Technical paper

# Pesticide Residues in Cauliflower, Eggplant, Endive, Lettuce, Pepper, Potato and Wheat of the Slovene Origin Found in 2009

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Received: 14-02-2010

#### Abstract

In the year 2009, 170 cauliflower, eggplant, endive, lettuce, pepper, potato and wheat samples from Slovene producers were analysed for pesticide residues. The samples were analysed for the presence of 214 different active compounds using three analytical methods. MRL exceedances have not been observed, which is better than the results obtained from the monitoring of pesticide residues in the products of plant origin in the European Union, Norway, Iceland and Liechtenstein for the years 2004 to 2006. We have observed that MRL exceedances in Slovenia have been reduced in recent times. We assume that the farmers have learned how to use PPP safely in accordance with good agricultural practice.

Keywords: GC/MS, LC/MS/MS, pesticides, plant protection products

#### **1. Introduction**

Monitoring of plant protection product (PPP) residues in agricultural products of Slovene producers allows to control the correct use of PPPs in accordance with the good agricultural practice applied in conventional, integrated and ecological production, and designation of origin of the residues.

In 2009, inspectors were sampling cauliflower, eggplant, endive, lettuce, pepper, potato and wheat. For the monitoring purposes, lettuce and potato are sampled each year while the other agricultural products are sampled every three years. The samples were taken randomly in eight production areas in Slovenia: Celje, Koper, Kranj, Nova Gorica, Novo mesto, Murska Sobota, Maribor, and Ljubljana. Agricultural products were taken directly in the field or in the storehouses after the expiration of pre-harvest interval of the PPPs.

For the monitoring purposes, laboratories need quick and reliable methods that enable simultaneous determination of a wide spectrum of active substances. The methods mainly use three types of solvents for extraction: ethylacetate,<sup>1-4</sup> acetonitrile (method also known as QuEC-hERS method)<sup>5,6</sup> or acetone.<sup>7–9</sup> Our laboratory used acetone because of its low toxicity, high volatility and miscibility with water in plant matrices. For better extraction of

active substances we added petroleumether and dichlorometane to acetone.<sup>10,11</sup> For the determination of extracted active substances, laboratories mainly use gas chromatography coupled to various detectors: flame ionisation detector (FID), electron capture detector (ECD), nitrogen phosphor detector (NPD), flame photometric detector (FPD) or as in our case mass spectrometer (MS) which is the only one to enable unequivocal qualitative and quantitative detection of active substances. In case of thermally labile compounds liquid chromatography coupled to UV, fluorescence detector or, as in our case, to MS is used, which is again, the only one to enable unequivocal qualitative and quantitative detection of active substances.

This paper presents the results of the 2009 Slovene monitoring of vegetables and cereals and the comparison with the previous monitoring results of the same agricultural products in Slovenia (period 2001–2008) and EU, Norway, Iceland and Liechtenstein (period 2001–2006).

In spite of the enhanced analytical capabilities of the laboratory (better equipment that enables lower limits of quantification, larger number of active substances sought) no Maximum Residue Levels (MRLs) were exceeded in the samples analysed in 2009. In comparison with the years 2001–2004, when a large number of potato samples violated dithiocarbamate MRLs, we can conclude that farmers' proper use of PPPs is today's reality.

#### 2. Experimental

Samples were analysed for the content of selected active substances.

In 2009, residues of 214 different compounds were determined using three different methods:

