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Pesticide Residues in Agricultural Products of Slovene Origin Found in 2001-2009

Helena Baša Česnik, Špela Velikonja Bolta and Ana Gregorčič
*Agricultural Institute of Slovenia, Central Laboratories
Slovenia*

1. Introduction

In the production of cereals, fruit and vegetables the appropriate protection from harmful organisms, which tend to appear in inappropriate places at inappropriate times, is needed. At present plant protection is based on the use of plant protection products (PPPs) which, when properly used, assure the most economical way of producing adequate quantities of high quality food. Incorrect and uncontrolled use of PPPs may cause great harm to people, animals and the environment. Agricultural experts have been constantly trying to develop new technologies of healthy food production including the development of PPPs which would be friendlier to people, animals and the environment.

The task of the government is to control the proper use of PPPs, which insures healthy food on the market (Akiyama et al., 2002; Andersen J. H. & Poulsen M. E., 2001; Dejonckheere et al., 1996; Dogheim et al. 2002; Fernandez et al., 2001; Ripley et al., 2000). This is why the 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 accordance to Slovenian legislation (RS 1999a; 1999b; 2001; 2004a; 2004b; 2007a; 2007b; 2009). The samples were taken randomly in eight production areas in Slovenia: Celje, Koper, Kranj, Nova Gorica, Novo mesto, Murska Sobota, Maribor, and Ljubljana. Each year (except in 2009) analyses of pesticide residues were performed on potato, lettuce and apple samples due to the characteristic nutrition of Slovenes (the Slovene Food Basket has not yet been demarcated). Selection of other agricultural commodities and active substances followed the guidelines given in the European Union monitoring recommendations (EC 2001; 2002a, 2002b; 2004; 2005; 2006; 2007; 2008a; 2008b).

Control of pesticide residues in agricultural products prior to the market allows assessment of the conformity of production with good agricultural practice and the determination of sources and/or causes of residues found. Random choice of producers enables a statistical approach to the estimation of food safety on the Slovene market.

The results are intended to:

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

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

For monitoring purposes quick and reliable multiresidual methods are needed that enable simultaneous determination of a wide spectrum of active substances. The methods mainly use three types of solvents for extraction: ethylacetate (Berrada et al., 2006; Čajka & Hajšlová, 2004; Ferrer et al., 2005; Sharif et al., 2006), acetonitrile (method also known as QuEChERS method) (Lehotay, 2007; Maštovská et al., 2005) or acetone (Díez et al., 2006; Pizzutti et al., 2009; Stan & Linkerhägner, 1996). Our laboratory used acetone because of its low toxicity, high volatility and miscibility with water. For better extraction of active substances we added petroleum ether and dichloromethane to the acetone (Baša Česnik & Gregorčič, 2003; Baša Česnik et al., 2006). For the determination of the extracted active substances laboratories mainly use gas chromatography coupled to various detections, i.e. flame ionisation detection (FID), electron capture detection (ECD), nitrogen phosphor detection (NPD) and flame photometric detection (FPD). We have used gas chromatography coupled to mass spectrometry (GC/MS) which enables simultaneous and unequivocal qualitative and quantitative determination of active substances. In the case of thermally labile compounds liquid chromatography coupled to UV detection or fluorescence detection is used. We have used liquid chromatography coupled to tandem mass spectrometry (LC/MS/MS) which enables simultaneous and unequivocal qualitative and quantitative determination of active substances.

2. Experimental

In nine years of monitoring we analysed 1504 samples: 102 cereal samples (9 barley samples, 72 wheat samples, 1 millet sample, 2 spelt samples, 7 corn samples, 1 triticale sample, 5 rye samples and 5 oat samples), 494 fruit samples and 908 vegetable samples. The sampling is presented in Table 1.

For the determination of PPP residues we used four different testing methods:

- method for the determination of benzimidazoles: tiabendazol and the sum of benomil and carbendazim (in 2001-2007) (van Zoonen, 1996),
- method for the determination of the maneb group: maneb, mankozeb, metiram, propineb, thiram and zineb, the sum is expressed as carbon disulfide (in the years 2001-2009) (Baša Česnik & Gregorčič, 2006)
- multiresidual GC/MS method (in 2001-2009) (Baša Česnik & Gregorčič, 2003; Baša Česnik et al., 2006)

In 2001 and 2002 the scope of analyses was: acephate, aldrin, azinphos-methyl, captan, carbofuran, chlorpyrifos, chlorpyrifos-methyl, cyhalotrin-lambda, DDT, deltamethrin, diazinon, dimethoate, endosulfan, endrin, fenitrothion, fenthion, fludioxonil, folpet, HCH-alpha, heptachlor, heptenophos, imazalil, iprodione, lindane, malathion, mecarbam, metalaxyl, methamidophos, methidathion, parathion, permethrin, phosalone, pirimiphos-methyl, procymidone, pyridaphenthion, quinalphos, thiabendazole, triazophos and vinclozolin.

