and short-term intake of pesticide residues in early vegetables in years 2009–2011 for toddlers and adults. The estimation of dietary exposure was based on pesticide residue data from research carried out by Laboratory of Pesticide Residue Analysis and was calculated using Pesticide Safety Directorate model. The highest long-term intake was for parsley leaves but did not exceed for adult 26.6 % ADI and for toddlers 17.3 % of the ADI. In case of consumption other early vegetables, long-term exposure in both age groups did not exceed 2.5 % ADI. The highest estimated values for short-term exposure were obtained for tomato, and in the group of toddlers it was 41.4 % ARfD, and in the adult group it was 10.4 % ARfD. In the remaining samples the short-term exposure did not exceed 5 % ARfD.

Keywords: pesticide residues, dietary exposure, early vegetables

Introduction

Early vegetables are young spring vegetables available for the first time in the season. Early vegetables include radishes, tomatoes, lettuce, cucumbers, dill and chives. In Poland the seasons for early vegetables falls in the period from March to June. It is the time when the human body is “tired” with winter weather, “hungry” and even demanding stocking up of vitamins and minerals warehouse depleted during the winter.

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Young, fresh looking vegetables doubtlessly bring some variation into the spring diet and are a good looking addition to a menu.

Vegetables are grown in 2 main ways: in a field or in a greenhouse. Early vegetables are grown in the second way, as in our climate cold days with small amount of sunshine and significant temperature variations prevail in the early spring. These are not conditions favourable for plant growth. Therefore, it is necessary to create an appropriate artificial environment for them. Cultivation of early vegetables is carried out in specially adapted greenhouses, ensuring temperature conditions, humidity and sunshine conditions favourable for plant growth.

To facilitate plant growth a large number of *plant protection products* (p.p.p) is used, as in unfavourable weather conditions they require more growth stimulators. Chemical substances also ensure protection against diseases and pests.

Besides bringing advantages to producers, p.p.p are also encumbered with undeniable negative effects on human health, as, obviously, food should have appropriate nutrition value, and contain as low as possible content of pesticide residues, being exceptionally toxic substances amongst those to which humans are exposed. Therefore, does the real nutrition value of early vegetables match their healthiness as expected by customers?

Tests of food are particularly important for assessment of human exposure to pesticide residues in food, as they allow determining those pesticides present in the largest amounts in food and those foods that most often contain their residues. A need to monitor residues of chemical p.p.p in food also results from their toxic effect and common use in agriculture [1].

The food safety strategy in force in the European Union requires the Member States to maintain monitoring programmes and official food monitoring for contamination, including pesticides, against *the maximum residue levels* (MRLs). Their objective is to evaluate the actual pesticide intake and, on that basis, assess the risk for consumers related to short-term (acute) and prolonged exposure. It should be emphasised here, however, that established and valid MRL values are not the safety limit. The safe level of pesticide residues can be established using the *Acceptable Daily Intake* (ADI) or the *Acute Reference Dose* (ARfD) for prolonged and acute exposure, respectively [2].

The evaluation of dietary exposure was based on data concerning residues found during official testing of Polish crops carried out at the Laboratory of Pesticide Residue Analysis in Rzeszow, and on food consumption in Great Britain, due to lack of Polish data.

The aim of this work was to assess the actual pesticide intake with early vegetables eaten in years 2009–2011 and to evaluate on that basis the risk for consumers related to short-term and long-term exposure.

Materials and methods

The studied material contained samples of greenhouse cucumbers (g), tomatoes (g), lettuce (g), parsley leaves, dill, chives, radishes and peppers. Analyses were conducted as a part of official monitoring ordered by the Ministry of Agriculture and Rural Development, and to orders of producers and companies processing, purchasing and

exporting fruit and vegetables. Data concerning residues for risk estimations were obtained in tests carried out in years 2009–2011 from March to June at the Laboratory of Pesticide Residue Analysis of the Plant Protection Institute at the Regional Experimental Station in Rzeszow. In total, 96 samples of early vegetables from the south-east Poland were analysed at the laboratory.

During the studies, from 126 in 2009 to 147 in 2011 of p.p.p substances, together with their metabolites and decomposition products, were determined. Samples were tested using chromatographic and spectrophotometric methods accredited in accordance with ISO/IEC 17025. Residues of pesticides were determined using the analytical method required by the European Commission [3].

