Technical Paper

Pesticide Residues in Agricultural Products of Slovene Origin in 2005

Helena Baša Česnik, Ana Gregorčič, Špela Velikonja Bolta

Agricultural Institute of Slovenia, Central Laboratories, Hacquetova 17, SI-1000 Ljubljana, Slovenia

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Abstract

In the Central Laboratories of Agricultural Institute of Slovenia 115 apple, carrot, cucumber, lettuce, pear, potato, spinach and string beans samples from Slovene producers were analysed for pesticide residues in the year 2005. Samples were analysed for the presence of 66 different active compounds using three analytical methods. Three samples (2.6%) exceeded maximum residue levels (MRLs) which is less than it was found during the national monitoring of the European Union in 2003 (5.5%).

Key words: pesticides, plant protection products.

Introduction

In accordance with the Law on Plant Protection Products[1] and Regulation on Pesticide Residues in/on Foodstuffs and Agricultural Products[2] Agricultural Institute of Slovenia was determining pesticide residues in agricultural products of Slovene producers prior to the market, i.e. after picking, digging or harvesting and in storage. In conformity with a good agricultural practice in the conventional, integrated and ecological production, the use of plant protection products has been surveyed. Each year analyses of pesticide residues were performed on potato, lettuce and apple samples, due to the characteristic nutrition of Slovenes. Selection of other agricultural commodities and active substances follows the guidelines given in the EU Recommendations[3].

Control of pesticide residues in agricultural products prior to the market allows assessment of conformity of production with good agricultural practice and determination of source and/or cause of residues found. Due to a random choice of producers the results obtained enable the estimation of the state and efficiency of previous measures. All this helps us to ensure food safety on Slovene market.

The results are intended for:

- Determination of conformity with the legally prescribed maximum residue levels (MRLs)
- Determination of conformity of the conventional, integrated and ecological production with the good agricultural practice
- Determination of source and/or cause of residues found

Beside potato, lettuce and apple samples agricultural inspectors took samples of carrot, cucumber, pear, spinach and string beans in 2005. The samples were taken randomly in eight production areas of Slovenia: Celje, Koper, Kranj, Nova Gorica, Novo mesto, Murska Sobota, Maribor and Ljubljana. Agricultural products were taken directly in the field or in the storehouse after the expiration of pre-harvest interval of the plant protection products used.

Legally prescribed MRLs are defined on the basis of field trials in accordance with good agricultural practice. Consideration of the pre-harvest interval and prescribed way of use of the plant protection products is therefore of key importance.

Experimental

Samples were analysed for the content of selected active substances.

In 2005, residues of 66 different compounds were determined in the Central Laboratories using three different methods:

1. *Multiresidual GC/MS method* for the determination of 64 compounds: acephate, aldrin, azinphos-methyl, azoxystrobin, bifenthrin, bromopropylate, bupirimate, captan, carbaryl, carbofuran, chlorothalonil, chlorpropham, chlorpyriphos, chlorpyriphos-methyl, cyhalotrin-lambda, cypermethrin, cyprodinil, DDT, deltamethrin, diazinon, dichlofluanid, dimethoate,

Table 1. List of agricultural products, analysed in 2005, and distribution of sample locations among individual production areas

	AGRICULTURAL PRODUCT								
AREA	apples	carrot	cucumbers	lettuce	pears	potatoes	spinach	string beans	Sum
Celje	3	2	4	3	2	2	1	1	18
Koper	0	0	0	2	1	0	0	3	6
Kranj	1	2	0	1	1	4	1	0	10
Ljubljana	2	7	3	3	2	3	5	5	30
Maribor	4	3	3	3	3	3	0	3	22
Murska Sobota	2	0	2	3	0	2	0	1	10
Nova Gorica	2	0	2	2	2	0	0	0	8
Novo mesto	3	1	3	0	1	2	0	1	11
SUM	17	15	17	17	12	16	7	14	115

diphenylamine, endosulfan, endrin, fenitrothion, fenthion, fludioxonil, folpet, HCH-α, heptachlor, heptenophos, imazalil, iprodione, kresoxim-methyl, lindane, malathion, mecarbam, metalaxyl, methamidophos, methidathion, myclobutanil, omethoate, oxydemeton-methyl, parathion, permethrin, phorate, phosalone, pirimicarb, pirimiphos-methyl, procymidone, propargite, propyzamide, pyridaphenthion, pyrimethanil, quinalphos, spiroxamine, thiabendazole, tolclofos-methyl, tolylfluanid, triadimefon, triadimenol, triazophos, vinclozolin[4].