- 1. Multiresidual GC/MS method for the determination of 100 compounds: acephate, acrinathrin, aldrin, azinphosmethyl, azoxystrobin, bifenthrin, boscalid, bromopropylate, bupirimate, captan, carbaryl, carbofuran, carboxin, chloridazon, chlorothalonil, chlorpropham, chlorpyriphos, chlorpyriphos-methyl, clomazone, cyhalotrinlambda, cypermethrin, cyproconazole, cyprodinil, dazomet, DDT, deltamethrin, desmethylpirimicarb, diazinon, dichlofluanid, dichlorvos, dimethachlor, dimethoate, diniconazole, diphenylamine, endosulfan, endrin, esfenvalerate, fenamidone, fenbuconazole, fenitrothion, fenthion, fenvalerate, flonicamid, fludioxonil, fluquinconazole, folpet, HCH-alpha, HCH-betha, HCH-deltha, heptachlor, heptenophos, hexachlorobenzene, imazalil, indoxacarb, iprodione, kresoxim-methyl, lindane, malathion, mecarbam, metalaxyl, metalaxyl-M, metconazole, methacrifos, methamidophos, methidathion, metrafenone, metribuzin, myclobutanil, omethoate, oxadixyl, oxydemeton-methyl, parathion, parathion-methyl, penconazole, permethrin, phorate, phosalone, pirimicarb, pirimiphos-methyl, procymidone, profenofos, propargite, propyzamide, pyridaphenthion, pyrimethanil, quinalphos, quinoclamine, quinoxyfen, spiroxamine, tebuconazole, tetraconazole, tetradifon, thiabendazole, tolclofosmethyl, tolylfluanid, triadimefon, triadimenol, triazophos, trifloxystrobin and vinclozolin. Extraction was performed by the mixture of acetone, petroleumether and dichlorometane, clean-up by gel permeation chromatography and determination by GC/MS.<sup>10,11</sup>
- 2. *GC/MS method* for the determination of dithiocarbamate group: maneb, mankozeb, metiram, propineb and zineb, the sum is expressed as carbon disulfide. Samples were heated in a two-phase system isooctane/stannous (II) chloride in diluted hydrochloric acid. The produced carbon disulfide was dissolved in the organic phase (isooctane) and determined by GC/MS.<sup>11,12</sup>
- 3. Multiresidual LC/MS/MS method for the determination of 113 compounds: 2,4-D, acetamiprid, aldicarb, aldicarb sulfone, aldicarb sulfoxide, amidosulfuron, amitrole, azinphos-ethyl, beflubutamid, benalaxyl, benalaxyl-M, bentazon, bitertanol, bromoxynil, buprofezin, carbendazim, carbosulfan, chlortoluron, clofentezine, clopyralid, clothianidin, cyazofamid, cycloxydim, cymoxanil, cyromazine, demeton-S-methyl sulphone, desmedipham, dichloprop-P, difenoconazole, diflufenican, dimethenamid-P, dimethomorph, epoxiconazole, ethofumesate, famoxadone, fenarimol, fenazaquin, fenhexamid, fenoxaprop-P-ethyl, fenoxycarb, fenpropidin, fenpropimorf, fenpyroximate, fenthion sulfone, fenthion sulfoxide, fipronil, florasulam, fluazifop-P-butyl, fluazinam, flufenacet, fluorochloridone, fluroxypyr, flusilazole, flutriafol, foramsulfuron, hexaconazole, hexythiazox, imidacloprid, iodosulfuron-methyl-sodium, iprovalicarb, isoproturon, isoxaflutole, linuron, lufenuron, malaoxon, mandipropamid, MCPA, metamitron, metazachlor, methiocarb, methiocarb sulfone, methiocarb sulfoxide, methomyl, methoxyfenozide, metosulam, monocrotophos, napropamide, nicosulfuron, oxamyl, paraoxon-methyl, pendimethalin, phenmedipham, phorate sulfone, phorate sulfoxide, phoxim, prochloraz, propamocarb, propaquizafop, propiconazole, prosulfocarb, prosulfuron, pymetrozine, pyraclostrobin, pyrazophos, pyridate, rimsulfuron, spinosad, spirodiclofen, tebufenozide, teflubenzuron, terbuthylazine, thiacloprid, thiamethoxam, thifensulfuron-methyl, thiodicarb, thiophanate-methyl, triasulfuron, tribenuronmethyl, trichlorfon, trifluralin, triflusulfuron-methyl, trinexapac-ethyl, zoxamide. Extraction was performed by mixture of acetone, petroleumether and dichlorometane, clean-up by gel permeation chromatography and determination by LC/MS/MS.13-15

Limits of quantification (LOQs) of all active substances determined were in the range of 0.003 to 1 mg/kg.

The trueness of methods is verified from recoveries which had to be from 70% to 120% and by participation in the inter-laboratory proficiency testing schemes: BIPEA (Bureau interprofessionnel d'etudes analytiques) and CRL European Proficiency Test 10.