In 2003 the scope was extended with the following active substances: azoxystrobin, bromopropylate, chlorothalonil, cypermethrin, dichlofluanid, omethoate, oxydemeton-methyl, phorate, propyzamide and tolylfluanid.

Commodity	2001	2002	2003	2004	2005	2006	2007	2008	2009	Sum
Apples	15	30	36	70	17	36	43	38	/	285
Beans	/	/	/	/	/	/	/	8	/	8
Carrot	/	/	/	/	15	/	/	17	/	32
Cauliflower	/	/	10	/	/	11	/	/	17	38
Cereals	31	/	15	/	/	26	10	/	20	102
Cherries	/	/	/	/	/	/	10	/	/	10
Cucumbers	/	/	/	/	17	/	/	20	/	37
Eggplant	/	/	/	/	/	/	/	/	9	9
Endive	/	/	/	/	/	/	/	/	28	28
Grapes	/	/	15	/	/	20	/	/	/	35
Head cabbage	/	/	/	15	/	/	21	/	/	36
Leek	/	/	/	/	/	/	9	/	/	9
Lettuce	15	30	24	28	17	16	25	24	23	202
Peaches	/	/	/	/	/	/	20	/	/	20
Pears	/	30	/	/	12	/	/	21	/	63
Peas	/	/	/	/	/	4	/	/	/	4
Pepper	/	/	15	/	/	16	/	/	21	52
Potatoes	30	30	35	61	16	33	36	32	52	325
Spinach	/	/	/	/	7	/	/	6	/	13
Strawberries	30	/	/	13	/	19	19	/	/	81
String beans	/	30	/	/	14	/	/	/	/	44
Tomatoes	30	/	/	24	/	/	17	/	/	71
Sum	151	150	150	211	115	181	210	166	170	1504

Table 1. Sampling of agricultural products in the years 2001 to 2009

In 2004 the scope was extended with the following active substances: cyprodinil, diphenylamine, kresoxim-methyl, myclobutanil, pyrimethanil and spiroxamine.

In 2005 the scope was extended with the following active substances: bifenthrin, bupirimate, carbaryl, chlorpropham, pirimicarb, propargite, tolclofos-methyl, triadimefon and triadimenol.

In 2006 the scope was extended with the following active substances: cyromazine, penconazole, trifloxystrobin.

In 2007 the scope was extended with the following active substances: boscalid, dichlorvos, fenamidone, quinoxifen, tebuconazole. Cyromazine was removed.

In 2008 the scope was extended with the following active substances: carboxin, chloridazon, clomazone, cyproconazole, diniconazole, fenbuconazole, indoxacarb, metconazole, methacrifos, metribuzin.

In 2009 the scope was extended with the following active substances: acrinathrin, dazomet, desmethylpirimicarb, dimethachlor, esfenvalerate, fenvalerate, flonicamid, fluquinconazole, HCH-betha, HCH-deltha, hexachlorobenzene, metalaxyl-M,

metrafenone, oxadixyl, parathion-methyl, profenofos, quinoclamine, tetraconazole, tetradifon.

- multiresidual LC/MS/MS method (in 2006-2009) (Bossi et al., 2002; Ortelli et al., 2004; Lehotay et al., 2005)

In 2006 the scope of analyses was: aldicarb, bentazone, cymoxanil, difenoconazole, fenazaquin, fenhexamid, fluroxypyr, imidacloprid, methiocarb, methomyl, phoxim, pymetrozine, spirodiclofen, tebufenozide, thiacloprid, thiamethoxam and zoxamide.

In 2007 the scope was extended with the following active substances: acetamiprid, amidosulfuron, benalaxyl, bitertanol, clofentezine, cyromazine, dimethomorph, epoxiconazole, ethofumesate, famoxadone, fenpropidin, fenpropimorph, fenpyroximate, flufenacet, fluquinconazole, hexythiazox, iprovalicarb, lufenuron, metosulam, pendimethalin, prochloraz, propamocarb, propiconazole, pyridate, spinosad, terbuthylazine, thiophanate-methyl and trichlorfon.