2. *GC/MS method* for the determination of dithiocarbamate group: maneb, mancozeb, metiram, propineb and zineb, the sum is expressed as carbon disulfide.
3. *HPLC method* for the determination of benzimidazoles: thiabendazole and sum of benomyl and carbendazim[5].

The trueness of methods is verified by participation in the French inter-laboratory proficiency testing scheme BIPEA (Bureau interprofessionnel d´etudes analytiques).

In January 2005 a range of analyses covering pesticide residues were accredited by the French accreditation body COFRAC.

Results and discussion

115 samples of agricultural products, presented in Table 1, were analysed in 2005.

17 **apple** samples were analysed: one sample (5.9%) exceeded MRL, 15 samples (88.2%) contained residues lower than MRLs, residues were not found in one sample (5.9%).

15 **carrot** samples were analysed: residues exceeding MRLs were not determined, 3 samples

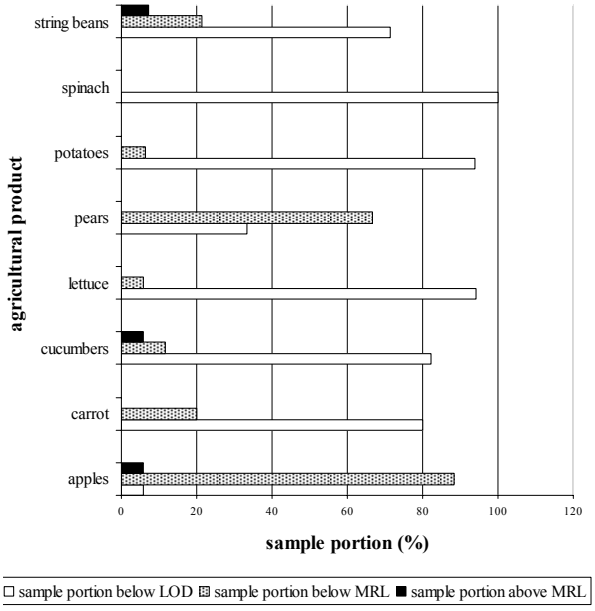

Figure 1. Pollution of agricultural products with pesticides

(20.0%) contained residues lower then MRLs, residues were not found in 12 samples (80.0%).

17 **cucumber** samples were analysed: one sample (5.9%) exceeded MRL, 2 samples (11.8%) contained residues lower than MRLs, residues were not found in 14 samples (82.4%).

17 **lettuce** samples were analysed: residues exceeding MRLs were not determined, one sample (5.9%) contained residues lower than MRLs, residues were not found in 16 samples (94.1%).

12 **pear** samples were analysed: residues exceeding MRLs were not determined, 8 samples (66.7%) contained residues lower than MRLs, residues were not found in 4 samples (33.3%).

16 **potato** samples were analysed: residues exceeding MRLs were not determined, one sample

(6.3%) contained residues lower than MRLs, residues were not found in 15 samples (93.8%).

7 **spinach** samples were analysed: residues were not found in 7 samples (100.0%).

14 **string beans** samples were analysed: one sample (7.1%) exceeded MRL, 3 samples (21.4%) contained residues lower than MRLs, residues were not found in 10 samples (71.4%).

Results are presented in Figure 1.

21 samples (18.3%) out of 115 samples contained **multiple residues**. Residues of two active substances were determined in 4 out of 17 apple samples (23.5%), 1 out of 17 cucumber samples (5.9%) and 3 out of 12 pear samples (25.0%). Residues of three active substances were determined in 2 out of 17 of apple samples (11.8%) and 1 out of 12 pear samples (8.3%). Residues of more than three active substances were determined in 8 out of 17 apple samples (47.1%) and 2 out of 12 pear samples (16.7%). In two apple samples six active substances were found, i.e. the highest number of different residues in one sample.

