JOURNAL OF PLANT PROTECTION RESEARCH
Vol. 42, No. 2 (2002)

PESTICIDE RESIDUES IN GREENHOUSE VEGETABLES OF SOUTH-EASTERN POLAND IN 1999–2001

Stanisław Sadło, Ewa Szpyrka

Institute of Plant Protection, Experimental Station
Langiewicza 28, 35-101 Rzeszów, Poland
e-mail: s.sadlo@ior.poznan.pl

Accepted: April 18, 2002

Abstract: The purpose of this paper is to estimate levels of pesticide residues present on or in greenhouse vegetables of the south-eastern Poland. Samples taken by trained inspectors of Inspectorates of Plant Protection (national monitoring program) and by personnel of the Experimental Station (surveillance programme) were generally analysed unwashed and unpeeled. The results obtained were compared to their MRLs and then were used for the assessment of the long (chronic) and short-term (acute) exposure of adult consumers. Detectable residues (above limit of determination) were found in 45%, 36%, and 20% of the tomato, pepper and cucumber samples (national monitoring program), respectively, and in 78%, and 52% of the tomato and cucumber samples (surveillance programme). Long-term intake of residues by an adult consumer of the south-eastern Poland did not exceed the level of 0.2% of the ADI, indicating that sufficient margin of safety exist for the consumer. From short-term exposure, only consumption of tomatoes containing DTCs and chlorothalonil residues were close to levels of respective ADIs.

Key words: pesticide residues, greenhouse vegetables, acute and chronic exposure, adult consumer

INTRODUCTION

Maximum **R**esidue **L**evels/**L**imits (**MRLs**) are defined as the highest concentrations of pesticides residues (expressed in milligrams of residues per kilogram of commodity) likely to occur in or on food commodities after the use of plant protection products according to **G**ood **A**gricultural **P**ractice (**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.

Estimates of pesticide intake need to be made in order to compare potential consumer dietary exposure with **A**cceptable **D**ietary **I**ntakes (**ADIs**) and **A**cute **R**eference Doses (ArfDs) derived from toxicological studies. If estimates of long or short-term intake are less than the ADI and ARfD levels, respectively, then the risks to the consumer may be regarded as acceptable.

The purpose of this work was to assess and evaluate pesticide residues present on or in greenhouse vegetables in relation to their MRLs. In addition, the long and short-term dietary exposure for adult consumers from the south eastern Poland have been calculated in accordance with methodology currently recommended by European Commission for the Member States of European Union.

METHODS

Sampling design. Polish national monitoring programme (1) for pesticides residues in products of plant origin is conducted by six analytical laboratories of the Institute of Plant Protection. Each year a total of 2200 laboratory (composite) samples were taken by trained inspectors from the local Plant Protection Services according to sampling plan designed at the beginning of each year. 480 of the samples collected were analysed by the analytical laboratory in Rzeszów.

Besides national monitoring programme, the analytical laboratory in Rzeszów has run specific surveillance programme (2) for pesticide residues in vegetables grown in six 1-ha greenhouses delivering tomatoes and cucumbers to dwellers of the south-eastern Poland. This programme has existed since 1999, and its aim was to work towards a system, which makes it possible to estimate actual dietary pesticide exposure throughout vegetation season. The samples were taken 6–7 times a year (from April to October) by trained personnel of the laboratory.

Samples were generally analysed unwashed and unpeeled by **M**ulti-**R**esidue **M**ethod (**MRM**) consisting of an extraction of residues into an organic solvent followed by a chromatographic separation and selective EC and NP detection (Ambrus et al. 1981; Luke et al. 1981; Sadło 1998). Along with this multiresidue method, spectrophotometric and **T**hin **L**ayer **C**hromatographic (**TLC**) determination of the sum of **d**ithio**c**arbamates (**DTCs**) and bennzimidazoles expressed as carbendazim residues were carried out (Chmiel 1979; Murawska 1980).

Both the monitoring (1) and the surveillance (2) data were used for the assessment of the long (chronic) and short-term (acute) consumer exposure.