In 2008 the scope was extended with the following active substances: aldicarb sulfon, aldicarb sulfoxid, buprofezin, carbendazim, clopyralid, clothianidin, cycloxydim, desmedipham, flutriafol, foramsulfuron, iodosulfuron-methyl-sodium, isoxaflutole, linuron, malaoxon, metamitron, metazachlor, methiocarb sulfon, methiocarb sulfoxid, methoxyfenozide, napropamide, phenmedipham, prosulfocarb, prosulfuron, pyraclostrobin, rimsulfuron, tetraconazole, thifensulfuron-methyl, thiodicarb, triasulfuron, trifluralin and triflusulfuron-methyl.

In 2009 the scope was extended with the following active substances: 2,4-D, amitrole, azinphos-ethyl, beflubutamid, benalaxyl M, bromoxynil, carbosulfan, chlortoluron, cyazofamid, demeton-S-methyl sulphone, dichloprop-P, diflufenican, dimethenamid-P, fenarimol, fenoxaprop-P-ethyl, fenoxycarb, fenthion sulfone, fenthion sulfoxide, fipronil, florasulam, fluazifop-P-butyl, fluazinam, fluorochloridone, flusilazole, hexaconazole, isoproturon, mandipropamid, MCPA, monocrotophos, nicosulfuron, oxamyl, paraoxon-methyl, phorate sulfone, phorate sulfoxide, propaquizafop, pyrazophos, teflubenzuron, tribenuron-methyl and trinexapac-ethyl. Fluquinconazole and tetraconazole were removed.

The trueness of testing methods was verified by recoveries which had to be from 70% to 120%.

The trueness was additionally verified by participation in the French inter-laboratory proficiency testing scheme BIPEA (Bureau interprofessionnel d'études analytiques) and CRL European Proficiency Tests.

In January 2005 determination of pesticide residues was accredited by the French accreditation body COFRAC.

3. Results and discussion

During the period, from 2001 to 2009, 1504 samples were analysed. **Sample portions below reporting level (RL), sample portions below or equal to MRLs and sample portions above MRLs** are presented in Figure 1, Figure 2 and Table 2.

In 946 samples (62.9%) PPP residues were not found, in 493 samples (32.8%) PPP residues were lower or equal to MRLs and in 65 samples (4.3%) PPP residues were above MRLs.

The highest portion of PPP residues, 50% and more, was found in fruit. The farmers have to protect fruit against rot, mould and insects. The highest portion of determined but not exceeding PPP residues, (residues lower or equal to MRLs), was found in cherry samples