Contribution of samples with multiple residues was 82.4% (14 samples) for apples, 5.9% (1 sample) for cucumbers and 50.0% (6 samples) for pears.

Residues of one active substance were found in carrot, lettuce, potato and string beans samples while no residues were found in spinach.

The results are shown in Fig. 2.

In 2005 apple, carrot, cucumber, lettuce, pear, potato, spinach and string beans samples contained following **active substances**: chlorpropham, folpet, pirimicarb and procymidone each in one sample (0.9%), chlorothalonil, chlorpyrifos-methyl and cyprodinil each

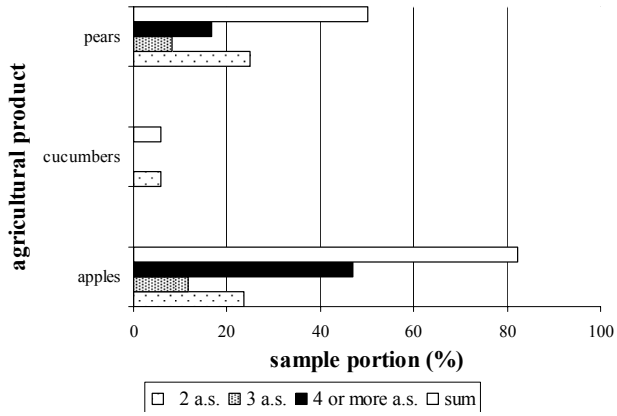

Figure 2. Distribution of samples with multiple residues

in 3 samples (2.6%), chlorpyrifos in 4 samples (3.5%), captan in 8 samples (7.0%), phosalone in 9 samples (7.8%), diazinon in 12 samples (10.4%), tolylfluanid in 16 samples (13.9%) and dithiocarbamates in 24 samples (20.9%). The residues most frequently found were those from the group of dithiocarbamates: maneb, mancozeb, metiram, propineb and zineb (fungicides) followed by tolylfluanid (fungicide) and diazinon (insecticide). The results are given in Table 2 and Fig. 3.

Active substances exceeding MRLs were the following: chlorothalonil, diazinon and tolylfluanid, each in one sample (0.9%). The results are shown in Table 3. Chlorothalonil content in string beans sample was 0.06 mg/kg (MRL is 0.01 mg/kg), diazinon content in cucumber sample was 0.21 mg/kg (MRL is 0.02 mg/kg) and tolylfluanid content in apple sample was 0.73 mg/kg (MRL is 0.21 mg/kg).

Table 2. Active substances found in fruit and vegetable samples

	apples	carrot	cucumbers	lettuce	pears	potatoes	spinach	string beans	sum	Portion of samples that contained active substance (%)
captan	**5**	0	0	0	**3**	0	0	0	**8**	**7.0**
chlorothalonil	0	0	2	0	0	0	0	1	**3**	**2.6**
chlorpropham	0	0	0	0	0	**1**	0	0	**1**	**0.9**
chlorpyrifos	**4**	0	0	0	0	0	0	0	**4**	**3.5**
chlorpyrifos-methyl	**1**	0	0	0	**2**	0	0	0	**3**	**2.6**
cyprodinil	**2**	**1**	0	0	0	0	0	0	**3**	**2.6**
diazinon	**7**	**2**	**2**	0	**1**	0	0	0	**12**	**10.4**
dithiocarbamates	**15**	0	0	**1**	**5**	0	0	**3**	**24**	**20.9**
folpet	**1**	0	0	0	0	0	0	0	**1**	**0.9**
phosalone	**4**	0	0	0	**5**	0	0	0	**9**	**7.8**
pirimicarb	**1**	0	0	0	0	0	0	0	**1**	**0.9**
procymidone	0	0	0	0	**1**	0	0	0	**1**	**0.9**
tolylfluanid	**12**	0	0	0	**4**	0	0	0	**16**	**13.9**

Table 3. Active substances in fruit and vegetable samples exceeding maximum residue levels

	apples	carrot	cucumbers	lettuce	pears	potatoes	spinach	string beans	sum	Portion of samples with exceeded MRL (%)
chlorothalonil	0	0	0	0	0	0	0	**1**	**1**	**0.9**
diazinon	0	0	**1**	0	0	0	0	0	**1**	**0,9**
tolylfluanid	**1**	0	0	0	0	0	0	0	**1**	**0.9**