 Table 1: List of vegetable and cereal samples analysed in 2009, and distribution of sample locations among individual production areas

Area			Agri	cultural p	roduct			Sum
Alea	Cauliflower	Eggplant	Endive	Lettuce	Pepper	Potatoes	Wheat	Sum
Celje	2	0	3	4	3	5	1	18
Koper	2	2	1	3	2	2	0	12
Kranj	1	1	3	0	1	18	1	25
Ljubljana	5	4	9	6	4	9	2	39
Maribor	3	1	4	4	3	8	4	27
Murska Sobota	0	0	1	2	2	3	1	9
Nova Gorica	1	1	3	2	3	1	10	21
Novo mesto	3	0	4	2	3	6	1	19
Sum	17	9	28	23	21	52	20	170

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

170 of the vegetable and cereal samples presented in Table 1 were analysed in 2009.

## 3. Results and Discussion

From the samples analysed in 2009, the **number** and portion of samples where residues were not found and number and portion of samples lower or equal to MRLs are presented in Table 2. In cauliflower, dithiocarbamates were the only active substance found. Some substances that are naturally present in cauliflower give responses for dithiocarbamates. So the question arises whether cauliflower was really treated with plant protection products containing active substances from the dithiocarbamate group.

Active substances that were found in agricultural products analysed in 2009 are presented in Table 3.

Multiple residues by matrices are presented in Table 4.

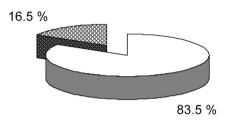
Detailed results of PPP residues found in 2009 are presented in Table 5.

Active substances not registered in the Republic of Slovenia were found in cauliflower (in cauliflower are naturally present compounds which give responses for dithiocarbamates) and endive (chlorothalonil, dithiocarbamates).<sup>16</sup>

Active substances not allowed in the integrated production in the Republic of Slovenia were found in endive (cyprodinil, fludioxonil, dithiocarbamates).<sup>17,18</sup>

Active substances not allowed in the ecological production in the Republic of Slovenia were not found.

In 142 samples (83.5%) out of 170 samples residues were not found, in 28 samples (16.5%) residues were lo-



□ sample portion <LOQ (%) ⊠ sample portion ≤MRL (%)

Fig. 1: Results of monitoring in 2009

Table 2: Samples where residues were not found and samples lower or equal to MRLs in 2009.

	No. of samples analysed	No. of samples <loq< th=""><th>Sample portion <loq (%)<="" th=""><th>No. of samples ≤MRL</th><th>Sample portion ≤MRL (%)</th></loq></th></loq<>	Sample portion <loq (%)<="" th=""><th>No. of samples ≤MRL</th><th>Sample portion ≤MRL (%)</th></loq>	No. of samples ≤MRL	Sample portion ≤MRL (%)
Cauliflower	17	0	0.0	17	100.0
Eggplant	9	9	100.0	0	0.0
Endive	28	24	85.7	4	14.3
Lettuce	23	18	78.3	5	21.7
Pepper	21	19	90.5	2	9.5
Potatoes	52	52	100.0	0	0.0
Wheat	20	20	100.0	0	0.0

Table 3: Active substances found in 2009.

	Cauliflower	Endive	Lettuce	Pepper	Sum	Sample portion (%)
Azoxystrobin	0	0	0	1	1	0.6
Chlorothalonil	0	1	0	0	1	0.6
Cyprodinil	0	1	1	1	3	1.8
Dithiocarbamates	17	2	1	0	20	11.8
Fludioxonil	0	1	1	1	3	1.8
Indoxacarb	0	1	0	0	1	0.6
Iprodione	0	0	2	0	2	1.2
Lufenuron	0	0	0	1	1	0.6
Thiamethoxam	0	0	3	0	3	1.8

Table 4: Multiple residues found in 2009.