Exposure assessment. The assessment of long-term (acute) dietary intakes (**L-TDI**) has been carried out using the following equation:

$$L-TDI = \frac{average\,consumption}{body\,weight} \times \frac{R}{ADI} \times 100\%$$

where R is a residue of a given pesticide found in composite samples of the food item. The intake was calculated only for those compounds for which the 90th percentiles of their residue were found to be above the **l**imit **o**f **d**etermination (**LOD**).

Assuming additive impact of different pesticides on a consumer, on the basis of individual analyses a daily intake have been calculated for each laboratory sample using the following equation:

$$L - TDI = \frac{average\ consumption}{body\ weight} \times \sum_{i=1}^{n} \frac{R_i}{ADI_i} \times 100\%$$

where: R_i is a residue of an "*i*" pesticide of the "n" different pesticides found in a given sample. The total long-term dietary intakes taking into account so called multiple residues were expressed by the average and 90^{h} percentile.

Short-term dietary intake estimates (**S-TDI**) have been carried out using the following equation:

$$S - TDI = \frac{97.5th\ percentile\ of\ consumption}{body\ weight} \times \frac{HR \times v}{ADI(ARfD)} \times 100\%$$

where: HR is the highest residue found in the food item, and ***v*** is a default **v**ariability/homogeneity factor. The **A**cute **R**eference **D**ose is the amount of a substance in food that can be ingested during one meal, or one day, without appreciable adverse health effect to the consumer. At present, ARfD have been fixed only for certain pesticides. Therefore, short-term dietary intakes have been estimated in relation to the ADIs taken from the "Pesticide Manual" (Tomlin 1994). The results obtained can be easily recalculated using actual ARfD values.

Quality assurance. All laboratories involving in the national monitoring program participated in proficiency testing exercises, including European Commission's Proficiency Tests and Food Analysis Performance Assessment Scheme (FAPAS). The results obtained allowed an independent check of the laboratories' performance to be made. Each time the analytical laboratory in Rzeszów obtained satisfactory results. Besides, the laboratory met the other requirements of **G**ood **L**aboratory **P**ractice (**GLP**).

RESULTS

Evaluation of pesticide residue levels

The summarised results of the monitoring (1) and surveillance (2) programmes are given in table 1, 2, and 5. A total of 657 samples of greenhouse vegetables were analysed. 48% of them were free of pesticide residues (R<**LOD**). Detectable residues (at or below MRL) were found in 51.5% of the samples. In 0.5% of the samples, the residues exceeded national MRLs.

Table 2 summarises samples in which more than one pesticide residue had been found. Residues of more than one pesticide were found in about 20% of the analysed samples. In most cases (19%), residues of two pesticides were found, followed by 1% of samples containing three residues. In 3 samples (0.5%), residues of four different pesticides were found.

In general, residues at or below the MRL (78%) and above MRL (1%) were found most often in tomatoes. Their highest residues found were 2.25 mg/kg DTCs and 1.80 mg/kg chlorothalonil. The most important pesticide-commodity combinations were found to be chlorothalonil/tomato and procymidone/tomato. With regard to MRL exceeding the most important pesticide-commodity combination

Table 1. Pesticide residues found in greenhouse vegetables analysed in the framework of the national monitoring (1) and surveillance (2) programmes in 1999–2001