Obtained results were compared against the maximum residue levels (MRLs) in force in Poland [4].

Each year the laboratory participates in the international proficiency tests organised by the European Union (University of Almeria, Spain), and also in interlaboratory comparative research, in which it achieves correct results. This proves that the system for monitoring of residue levels is correct. This way the laboratory confirms its competences for carried out tests, ensuring obtaining correct results.

Gas chromatography with an *electron capture detector* and ion monitoring (GC/ECD/NPD) for simultaneous detection of many compounds and the spectrophotometric method were used in analyses.

Determination of plant protection products residues using the gas chromatography method

100 g of the analytic sample was homogenised with acetone and filtered in vacuum through a filter placed in a Büchner funnel. A homogeniser container was rinsed with acetone and the washings were used to rinse the filter. For further analysis, 1/5 of obtained filtrate was sampled (sample of 20 g) and placed in a separator containing 2.5 % sodium sulphate(VI). Pesticide residues were extracted three times with dichlorometane. The combined extracts were evaporated until dryness using a rotary evaporator Rotavapor-R from the company Büchi in a temperature below 40 °C, and then transferred with petroleum ether into a measuring flask, of 10 cm³ capacity. The obtained extracts were purified in the florisil column. Pesticides were eluated with a mixture of diethylene ether : petroleum ether, 3:7 (v/v) and then with a mixture of petroleum ether : acetone 7:3 (v/v). Eluates were vaporated until dryness in the rotary evaporator and the residues transferred quantitatively to measuring flasks and made up to volume with petroleum ether [5–8].

Purified extracts were analysed in a gas chromatograph Agilent 6890 equipped with EC and NP detectors (DB-1701 column; sequence of temperatures: initial temperature 100 °C → 20 °C/min → 180 °C – 4 min → 20 °C/min → 220 °C – 5 min → 20 °C/min → 260 °C – 43 min; the total analysis time of 60 minutes). The results were confirmed in a chromatograph Hewlett Packard 7890 equipped with EC and NP detectors (HP-5MS column; sequence of temperatures: initial temperature 100 °C → 10 °C/min

→ 180 °C – 4 min → 3 °C/min → 220 °C – 15 min → 10 °C/min → 260 °C – 11 min; the total analysis time of 55 minutes) for linearity of their determinations.

Determination of plant protection products residues using the spectrophotometric method

Determination of dithiocarbamates residues were by spectrophotometric method through decomposition to CS₂ in the acid environment in a presence of tin(II) chloride and transfer to the methylene blue analysed at the spectrophotometer Unicam Helios at the wavelength $\lambda = 662$ nm [9].

Intake estimation

For consumer residues intake estimation, new models from Pesticides Safety Directorate of the Department for Environment, Food and Rural Affairs (PSD-Defra, UK) were applied. Calculations were performed using a Chronic_and Acute_Consumer_ver1.1 software with built-in consumption database for 10 groups of people [10].

Long-term risk was calculated as follows:

$$\text{NEDI} = \Sigma [(F_i \times RL_i \times P_i)/\text{mean body weight}]$$

where: NEDI – *National Estimated Daily Intake*,

F_i – food consumption data for given food commodity,

RL_i – appropriate residue level corresponding to that commodity,

P_i – correction value that takes into account the reduction or increase in residue which might occur on storage and/or processing.

Short-term risk was calculated according to the following formula:

$$\text{NESTI} = \Sigma [(F \times HR)/\text{mean body weight}]$$

where: NESTI – *National Estimates of Short-Term Intake*,

F – full portion consumption data for the commodity unit,

HR – *the highest residue level* detected incorporating processing or edible portion factor.

Values of ADI and ARfD are elaborated by the European Commission, European Food Safety Authority (EFSA), Standing Committee on the Food Chain and Animal Health (SCoFAH) and the values are derived from pesticide database [11].