	No. of samples with 2 a.s.	Sample portion with 2 a.s. (%)	No. of samples with 3 a.s.	Sample portion with 3 a.s. (%)
Pepper	2	9.5	0	0.0
Lettuce	3	13.0	0	0.0
Endive	0	0.0	1	3.6

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		Cauliflowe	r		Endive	
Active substance	No. of samples	Portion (%)	Range (mg/kg)	No. of samples	Portion (%)	Range (mg/kg)
Azoxystrobin	_	-	_	_	_	_
Chlorothalonil	_	-	_	1	3.6	0.01
Cyprodinil	_	_	_	1	3.6	0.32
Dithiocarbamates	17	100.0	0.07-0.72	2	7.1	0.26-0.46
Fludioxonil	_	_	_	1	3.6	0.26
Indoxacarb	_	_	_	1	3.6	0.06
Iprodione	_	-	_	_	_	_
Lufenuron	_	_	_	_	_	_
Thiamethoxam	_	-	_	_	_	_

**Table 5a:** Active substances found in each matrix analysed in 2009, range of each active substance found and portion of samples which contained active substances.

**Table 5b:** Active substances found in each matrix analysed in 2009, range of each active substance found and portion of samples which contained active substances.

		Lettuce			Pepper	
Active substance	No. of samples	Portion (%)	Range (mg/kg)	No. of samples	Portion (%)	Range (mg/kg)
Azoxystrobin	_	-	_	1	4.8	0.19
Chlorothalonil	_	-	_	_	_	_
Cyprodinil	1	4.3	0.08	1	4.8	0.03
Dithiocarbamates	1	4.3	0.06	_	_	_
Fludioxonil	1	4.3	0.04	1	4.8	0.04
Indoxacarb	_	_	_	_	_	_
Iprodione	2	8.7	1.56-1.71	_	_	_
Lufenuron	_	-	_	1	4.8	0.04
Thiamethoxam	3	13.0	0.03-0.23	_	-	_

wer or equal to MRLs and no samples contained residues above MRLs in 2009 (Fig. 1).

Results from previous years (2001–2008) showed that wheat was sampled in the years 2001, 2003 and 2006 and no residues were found. Eggplants and endive were never sampled during that period. Comparison of PPP residues obtained during that period in lettuce, potato, cauliflower and pepper is shown in Tables 6–9.

Active substances found in 2003 and 2006 in pepper do not match the ones found in 2009, but the number of different active substances in 2006 matches the number of active substances in pepper found in 2009. Pesticide residues found in pepper are rare. Among 51 active substances sought in 2003 only one was found. Among 86 active substances sought in 2006 only four active substances were found. Among 214 active substances sought in 2009 only four active substances were found.

In potato, no active substances were found in 2009. Results from previous years showed mainly the use of dithiocarbamates. We can conclude that potato treatment has been significantly reduced.

In cauliflower, the same active substance found in 2003, 2006 and 2009 are dithiocarbamates. As already mentioned, in cauliflower there are naturally present substances that give the same responses as dithiocarbamates. Since we can not say that cauliflower was really treated with dithiocarbamates and beside dithiocarbamates only one active substance was found (difenoconazole in 2006), we can conclude the same as for pepper. Pesticide residues found in cauliflower are rare.

In lettuce, the same active substances as present in 2009 were found at least in one year in the period 2001–2008. In the years 2003, 2005 and 2006 only 1–2 active substances were found in lettuce. In 2007 that number increased and remained on the same level until 2009. Among products analysed, lettuce contains the highest level of active substances sought. But still the number is small (5 active substances among 45 sought in 2002, 2 active substances among 51 sought in 2003, 5 active substances among 57 sought in 2004, 1 active substance among 66 sought in 2005, 1 active substance among 86 sought in 2007, 4 active substances among 158 sought in 2008, 5 active substances among 214 sought in 2009).

In 2009, no **MRL exceedances** were observed. In 2003 and 2006, no MRL exceedances were observed in pepper and cauliflower as well. In lettuce, MRL exceedances were observed in 2001 (13.3% of lettuce samples), 2002 (3.3% of lettuce samples), 2007 (4.0% of lettuce samples) and in 2008 (4.2% of lettuce samples). In potato, MRL exceedances were observed for dithiocarbamates