Compound	Food item	N	R<LOD		R>LOD		R>MRL	
			n	%	n	%	n	%
Procymidone	pepper (1)	100	72	72	28	28	0	0
Chlorothalonil			95	95	5	5	0	0
Bifenthrin			96	96	4	4	0	0
Iprodione			96	96	4	4	0	0
	Total		**64**	**64**	**36**	**36**	**0**	**0**
Chlorothalonil	tomato (1)	310	231	75	79	25	0	0
Procymidone			256	83	54	17	0	0
Iprodione			279	90	31	10	0	0
DTC			283	91	27	9	3	1
Tolylfluanid			294	95	16	5	0	0
Dichlofluanid			301	97	9	3	0	0
Vinclozolin			307	99	3	1	0	0
Pyrimethanil			308	99	2	1	0	0
	Total		**172**	**55**	**138**	**45**	**3**	**1**
Procymidone	cucumber (1)	139	125	90	14	10	0	0
Chlorothalonil			129	93	10	7	0	0
Iprodione			132	95	7	5	0	0
Dichlofluanid			137	99	2	1	0	0
Bifenthrin			137	99	2	1	0	0
Carbendazim			138	99	1	1	0	0
Tolylfluanid			138	99	1	1	0	0
	Total		**111**	**80**	**28**	**20**	**0**	**0**
Procymidone	tomato (2)	85	37	44	48	56	0	0
Chlorothalonil			52	61	33	39	0	0
Iprodione			59	69	26	31	0	0
Dichlofluanid			78	92	7	8	0	0
Tolylfluanid			81	95	4	5	0	0
Pyrimethanil			83	98	2	2	0	0
Pirimicarb			84	99	1	1	0	0
Pyrazophos			84	99	1	1	0	0
	Total		**19**	**22**	**66**	**78**	**0**	**0**
Procymidone	cucumber (2)	23	13	57	10	43	0	0
Iprodione			18	78	5	22	0	0
Chlorothalonil			22	96	1	4	0	0
Dichlofluanid			22	96	1	4	0	0
	Total		**11**	**48**	**12**	**52**	**0**	**0**

N, n,% – number of samples analysed, and number and percentage of samples with residues in a given range

was DTC/tomato. It is evident from table 1 that commodity where most often residues were detected and exceeded the MRLs levels, and where the highest residues were found, was tomato.

Table 2. Numbers of samples in which 2 or more pesticides were detected

Food item	N	2	3	4	≤ 5	Multiple residues	
						n	%
Pepper (1)	100	5	0	0	0	5	5
Tomato (1)	310	42	9	0	0	51	16
Cucumber (1)	139	8	0	0	0	8	6
Tomato (2)	85	33	6	3	0	42	49
Cucumber (2)	23	3	1	0	0	4	17
Total	657	91	16	3	0	110	17

N, 2, 3, 4, ≤ 5, n,% – number of samples analysed, and number and percentage of samples with multiple residues

Exposure assessment

Long-term (chronic) exposure. Long-term consume exposures were calculated for an adult with an average bodyweight of 60 kg using the average consumption figures from Kubiak et al. (2000) and the 90th percentiles of the residue levels (mg/kg) found in laboratory (composite) samples of greenhouse vegetables analysed in the framework of the monitoring (1) and surveillance (2) programmes. The intake of a given pesticide via a specific commodity was calculated and expressed as percentage of its ADI level.

As shown by the results in table 3 and 4 the intake of pesticide residues within vegetation season did not exceed the level of 0.2% of the ADI for all pesticides. The exposure ranged from 0.00% for cucumber/procymidone combination to 0.179% of the ADI for tomato/chlorothalonil combination. Therefore, the obtained results were 8-fold lower than those obtained for the case of pepper/endosulfan combination (SANCO/397/01-Final), indicating that a sufficient margin of safety existed for the adult consumer.

Since a number of composite samples were found to contain residues of more than one compound it was necessary to consider the intakes of multiple residues from any one crop. Representative calculation shown in table 4 indicate that food

Table 3. Long-term dietary intake of any one pesticide residue from greenhouse vegetables

Compound	Food item	90th percentile (mg/kg)	ADI	Average consumption (kg/day)	Intake via commodity (mg/day/kg)	Intake in% of the ADI
Procymidone	pepper (1)	0.051	0.100	0.003	0.000002	0.002
Chlorothalonil		0.090	0.030		0.000025	0.082
Procymidone	tomato (1)	0.050	0.100	0.016	0.000014	0.014
Iprodione		0.001	0.200		0.000000	0.000
Procymidone	cucumber (1)	0.002	0.100	0.007	0.000000	0.000
Chlorothalonil		0.196	0.030		0.000054	0.179
Procymidone	tomato (2)	0.206	0.100	0.016	0.000056	0.056
Iprodione		0.110	0.200		0.000030	0.015
Procymidone	cucumber (2)	0.048	0.100	0.007	0.000006	0.006
Iprodione		0.028	0.200		0.000003	0.002