Results and their discussion

96 samples in total were analysed at the laboratory. Residues of p.p.p were found in 35 of tested samples, corresponding to 36.5 % of all samples. The largest amounts of pesticide residues were found in chives 100 %, pepper (g) 71 %, parsley leaves and dill,

50 %, and tomatoes (g) 47 %, of tested crops. The most often found substances were fungicide residues: chlorothalonil – 14 samples, azoxystrobin – 9 samples, dithiocarbamates – 7 samples, cyprodinil and fludioxonil – in 5 samples, and of insecticides: bifenthrin – 7 samples. In 3 samples determined levels of pesticide residues exceeded MRLs. Presence of multiple residues was also found. In the tomato samples residues of 4 active substances were found, with one substance exceeding MRL. In the green parsley sample residues of 4 active substances were found, with 3 substances exceeding MRLs, and in the dill sample 3 residues were found, all of which exceeded MRLs. The details are shown in Table 1.

Table 1

Occurrence of pesticide residues in early vegetables in 2009–2011

Crop	Number of analyzed samples	Active substance	Samples with residues		Range of found residues		MRL [mg/kg]
			number	[%]	min [mg/kg]	max [mg/kg]	
Greenhouse cucumber	27	Azoxystrobin	3	11	0.09	0.23	1
		Bifenthrin	3	11	0.02	0.02	0.1
		Chlorothalonil	3	11	0.02	0.35	1
Greenhouse tomato	45	Azoxystrobin	2	4.4	0.007	0.05	3
		Bifenthrin	3	6.6	0.02	0.3	0.2
		Boscalid	3	6.6	0.05	0.14	1
		Chlorothalonil	8	17.8	0.01	0.09	2
		Cyprodinil	5	8.9	0.01	0.07	1
		Dithiocarbamates	6	13.3	0.03	0.95	3
		Fludioxonil	5	8.9	0.02	0.08	1
Iprodione	2	4.4	0.08	0.19	5		
Greenhouse lettuce	5	Dithiocarbamates	1	20	0.03	—	5
Parsley leaves	6	Azoxystrobin	1	16.7	0.24	—	70
		Chlorpyrifos	1	16.7	1.45	—	0.05
		Chlorothalonil	2	33.3	1.18	45.9	5
		Cypermethrin	1	16.7	0.25	—	2
		Propiconazole	1	16.7	0.65	—	0.05
		Tetraconazole	1	16.7	0.3	—	0.02
Dill	4	Chlorpyrifos	1	25	0.12	—	0.05
		Diazynon	1	25	0.08	—	0.01
		Captan	1	25	0.05	—	0.02
		Pendimethalin	1	25	0.6	—	0.05
Chive	1	Azoxystrobin	1	100	0.28	—	3
Radish	1	—	—	—	—	—	—
Greenhouse peppers	7	Azoxystrobin	2	28.5	0.02	—	3
		Bifenthrin	1	14.3	0.03	—	0.2
		Chlorpyrifos	1	14.3	0.09	—	0.5
		Chlorothalonil	1	14.3	0.08	—	2
		Cypermethrin	1	14.3	0.02	—	0.5
		Iprodione	1	14.3	0.02	—	5

Table 2

Estimation of long-term dietary exposure to pesticide residues for early vegetables in years 2009–2011

Crop	Number of analyzed samples	Active substance	Average residue level [mg/kg]	ADI [mg/kg body weight]	High level (97.5 percentile) of long term consumption [kg/person/day for]				Intake		
					adults		toddlers		adults [76 kg]		toddlers [14.5 kg]
					adults	toddlers	adults	toddlers	mg/kg body weight	% ADI	mg/kg body weight
Greenhouse cucumber	27	Azoxystrobin	0.15	0.2	0.0309	0.0351	0.00036	0.00006	0.180	0.030	
		Bifenthrin	0.02	0.15	0.0309	0.0351	0.00005	0.00001	0.033	0.006	
		Chlorothaloniol	0.14	0.015	0.0309	0.0351	0.00034	0.00006	2.267	0.400	
Greenhouse tomato	45	Azoxystrobin	0.03	0.2	0.1047	0.0382	0.00008	0.00004	0.040	0.020	
		Bifenthrin	0.12	0.15	0.1047	0.0382	0.00032	0.00017	0.213	0.113	
		Boscalid	0.11	0.04	0.1047	0.0382	0.00029	0.00015	0.725	0.375	
		Chlorothaloniol	0.04	0.015	0.1047	0.0382	0.00011	0.00006	0.733	0.400	
		Cyprodinil	0.04	0.03	0.1047	0.0382	0.00011	0.00006	0.367	0.200	
		Ditocarbamates	0.23	0.03	0.1047	0.0382	0.00061	0.00032	2.033	1.067	
		Fludioxonil	0.05	0.37	0.1047	0.0382	0.00013	0.00007	0.035	0.019	
Iprodione	0.135	0.06	0.1047	0.0382	0.00036	0.00019	0.600	0.317			
Greenhouse lettuce	5	Ditocarbamates	0.03	0.03	0.0471	0.0124	0.00003	0.00002	0.100	0.067	