Active substanceNo. of samplesPortionRange (%)No. of magNo. of samplesChlorothalonil $n.a$ $n.a$ $n.a$ $n.a$ Chlorothalonil $n.a$ $n.a$ $n.a$ $n.a$ Cypendinil $n.a$ $1$ $6.7$ $2.56$ $3$ Ditthiccarbamates $3$ $2.00$ $0.07-6.36$ $7$ Ditthiccarbamates $1$ $6.7$ $2.56$ $3$ Ditthiccarbamates $1$ $6.7$ $2.56$ $3$ Ditthiccarbamates $1$ $6.7$ $2.56$ $3$ Ditthiccarbamates $1$ $6.7$ $2.26$ $2$ Programide $n.a$ $n.a$ $n.a$ $n.a$ Programide $n.a$ $n.a$ $n.a$ $n.a$ Discore $n.a$ $n.a$ $n.a$ $n.a$ Discore $n.a$ $n.a$ $n.a$ $n.a$ Programide $n.a$ $n.a$ $n.a$ $n.a$ Programide $n.a$ $n.a$ $n.a$ $n.a$ Discore $n.a$ $n.a$ $n.a$ $n.a$ Discore $n.a$ $n.a$ $n.a$ $n.a$ Discore $n.a$ $n.$	Portion (%) (%) (%) (%)	Range (mg/kg) 0.03-0.38 0.03-0.38 0.12 0.03-0.14 0.03 0.03	No. of samples 0 0 1 1 1 1 1 1 1 0 0 0 0 0 0 0 0 0 0	<b>Portion</b> (%) (%) 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	Range (mg/kg) 0.04 0.08-0.92	No. of samples 0 0 0 144 14 144 144 144 144 144 144 0 0 0 0	g	Range (mg/kg) (mg/kg) (0.02-0.11 0.02-0.09 0.02-0.09 0.02-0.09 0.02 0.09 0.02 0.09 0.02 0.09 0.02 0.02
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$ \begin{array}{cccccc} 0 & 0.0 & - & \\ n.a. & n.a. & & \\ n.a. & n.a. & \\ n.a. & & \\ n.a. & & \\ n.a. & & \\ n.a. & \\ 0 & 0.0 & 0.0 & - \\ 0 & 0.0 & 0.0 & - \\ 0 & 0.0 & 0.0 & - \\ 1 & 5.9 & 0.05 & \\ 0 & 0.0 & 0 & - \\ 1 & 5.9 & 0.05 & \\ 1 & 5.9 & 0.05 & \\ 1 & 0 & 0.0 & - \\ 1 & 0 & 0.0 & - \\ 1 & 0 & 0.0 & - \\ 1 & 0 & 0.0 & - \\ 1 & 0 & 0.0 & - \\ 1 & 1 & 5.9 & 0.05 & \\ 1 & 1 & 1 & \\ 1 & 1 & 1 & \\ 1 & 1 &$	6.7 3.3 0.0	0.03-0.14 0.03 0.03	0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	0.0 0.0 0.0 0.0 0.0		0 1 1. 0 0 1. 0 1. 0 1. 0 1. 0 1.	0.0 3.6 0.0	0.01 - 0.02 
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thyl 0 0.0 $-$ n.a. $0.0 - 0.0 -$ n.a. $0.a.$ n.a. $0.a.$ n.a. $0.a.$ n.a. $0.a.$ it protection product residues obtained in 2001–2008 in lettuc a n.a. $0.0$ $0.02-0.10$ a $0.00$ $0.00-0.10$ therefore the state obtained in 2001–2008 in lettuc a $0.00$ $0.00-0.00$ $0.00$	3.3 3.3 0.0	0.03	0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	0.0 0.0 0.0 0.0		0 1 0. 1. 1. 0	0.0 3.6 0.0	0.01 - 0.02 - 0.02
$ \begin{array}{ccccccc} 1 & 6.7 & 1.28 \\ n.a. & n.a. \\ n.a. & 0.02-0.10 \\ \hline \end{array} \\  \begin{array}{cccccccc} 1 & 2001-2008 \text{ in lettuc} \\ 1 & 1001-2008 \text{ in lettuc} \\ \hline \end{array} \\  \begin{array}{cccccccccccccccccccccccccccccccccc$	3.3 0.0	0.03	0 0 11.8. 0 0 0	0.0 0.0 0.0	1 1 1 1	1 0 1.a. 0	3.6 0.0	0.01 0.02
$ \begin{array}{ccccccc} n.a. & 20.0 0.02-0.10 \\ \hline                                  $	0.0		0 п.а. п.а. 0	0.0	1 1 1	0 n.a. n.a. 1	0.0	0.02
$\begin{array}{ccccc} & & & & & & & & & & & & & & & & &$	0.0	I	п.а. п.а. 0 0	0.0		n.a. n.a. 1 0		0.02
$ \begin{array}{ccccc} & & & & & & & & & & & & & & & & &$	0.0	I	п.а. п.а. 0 0	0.0	1 1	n.a. n.a. 1	v c	0.02
$\begin{array}{ccccc} n.a. \\ n.a. \\ n.a. \\ n.a. \\ n.a. \\ n.a. \\ 1.2000 \\  protection product residues obtained in 2001-2008 in lettuc \\ \hline \                                 $	0.0	I	п.а. 0 0 0	0.0	1 1	n.a. 1 0	9 c	0.02
$\begin{array}{c cccc} n.a. \\ n.a. \\ n.a. \\ 3 & 20.0 & 0.02-0.10 \\ \hline and a & 200S & and a & and &$	0.0	I	п.а. 0	0.0	1 1	n.a. 1 0	2 6	0.02
n.a. $3$ $20.0$ $0.02-0.10$ Plant protection product residues obtained in 2001-2008 in lettuc $2005$ $1001-2008$ n $2005$ $1001-2008$ $10110$ n $0$ $0$ $0$ $001-2008$ $10110$ n $0$	0.0	1	00	0.0	1 1	1 0	У c	0.02