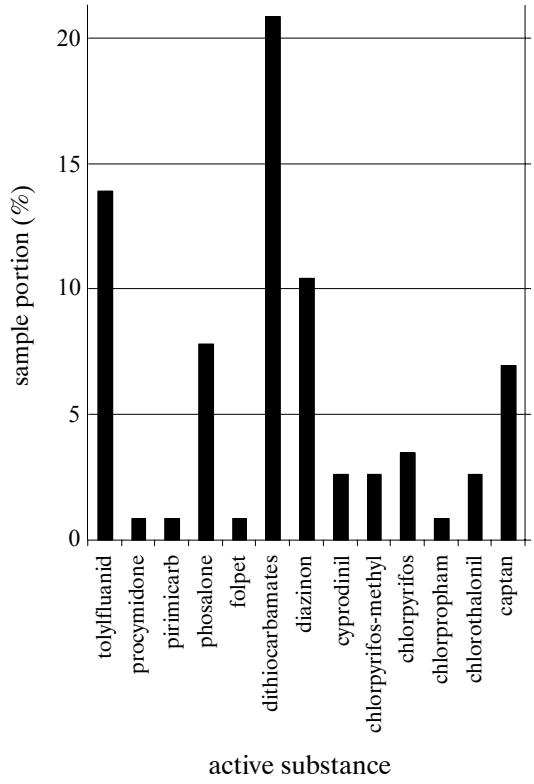

Figure 3. Samples with active substances, found in 2005

In 2005 79 samples (68.7%) out of 115 samples analysed did not contain any residue or the contents were below the limit of detection of the method, 33 samples (28.7%) contained residues lower or equal to MRLs and 3 samples (2.6%) contained residues above MRLs (Fig. 4).

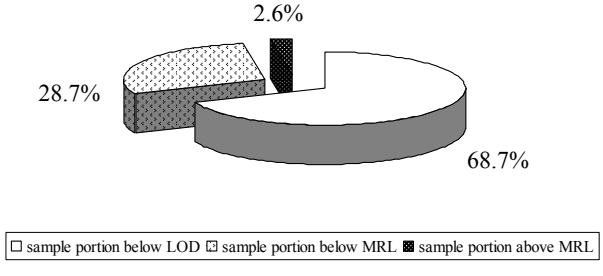

Figure 4. Results of monitoring in 2005

The results of monitoring obtained from 2001 to 2004 are worse than the results in 2005. From 2001 to 2004 662 samples were analysed: 375 samples (56.6%) did not contain any residue or the contents were below the limit of detection of the method, 240 samples (36.3%) contained residues lower or equal to MRLs and 47 samples (7.1%) contained residues above MRLs.

Conclusions

The pollution of agricultural products with pesticide residues in Slovenia in 2005 does not give any cause for alarm. 68.7% samples examined did not contain any residues. Exceeding maximum residue levels were found only in 2.6% samples of agricultural products.

For comparison, the results of national monitoring in 2003, performed in fifteen EU countries and in Norway, Iceland and Liechtenstein, are presented. They have shown that 56% of all examined fresh (unprocessed) fruit, vegetable and cereals samples did not contain pesticide residues, 38.5% of fresh (unprocessed) samples contained residues lower or equal to MRLs and 5.5% of examined fresh (unprocessed) samples contained residues above MRLs.[6] The results for 2004 and 2005 are not available yet.

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Povzetek

Na Kmetijskem inštitutu Slovenije smo na ostanke pesticidov v letu 2005 analiziral 115 vzorcev jabolk, korenja, kumar, solate, hrušk, krompirja, špinače in stročjega fižola slovenskih tržnih pridelovalcev. Vse vzorce smo analizirali s tremi analitskimi metodami na prisotnost 66 različnih aktivnih spojin. Trije vzorci (2,6%) so presegli maksimalno dovoljene količine ostankov kar je manj, kot je bilo ugotovljenih preseženih vzorcev v nacionalnem monitoringu evropske skupnosti v letu 2003 (5,5%).