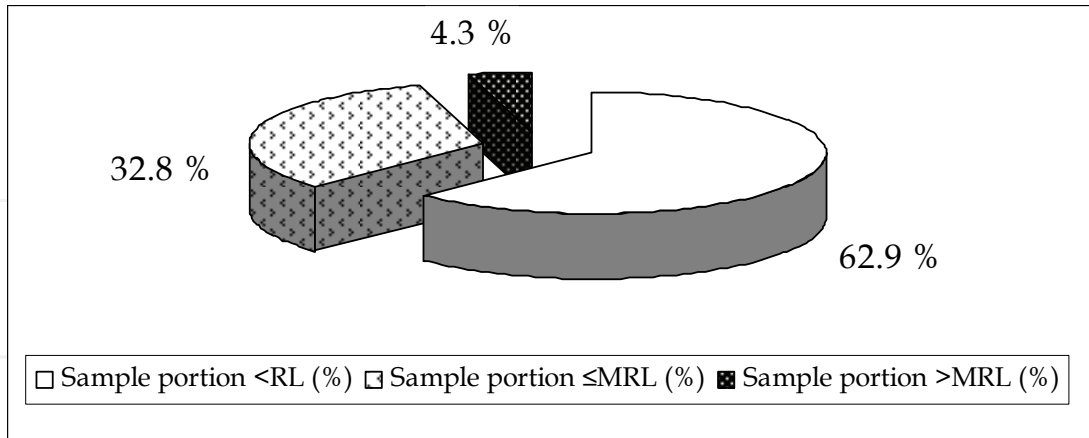


Fig. 1. Results of monitoring from 2001 to 2009

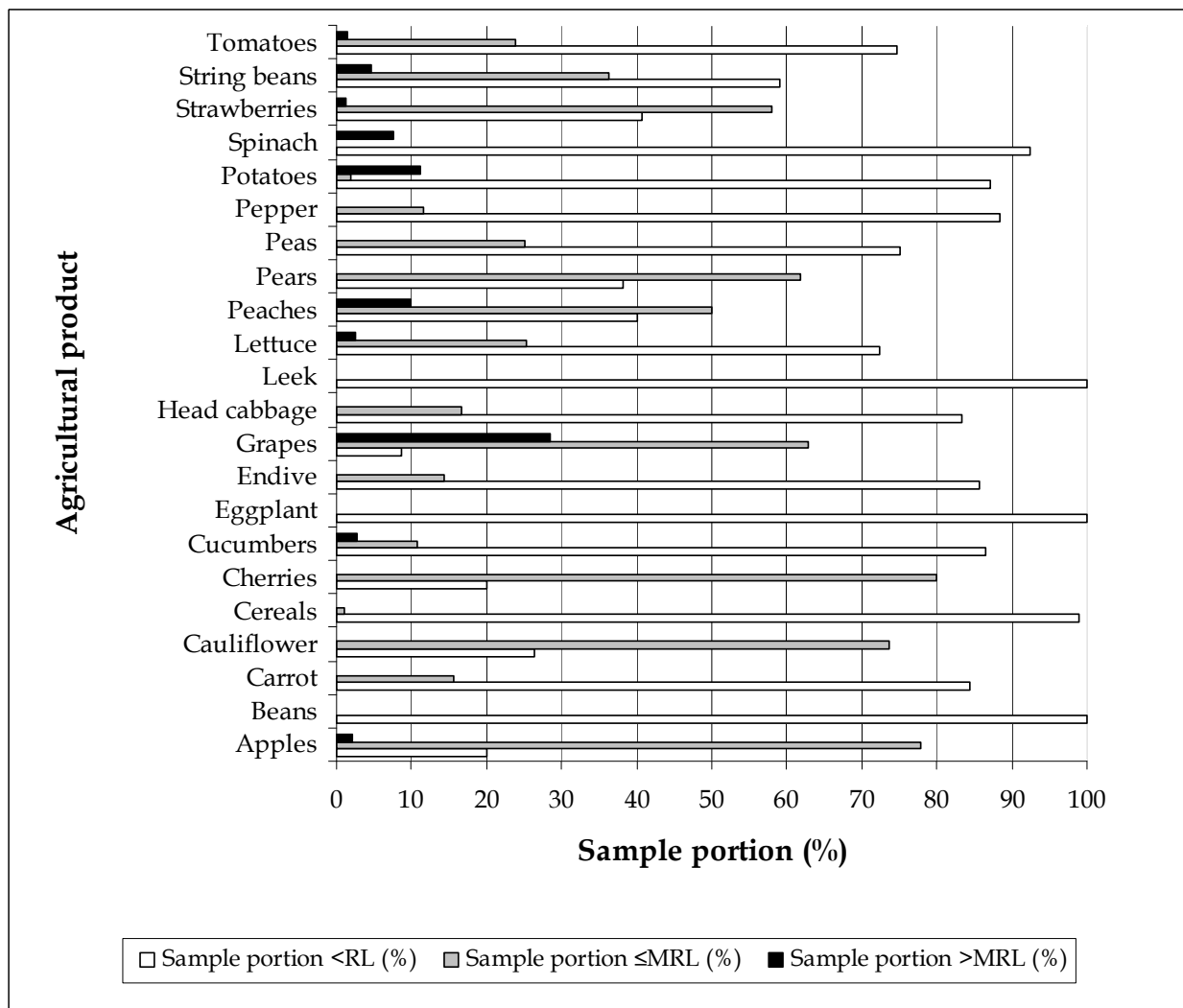


Fig. 2. Sample portions of PPP residues for each analysed matrix from 2001 to 2009

Commodity	Sample portion <RL (%)	Sample portion ≤MRL (%)	Sample portion >MRL (%)
Apples	20.0	77.9	2.1
Beans	100.0	0.0	0.0
Carrot	84.4	15.6	0.0
Cauliflower	26.3	73.7	0.0
Cereals	99.0	1.0	0.0
Cherries	20.0	80.0	0.0
Cucumbers	86.5	10.8	2.7
Eggplant	100.0	0.0	0.0
Endive	85.7	14.3	0.0
Grapes	8.6	62.9	28.6
Head cabbage	83.3	16.7	0.0
Leek	100.0	0.0	0.0
Lettuce	72.3	25.2	2.5
Peaches	40.0	50.0	10.0
Pears	38.1	61.9	0.0
Peas	75.0	25.0	0.0
Pepper	88.5	11.5	0.0
Potatoes	87.1	1.8	11.1
Spinach	92.3	0.0	7.7
Strawberries	40.7	58.0	1.2
String beans	59.1	36.4	4.5
Tomatoes	74.6	23.9	1.4

Table 2. Sample portions of PPP residues for each analysed matrix from 2001 to 2009

(80.0%), apple samples (77.9%), grape samples (62.9%), pear samples (61.9%), strawberry samples (58.0%) and peach samples (50.0%). Some fruit samples contained also exceeding PPP residues (residues above MRLs), i.e. grape samples (28.6%), peach samples (10.0%), apple samples (2.1%) and strawberry samples (1.2%).