3       20.0 $0.02-0.10$ Plant protection product residues obtained in 2001–2008 in lettuc $2005$ nance       No. of       Portion       Range         n       0       0       0 $-$ n       0       0       0 $-$ n       0       0.00 $ -$ n       0       0.00 $ -$ olde       1       5.9       0.05 $-$ nates       1       5.9       0.05 $-$ in       0       0.00 $ -$ methyl       0       0.00 $ -$ nates       1.3.       5.9       0.05 $-$ nates       1       5.9       0.05 $-$ nates       0       0.00 $  -$ nethyl       0       0.00 $  -$ nethyl       0       0.00 $  -$	0.0	1	0	0.0	1	0	5.0	I
rotection product residues obtained in 2001–2008 in lettue <b>2005 No. of Portion Range samples</b> $(\%)$ $(\mathbf{mg/kg)}$ $\mathbf{y}$							0.0	
2005         2005           No. of         Portion         Range           samples         (%)         (mg/kg)         r           0         0         0         -         -           0         0.00         -         -         -           0         0.00         -         -         -           0         0.00         -         -         -           1         5.9         0.05         -         -           0         0.00         -         -         -         -           1         5.9         0.05         -         -         -           1         0.00         -         -         -         -         -           1         0.00         - </th <th></th> <th></th> <th></th> <th></th> <th></th> <th></th> <th></th> <th></th>								
	2006			2007			2008	
samples         (%)         (mg/kg)           0         0         0         -           0         0.0         -         -           0         0.0         0.0         -           1         5.9         0.05         -           1         5.9         0.05         -           0         0.0         -         -           0         0.0         -         -           1         5.9         0.05         -           0         0.0         -         -           1         0.0         -         -           1         0.0         -         -           1         0.0         -         -           1         0.0         -         -           1         0         -         -           1         0         -         -           1         0         -         -         -           1         0         -         -         -           1         0         -         -         -           1.3         -         -         -	Portion	Range	No. of	Portion	Range	No. of	Portion	Range
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	(%)	(mg/kg)	samples	(%)	$\cup$	samples	$(\mathscr{Y}_{o})$	(mg/kg)
e 0 0.0 1. 1. 1. 2.9 0.0 1. 1. 1. 2.9 0.0 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1	0	1	-	4.0	0.05	0	0	1
thyl $0.0$ $1$ $1.1$ $1.3$	0.0	I	0	0.0	I		4.2	0.04
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	0.0	I	0 0	0.0	I	. 0	00	-
tes $n.a.$ 5.9 0.05 tes 1 5.9 0.05 0 0.0 $         -$	0.0	I	0	0.0	I	0	0.0	I
tes 1 5.9 $0.05$ 0 0.0 $         -$	0.0	I		4.0	0.07		0.0	I
thyl 0 0.0 0 0.0 0 0.0 0 0.0 0 0.0 0 0.0 1.a. 1	6.9	0.05		0.1	20:0		2.5 C 7	0.00
thyl 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.		CO.0			10.0		1 C	20.0
thyl 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.	0.0	l		0.0	I		0.0	l
u 0.0 n.a. 0.0 0 0.0 0 0.0 n.a. 1.0	0.0	I		0.0	I		0.0	I
thyl n.a. 0 0.0	0.0	I	0	0.0	I	<b>D</b> .	0.0	I
thyl 0 0.0			0	0.0	I	1	4.2	0.06
0 0.0 0 0 0.0	0.0	I	0	0.0	I	0	0.0	I
0 0.0 – 1.0.0 – –	0.0	I	0	0.0	I	0	0.0	I
n.a.	0.0	I	1	4.0	0.03	0	0.0	I
			1	4.0	0.02	0	0.0	I
n.a.	0.0	Ι	-	4.0	0.03	0	0.0	Ι
am	0.0	I	1	4.0	0.20	1	4.2	0.03
0 0.0 -	0.0	I	0	0.0	I	0	0.0	I
0 0.0 -	0.0	I	0	0.0	Ι	0	0.0	I