Table 2. contd.

Crop	Number of analyzed samples	Active substance	Average residue level [mg/kg]	ADI [mg/kg body weight]	High level (97.5 percentile) of long term consumption [kg/person/day for]		Intake				
					adults	toddlers	adults [76 kg]	toddlers [14.5 kg]	adults [76 kg]	toddlers [14.5 kg]	adults [76 kg]
Parsley leaves	6	Azoxystrobin	0.24	0.2	0.0129	0.0016	0.00003	0.00004	0.015	0.00004	0.020
		Chlorpyrifos	1.45	0.01	0.0129	0.0016	0.00016	0.00025	1.600	0.00025	2.500
		Chlorothaloniil	23.5	0.015	0.0129	0.0016	0.00259	0.00399	17.267	0.00399	26.600
		Cypermethrin	0.25	0.05	0.0129	0.0016	0.00003	0.00004	0.060	0.00004	0.080
		Propiconazole	0.65	0.04	0.0129	0.0016	0.00007	0.00011	0.175	0.00011	0.275
		Tetraconazole	0.3	0.004	0.0129	0.0016	0.00003	0.00005	0.750	0.00005	1.250
Dill	4	Chlorpyrifos	0.12	0.01	0.0291	L/C	L/C	0.00005	—	0.00005	0.500
		Diazynon	0.08	0.0002	0.0291	L/C	L/C	0.00003	—	0.00003	15.00
		Captan	0.05	0.1	0.0291	L/C	L/C	0.00002	—	0.00002	0.020
		Pendimethalin	0.6	0.125	0.0291	L/C	L/C	0.00023	—	0.00023	0.184
Chive	1	Azoxystrobin	0.28	0.2	0.0190	0.0023	0.00004	0.00007	0.020	0.00007	0.035
Radish	1	—	—	—	—	—	—	—	—	—	
Greenhouse peppers	7	Azoxystrobin	0.02	0.2	0.0281	0.0117	0.00002	0.00001	0.010	0.00001	0.005
		Bifenthrin	0.03	0.15	0.0281	0.0117	0.00002	0.00001	0.013	0.00001	0.007
		Chlorpyrifos	0.09	0.01	0.0281	0.0117	0.00007	0.00003	0.700	0.00003	0.300
		Chlorothaloniil	0.08	0.015	0.0281	0.0117	0.00006	0.00003	0.400	0.00003	0.200
		Cypermethrin	0.02	0.05	0.0281	0.0117	0.00002	0.00001	0.040	0.00001	0.020
Iprodione	0.02	0.06	0.0281	0.0117	0.00002	0.00001	0.030	0.00001	0.017		

Table 3
 Estimation of short-term exposure to pesticide residues for early vegetables in years 2009–2011

Crop	Active substance	HR [mg/kg]	ARfD [mg/kg body weight]	Full portion consumption data (97.5 percentile) [kg]		Intake			
				toddlers	adults	toddlers [14.5 kg]	% ARfD	adults [76 kg]	% ARfD
Greenhouse tomato	Bifenthrin	0.3	0.03	0.2830	0.0905	0.01242	41.41	0.00313	10.43
Parsley leaves	Chlorpyrifos	1.45	0.1	0.0497	0.0045	0.00045	0.45	0.00095	0.95
	Chlorothalonil	45.9	0.6	0.0497	0.0450	0.014245	2.37	0.03016	5.03
	Propiconazole	0.65	0.3	0.0497	0.0450	0.000202	0.07	0.00042	0.14
Dill	Chlorpyrifos	0.12	0.1	0.1558	—	—	—	0.00172	1.72
	Diazynone	0.08	0.025	0.1558	—	—	—	0.00115	4.60
	Pendimethalin	0.6	no applicable	—	—	—	—	—	—

Tests for p.p.p residues showed presence of active substances not recommended for protection of a given crop [12]. The largest amount of not recommended substances was found in dill, and they were: chlorpyrifos, diazinon and captan, and in parsley leaves and pepper (g): propiconazole and chlorpyrifos, respectively.