The portion of PPP residues found in vegetables and cereals was less than 50%. Cauliflower was the only exception. In cauliflower the same active substance found in 2003, 2006 and 2009 was dithiocarbamates (maneb group). In cauliflower there are naturally present substances that give the same responses as dithiocarbamates. This is why we cannot say that cauliflower was really treated with dithiocarbamates. Besides dithiocarbamates, only one active substance was found in one sample (difenoconazole in 2006).

The highest portion of exceeding PPP residues (residues above MRLs) were found in grape samples (28.6%) and potato samples (11.1%).

MRL exceedances in grape samples were found for cyprodinil in 2006 and for fludioxonil in 2003 and 2006. This suggests that the farmers used PPP Switch authorised for grapes that contains both active substances. The national MRL for both compounds was 0.02mgkg⁻¹ in

2003 and 2006. Today the European Community MRL for cyprodinil is 5mgkg^{-1} (Commission Regulation (EC) No. 459/2010) and for fludioxonil 2mgkg^{-1} (Commission Regulation (EC) No. 822/2009). The highest value obtained in grape samples was 0.40mgkg^{-1} for cyprodinil and 0.04mgkg^{-1} for fludioxonil. Taking into account today's MRLs none of the samples would be exceeding. The risk assessment performed with Pesticide Safety Directorate (PSD, York, UK), model for acute exposure for cyprodinil at concentration level 0.40mgkg^{-1} and Acceptable Daily Intake (ADI) 0.03mgkg^{-1} body weight⁻¹ day⁻¹ (Acute Reference Dose-ARfD for cyprodinil was not determined) showed that the National Estimate of Short Term Intake (NESTI) expressed in ADI percentage ranged from 2.5% for 7-10 years old children to 31.6% for adults. The risk assessment performed with the PSD model for acute exposure for fludioxonil at concentration level 0.04mgkg^{-1} and ADI 0.37mgkg^{-1} body weight⁻¹ day⁻¹ (ARfD for fludioxonil was not determined) showed that NESTI expressed in ADI percentage ranged from 0.0% for 7-10 years old children and residential elderly people to 0.3% for adults. ADIs were found on the internet (http://ec.europa.eu/sanco_pesticides/public/index.cfm?event=activesubstance.detail) for cyprodinil and

http://ec.europa.eu/sanco_pesticides/public/index.cfm?event=activesubstance.detail

for fludioxonil), as well as the PSD model for acute exposure

(<http://www.pesticides.gov.uk/approvals.asp?id=1687>). The risk assessment showed that the exceeding grape samples did not present any risk for health (NESTI in % of ADI was below 100%) and were therefore safe for consumers.

MRL exceedances in potato samples were found exclusively for dithiocarbamates in 2001-2004. Dithiocarbamates were the only active substances found in potato in these years. The reporting level for dithiocarbamates was 0.05mgkg^{-1} , which was at the same time the MRL for potato during these years (Official Gazette of the Republic of Slovenia No. 73/03). In January 2005 the MRL was raised to 0.1mgkg^{-1} (Commission Directive 2004/115/EC) and in 2008 it was raised to 0.3mgkg^{-1} (Commission Regulation (EC) No. 839/2008). If MRL 0.3mgkg^{-1} were valid from 2001 to 2004 only 8 samples instead of 36 would be exceeding. Among dithiocarbamates, ziram has the lowest ARfD

(http://ec.europa.eu/sanco_pesticides/public/index.cfm?event=activesubstance.selection)

which is 0.08mgkg^{-1} body weight⁻¹ day⁻¹. The highest value obtained in potato samples for dithiocarbamates during 2001-2004 was 0.51mgkg^{-1} , which is equivalent to 1.02mgkg^{-1} of ziram. The risk assessment performed with the PSD model showed, that for that sample acute exposure for ziram was exceeding (NESTI in % of ARfD was above 100%) for infants (196.0% ARfD), toddlers (135.6% ARfD) and 4-6 year old children (102.1% ARfD). Among dithiocarbamates thiram has the highest ARfD

(http://ec.europa.eu/sanco_pesticides/public/index.cfm?event=activesubstance.selection)

which is 0.6mgkg^{-1} body weight⁻¹ day⁻¹. The highest value 0.51mgkg^{-1} , obtained in potato samples for dithiocarbamates in the years 2001 to 2004, is equal to 0.81mgkg^{-1} of thiram. The risk assessment performed with the PSD model showed, that for that sample acute exposure for thiram was not exceeding (NESTI in % of ARfD was below 100%) for all groups. The highest acute exposure was 20.8% ARfD for infants and the lowest was 3.2% ARfD for adults. The active substances from the maneb group in potato were not determined separately and we cannot conclude if the samples presented any risk for the health of consumers. From 2005 to 2009 only two potato samples contained dithiocarbamates: one in 2006 and one in 2007 (dithiocarbamates content was 0.06mgkg^{-1} for both samples). Results for 2005 to 2009 show that farmers had learned how to use PPPs containing active substances from the maneb group in accordance with good agricultural practice.