Table 4. Total long-term dietary intake of pesticide residues from greenhouse vegetables

Food item	Average intake in% of the ADI	90[th] percentile intake in% of the ADI
Pepper (1)	0.001	0.004
Tomato (1)	0.045	0.101
Cucumber (1)	0.003	0.007
Total*	**0.049**	**0.112**
Tomato (2)	0.082	0.200
Cucumber (2)	0.003	0.010
Total*	**0.085**	**0.210**

*The average consumption (0.026 kg/day) of greenhouse vegetables constituted about 7.5% of the total consumption of fresh vegetables in Poland in 1998 (Kubiak et al. 2000)

items with multiple residues do not pose increased risk to consumers because exposition from this source is little if any larger than that from the most frequently single residue detected.

Short-term (acute) exposure. Since all chemicals have the potential to show a toxicological effect, it was considered necessary to assess short-term exposure to pesticide residues resulting from the consumption of one meal. This has been carried out using the highest residue (mg/kg) level found in composite samples of greenhouse vegetables analysed in the framework of the monitoring (1) and surveillance (2) programmes and the 97.5[th] percentile consumption of any one of food item over one day. In order to reflect a theoretical worst case situation, the average variability factor of 3.44 was used. On the basis of those data an exposure assessment for an adult of 70.1 kg has been carried out and the intake of a specific pesticide via a specific commodity was calculated and compared with the ADI.

As table 5 shows the intakes for the highest residues in composite samples of greenhouse vegetables for all the pesticides found were well below the ADI. Their values ranged from 0.00% of the ADI for cucumber/tolylfluanid to 57.8% and 46.2% of the ADI for tomato/DTC and for tomato/chlorothalonil. The latter cases showed that even the highest values constituted only a fraction of the ADI levels. Taking into account that the ARfD values now available are 2–10-fold higher than those fixed for the ADI (SANCO/397/01-Final), the safety factor of 4–20 for an adult consumer still existed.

CONCLUSIONS

1. Detectable residues (R>LOD) were found in 78% (2) and 45% (1) of the tomato samples, in 52% (2) and 20% (1) of the cucumber samples, and in 36% (1) of the pepper samples.
2. Long-term intakes of residues by an adult consumer of the south-eastern Poland did not exceed the level of 0.2% of the ADI, indicating that a sufficient margin of safety still existed.
3. From short-term exposure, only consumption of tomatoes containing DTCs and chlorothalonil residues could occasionally be close to levels of respective ADIs.

Table 5. Short-term dietary intake of pesticide residues from greenhouse vegetables

Compound	Food item	Residue	ADI	Consumption	Intake via commodity	Intake in% of the ADI
Procymidone	pepper (1)	0.400	0.100	0.089	0.00175	1.7
Chlorothalonil		0.050	0.030		0.00022	0.7
Bifenthrin		0.030	0.020		0.00013	0.7
Iprodione		0.060	0.200		0.00026	0.1
DTC	tomato (1)	2.250	0.030	0.157	0.01733	57.8
Chlorothalonil		1.800	0.030		0.01387	46.2
Procymidone		0.990	0.100		0.00763	7.6
Vinclozolin		0.560	0.070		0.00431	6.2
Dichlofluanid		0.810	0.300		0.00624	2.1
Iprodione		0.500	0.200		0.00385	1.9
Pyrimethanil		0.240	0.200		0.00185	0.9
Tolylfluanid		0.110	0.100		0.00085	0.8
Carbendazim	cucumber (1)	0.050	0.010	0.084	0.00021	2.1
Chlorothalonil		0.140	0.030		0.00058	1.9
Procymidone		0.200	0.100		0.00082	0.8
Bifenthrin		0.030	0.020		0.00012	0.6
Iprodione		0.140	0.200		0.00058	0.3
Dichlofluanid		0.060	0.300		0.00025	0.1
Tolylfluanid		0.010	0.100		0.00004	0.0
Chlorothalonil	tomato (2)	0.920	0.030	0.157	0.00709	23.6
Iprodione		1.300	0.200		0.01002	5.0
Procymidone		0.330	0.100		0.00254	2.5
Pirimicarb		0.050	0.020		0.00039	1.9
Pyrazophos		0.010	0.004		0.00008	1.9
Tolylfluanid		0.090	0.100		0.00069	0.7
Pyrimethanil		0.060	0.200		0.00046	0.2
Dichlofluanid		0.080	0.300		0.00062	0.2
Procymidone	cucumber (2)	0.070	0.100	0.084	0.00029	0.3
Chlorothalonil		0.020	0.030		0.00008	0.3
Iprodione		0.130	0.200		0.00054	0.3
Dichlofluanid		0.010	0.300		0.00004	0.0