Long-term and short-term exposure was estimated for 2 age groups: toddlers and adults. As acceptable and not health-threatening were considered values of evaluated consumer exposure not exceeding 100 % of ADI or ARfD value.

Table 2 shows evaluated long-term exposure of humans following consumption of all determined p.p.p. The highest long-term consumer exposure was found for both groups, of adults and of toddlers, in case of consumption of products such as parsley leaves (17.3 % ADI – toddlers, 26.6 % ADI – adults) and dill (15 % ADI – adults). In case of consumption of other early vegetables, long-term exposure in both age groups did not exceed 2.5 % ADI. The intake values for toddlers marked as L/C mean the consumption (very low) was determined as being below 0.1 g/day.

Short-term exposure is shown in Table 3. It is estimated by comparing a single intake of pesticide residues to the amount of its acute reference dose (ARfD). It was calculated for compounds exceeding MRLs. The highest values of short-term exposure were obtained for tomato, and for the group of toddlers it was 41.4 % ARfD, and for the adult group it was 10.4 % ARfD. In both cases these values did not exceed the acceptable 100 % threshold. In case of consumption of other products the short-term exposure did not exceed 5 % ARfD.

On a basis of the determined levels of pesticide residues in analysed crops, estimation of the risk to human health, both long- and short-term, it can be stated that intake of pesticide residues with Polish early vegetables did not pose a risk to consumers' health.

Conclusions

1. The substances most often found in early vegetables were residues of the fungicide group.
2. The highest estimated long-term consumer exposure was found for both groups of adults and toddlers in case of consumption of products such as parsley leaves (17.3 % ADI – toddlers, 26.6 % ADI – adults) and dill 15 % ADI – adults. In case of consumption of other early vegetables, long-term exposure in both age groups did not exceed 2.5 % ADI.
3. The highest estimated values of short-term exposure were obtained for tomato, and in the group of toddlers it was 41.4 % ARfD, and in the adult group it was 10.4 % ARfD. In the remaining samples the short term exposure did not exceed 5 % ARfD.

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POZOSTAŁOŚCI ŚRODKÓW OCHRONY ROŚLIN W NOWALIJKACH JAKO POTENCJALNE RYZYKO NARAŻENIA KONSUMENTÓW

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Abstrakt: W latach 2009–2011 w Laboratorium Badania Pozostałości Środków Ochrony Roślin od marca do czerwca przeprowadzono badania 96 próbek nowalijek. W 35 próbkach stwierdzono obecność pozostałości pestycydów. Celem pracy była ocena długo- i krótkoterminowego spożycia pozostałości pestycydów w nowalijkach dla dwóch grup konsumentów: małych dzieci i dorosłych. Oszacowane wartości narażenia wyznaczono z danych dotyczących pozostałości środków ochrony roślin z badań przeprowadzonych w Laboratorium. Wartości te zostały oszacowane na podstawie modelu brytyjskiego Urzędu Bezpieczeństwa Pestycydów Ministerstwa ds. Środowiska, Żywności i Rolnictwa. Najwyższe pobranie oszacowano dla liści pietruszki, jednak nie przekraczało ono: dla dorosłych 26,6 % ADI, a dla małych dzieci 17,3 % ADI. W przypadku konsumpcji innych nowalijek długoterminowe narażenie nie przekraczało 2,5 % ADI. Największe szacowane wartości krótkotrwałego narażenia uzyskano dla pomidorów w grupie małych dzieci – 41,4 % ARfD i w grupie dorosłych – 10,4 % ARfD. W pozostałych próbkach krótkoterminowe narażenie nie przekraczało 5 % ARfD.

Słowa kluczowe: pozostałości środków ochrony roślin, narażenie, nowalijki