Annual results for the most frequently inspected commodities, i.e. apple, lettuce and potato, are presented in Tables 3-5 and Figures 3-5. Lettuce and potato were sampled each year while apples were not sampled in 2009. The highest percentage of apple samples with determined but not exceeding PPP residues was found in 2005 (88.2%) and the lowest in

Year	Sample portion <RL (%)	Sample portion ≤MRL (%)	Sample portion >MRL (%)
2001	26.7	73.3	0.0
2002	30.0	66.7	3.3
2003	16.7	83.3	0.0
2004	17.1	80.0	2.9
2005	5.9	88.2	5.9
2006	16.7	77.8	5.6
2007	18.6	81.4	0.0
2008	28.9	71.1	0.0

Table 3. PPP residues in apple samples for the period from 2001 to 2008

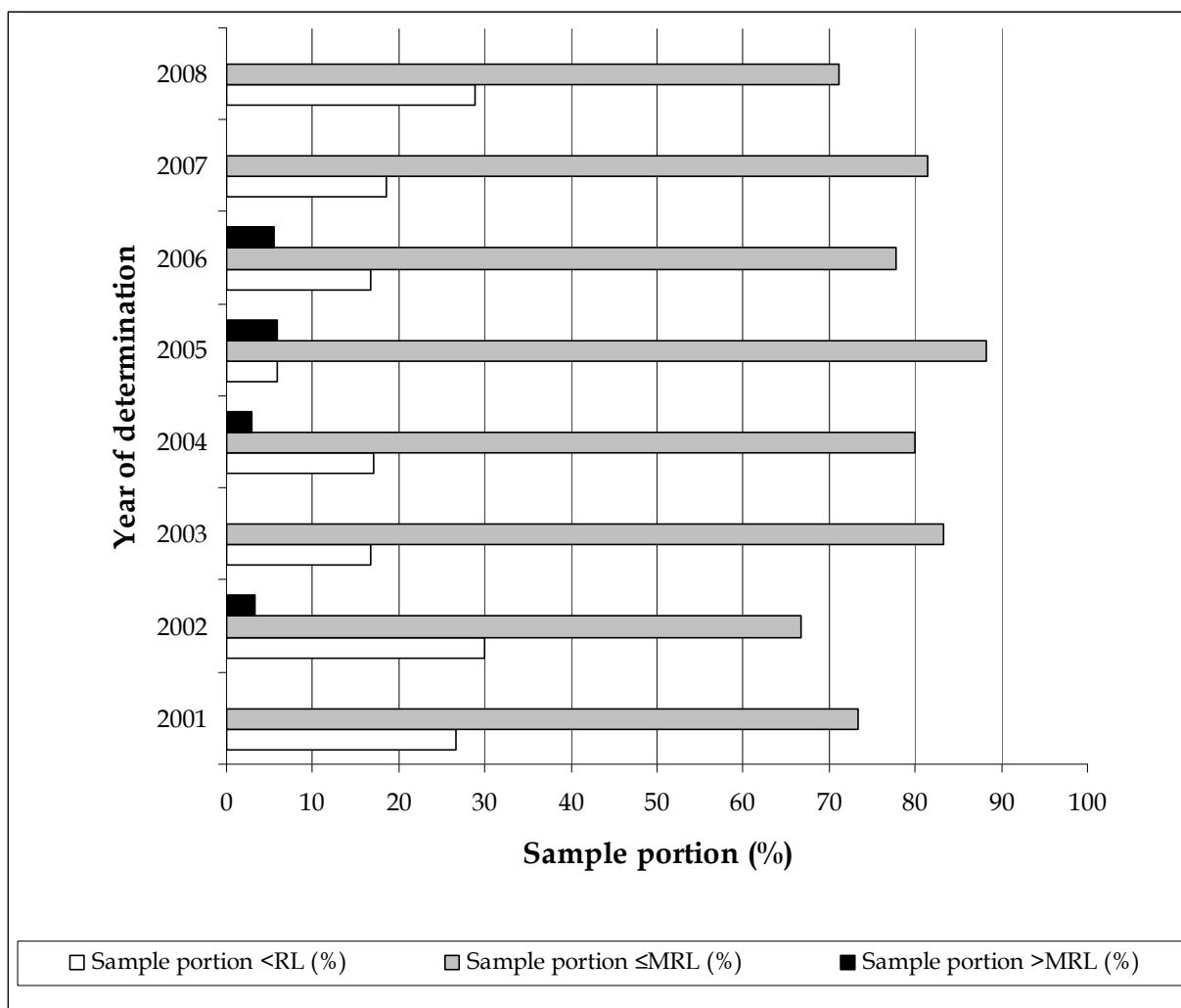


Fig. 3. Annual results for apple samples from 2001 to 2008

Year	Sample portion <RL (%)	Sample portion ≤MRL (%)	Sample portion >MRL (%)
2001	60.0	26.7	13.3
2002	63.3	33.3	3.3
2003	70.8	29.2	0.0
2004	42.9	57.1	0.0
2005	94.1	5.9	0.0
2006	93.8	6.3	0.0
2007	80.0	16.0	4.0
2008	83.3	12.5	4.2
2009	78.3	21.7	0.0