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Table 6a: Plant protection product residues obtained in 2001–2008 in lettuce.

		2001			2002			2003			2004	
Active substance	No. of samples	Portion (%)	Range (mg/kg)	No. of samples	Portion (%)	Range (mg/kg)	No. of samples	Portion (%)	Range (mg/kg)	No. of samples	Portion (%)	Range (mg/kg)
Chlorpropham	n.a.			n.a.			n.a.			n.a.		
Dithiocarbamates	9	20.0	0.06 - 0.27	13	43.3	0.05 - 0.44	14	40.0	0.05 - 0.51	S	8.2	0.06 - 0.14
Phosalone	0	0.0	I	0	0.0	I	0	0.0	I	0	0.0	Ι
A otivo cuhatanao	Ao of	2005 Dortion	Dongo	No of	2006 Dortion	Dance	No of	2007 Dortion		No of	2008 Dortion	Dange
	samples	(%)	(mg/kg)									
Chlorpropham	1	6.3	0.17	0	0.0	I	0	0.0	I	0	0.0	
Dithiocarbamates	0	0.0	I	1	3.0	0.06	1	2.8	0.06	0	0.0	I
Phosalone	0	0.0	I	1	3.0	0.01	0	0.0	I	0	0.0	I

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only: in 2001 (20.0% of potato samples), in 2002 (40% of potato samples), in 2003 (37.1% of potato samples) and in 2004 (8.2% of potato samples). Over the years we have observed that MRL exceedances are lower, which suggests that the farmers have learned to use PPP safely, in accordance with good agricultural practice. The results are presented in Table 10.

The results of monitoring during the years 2001-2006 for lettuce, potato, cauliflower, pepper, eggplants and wheat in the EU countries and in Norway, Iceland and Liechtenstein<sup>19</sup> are presented in Table 11. Endive was not sampled on the EU level. Lettuce in EU, Norway, Iceland and Liechtenstein in 2001 had less exceedances than lettuce in Slovenia in the same year. But in 2004, lettuce had no exceedances in Slovenia while in EU, Norway, Iceland and Liechtenstein it kept the same level of exceedances as in 2001. The same is valid for potato. Potato in EU, Norway, Iceland and Liechtenstein in 2002 had much less exceedances than potato in Slovenia in the same year. But in 2005, potato had no exceedances in Slovenia while in EU, Norway, Iceland and Liechtenstein it kept the same level of exceedances as in 2002. Cauliflower, pepper and eggplants in the years 2003 and 2006 and wheat in 2006 had some exceedances in EU, Norway, Iceland and Liechtenstein while the same agricultural products in Slovenia had none.

#### 4. Conclusions

Levels of pesticide residues in cauliflower, eggplant, endive, lettuce, pepper, potato and wheat in Slovenia in 2009 do not give any cause for alarm. 83.5% samples examined did not contain any residues and exceeding maximum residue levels were not found.