REFERENCES

Ambrus A., Lantos J., Visi E., Csatlos I., Sarvari L. 1981. General method for determination of pesticide residues of plant origin, soil, and water. I. Extraction and cleanup. J. Assoc. Off. Anal. Chem., 64: 733–742.

Chmiel Z. 1979. Spektrometryczne oznaczanie śladowych pozostałości dwutiokarbaminianów w materiale roślinnym. Chemia Analityczna 24: 505–512.

Kubiak K., Krajewski A., Mirkowska Z., Strojewska I. 2000. Spożycie produktów ogrodniczych w Polsce i wybranych krajach. Centralny Ośrodek Badawczo-Rozwojowy Ogrodnictwa: 9–14.

Luke M.A., Froberg J.E., Dosse G.M., Masumoto H.T. 1981. Improved multiresidue gas chromatographic determination of organophosphorus, organonitrogen and organohalogen pesticides in produce, using flame photometric and electrolytic conductivity detectors. J. Assoc. Off. Anal. Chem., 64: 1187–1192.

Murawska M. 1980. Metoda bioautografii w zastosowaniu do oznaczania śladowych ilości fungicydów benzimidazolowych. Prace Nauk. IOR 22 (1): 139–146.
Sadło S. 1998. Partition coefficient – its determination and significance in estimation of pesticide residue losses in the course of extraction procedure. J. Plant Protection Res., 38 (2): 179–184.
Tomlin C. 1994. "The Pesticide Manual", 10^{th} Edition; British Crop Protection Council: Croydon, UK.

POLISH SUMMARY

POZOSTAŁOŚCI ŚRODKÓW OCHRONY ROŚLIN W WARZYWACH SZKLARNIOWYCH POŁUDNIOWO-WSCHODNIEJ POLSKI

Celem pracy było oszacowanie poziomów pozostałości środków ochrony roślin w warzywach szklarniowych z południowo-wschodniej Polski. Próbki tych warzyw, pobrane przez inspektorów Wojewódzkich Inspektoratów Ochrony Roślin (w ramach monitoringu krajowego) i przez personel Terenowej Stacji Doświadczalnej Instytutu Ochrony Roślin (w ramach kontroli pozostałości), analizowano bez obierania i mycia. Uzyskane wyniki porównywano do Najwyższych Dopuszczalnych Pozostałości (NDP) a następnie wykorzystywano do oceny długotrwałej i krótkotrwałej ekspozycji dorosłego konsumenta.

Wykrywalne pozostałości (powyżej dolnej granicy oznaczalności) znaleziono w 45, 36 i 20% próbek pomidora, papryki i ogórka (monitoring krajowy) oraz w 78 i 52% próbek pomidora i ogórka (kontrola pozostałości). Dzienne pobieranie pozostałości środków ochrony roślin przez dorosłego konsumenta z południowo-wschodniej Polski nie przekraczało poziomu 0,2% dopuszczalnego dziennego pobrania (ADI) i wykazało, że istnieje dla niego dostateczny margines bezpieczeństwa. Jednorazowe pobranie pozostałości mogło się zbliżyć do odpowiednich poziomów ADI tylko po spożyciu pomidorów zawierających pozostałości ditiokarbaminianów lub chlorotalonilu.