Table 4. PPP residues in lettuce samples for the period from 2001 to 2009

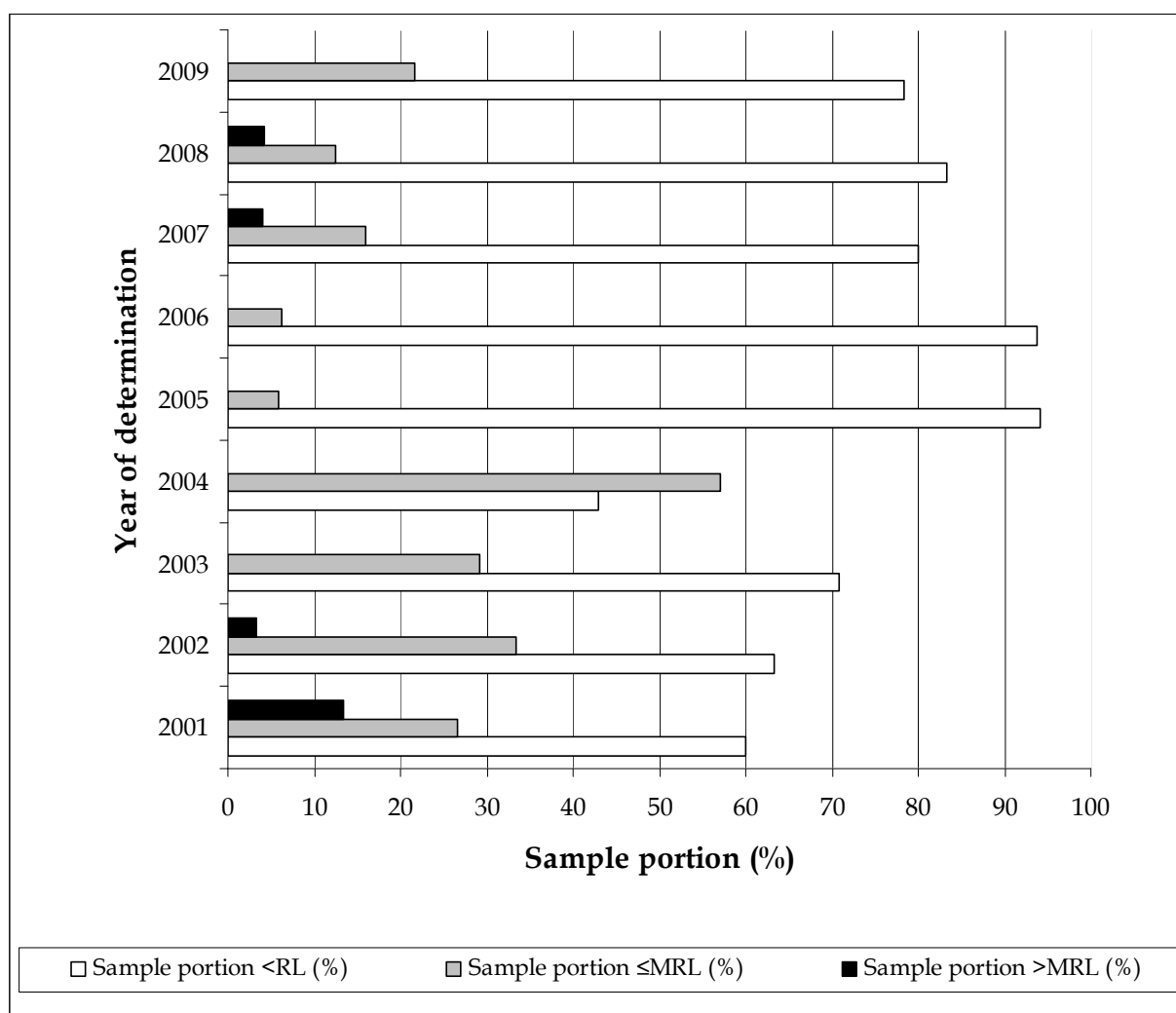


Fig. 4. Annual results for lettuce samples from 2001 to 2009

Year	Sample portion <RL (%)	Sample portion ≤MRL (%)	Sample portion >MRL (%)
2001	80.0	0.0	20.0