For comparison, the results of national monitoring in the same agricultural products performed in Slovenia in 2001–2008 are presented. MRL exceedances were found only in lettuce in 2001, 2002, 2007 and 2008 and in potato in 2001–2004.

Also, the results of national monitoring performed in the EU countries and in Norway, Iceland and Liechtenstein in 2001–2006 are presented.<sup>19</sup> MRL exceedances for potato in EU, Norway, Iceland and Liechtenstein are not so high as for potato in Slovenia, but there are some MRL exceedances in EU, Norway, Iceland and Liechtenstein in cauliflower, pepper, eggplants and wheat while in Slovenia there are none.

#### 5. Acknowledgements

The authors thank those who contributed to the work: Mateja Fortuna and co-workers at the Central Laboratories of Agricultural Institute of Slovenia. For financial support we express our thanks to the Inspectorate of the Republic of Slovenia for Agriculture, Forestry and Food, MAFF.

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n.a. means not analysed

Table 8: Plant protection product residues obtained in 2003 and 2006 in cauliflower.

		2003			2006	
Active substance	No. of samples	Portion (%)	Range (mg/kg)	No. of samples	Portion (%)	Range (mg/kg)
Difenoconazole	n.a.			1	9.1	0.01
Dithiocarbamates	1	10.0	0.98	10	90.9	0.05-0.41

n.a. means not analysed

Table 9: Plant protection product residues obtained in 2003 and 2006 in pepper.

		2003			2006	
Active substance	No. of samples	Portion (%)	Range (mg/kg)	No. of samples	Portion (%)	Range (mg/kg)
Difenoconazole	n.a.			1	6.3	0.04
Chlorothalonil	0	0.0	_	1	6.3	0.04
Dithiocarbamates	1	6.7	0.14	1	6.3	0.14
Imidacloprid	n.a.			2	12.5	0.01

n.a. means not analysed

Table 10a: MRL exceedances in 2001 to 2008.

	2001			2002			2003	
Matrix	Active substance	No. of samples	Matrix	Active substance	No. of samples	Matrix	Active substance	No. of samples
Lettuce	Dimethoate	1	Lettuce	Metalaxyl	1	Potato	Dithiocarbamates	13
Lettuce	Dithiocarbamates	1	Potato	Dithiocarbamates	12			
Potato	Dithiocarbamates	6						

Table 10b: MRL exceedances in 2001 to 2008.

	2004			2007			2008	
Matrix	Active substance	No. of samples	Matrix	Active substance	No. of samples	Matrix	Active substance	No. of samples
Potato	Dithiocarbamates	5	Lettuce	Chlorothalonil	1	Lettuce	Pendimethalin	1

Table 11: Results of the EU, Norway, Iceland and Liechtenstein monitoring in 2001–2006.

	Lettuce		Potato		Cauliflower		Pepper		Eggplants		Wheat	
	2001	2004	2002	2005	2003	2006	2003	2006	2003	2006	2003	2006
No residues (%)	47	49	89	74	82	78	60	55	80	63	78	73
Residues ≤ MRL (%)	49	48	10	25	17	20	34	42	18	33	22	27
Rresidues > MRL (%)	3.9	3.3	1	1.2	1	1.6	6	3.5	3	4.3	0	0.1

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# Povzetek

V letu 2009 smo analizirali ostanke pesticidov v 170 vzorcih cvetače, jajčevcev, endivije, solate, paprike, krompirja in pšenice slovenskih pridelovalcev. Vzorce smo analizirali na prisotnost 214 različnih aktivnih spojin s tremi analitskimi metodami. Preseženih maksimalno dovoljenih količin ostankov nismo določili, kar je boljše od rezultatov monitoringa ostankov pesticidov v rastlinskih proizvodih v Evropski skupnosti, Norveški, Islandiji in Liechtensteinu v letih od 2004 do 2006. Opazili smo, da je zadnje čase v Sloveniji manj preseženih MRL-jev. Domnevamo, da so se kmetovalci nauči-li varno uporabljati fitofarmacevtska sredstva, v skladu z dobro kmetijsko prakso.