2002	56.7	3.3	40.0
2003	60.0	2.9	37.1
2004	91.8	0.0	8.2
2005	93.8	6.3	0.0
2006	93.9	6.1	0.0
2007	97.2	2.8	0.0
2008	100.0	0.0	0.0
2009	100.0	0.0	0.0

Table 5. PPP residues in potato samples for the period 2001 to 2009

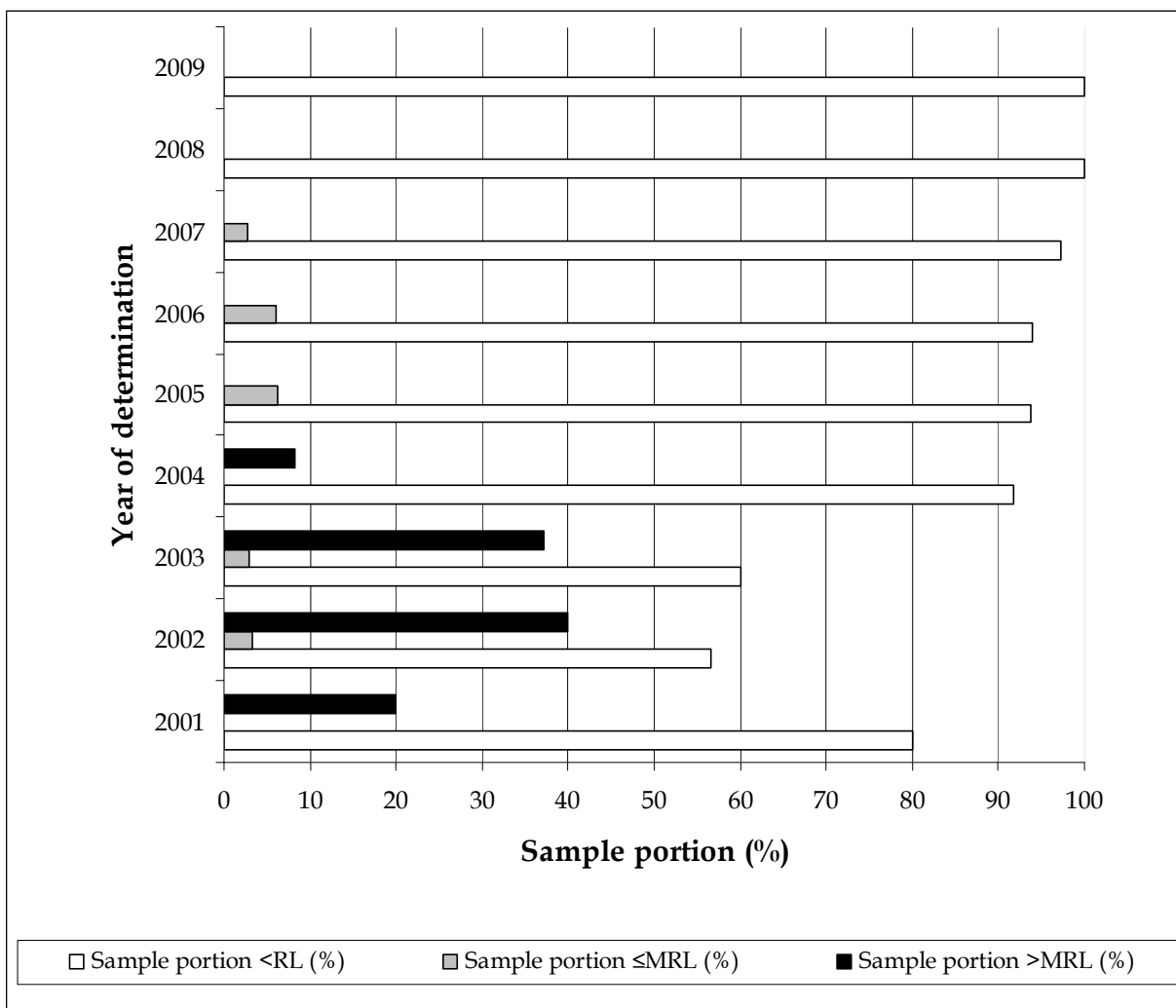
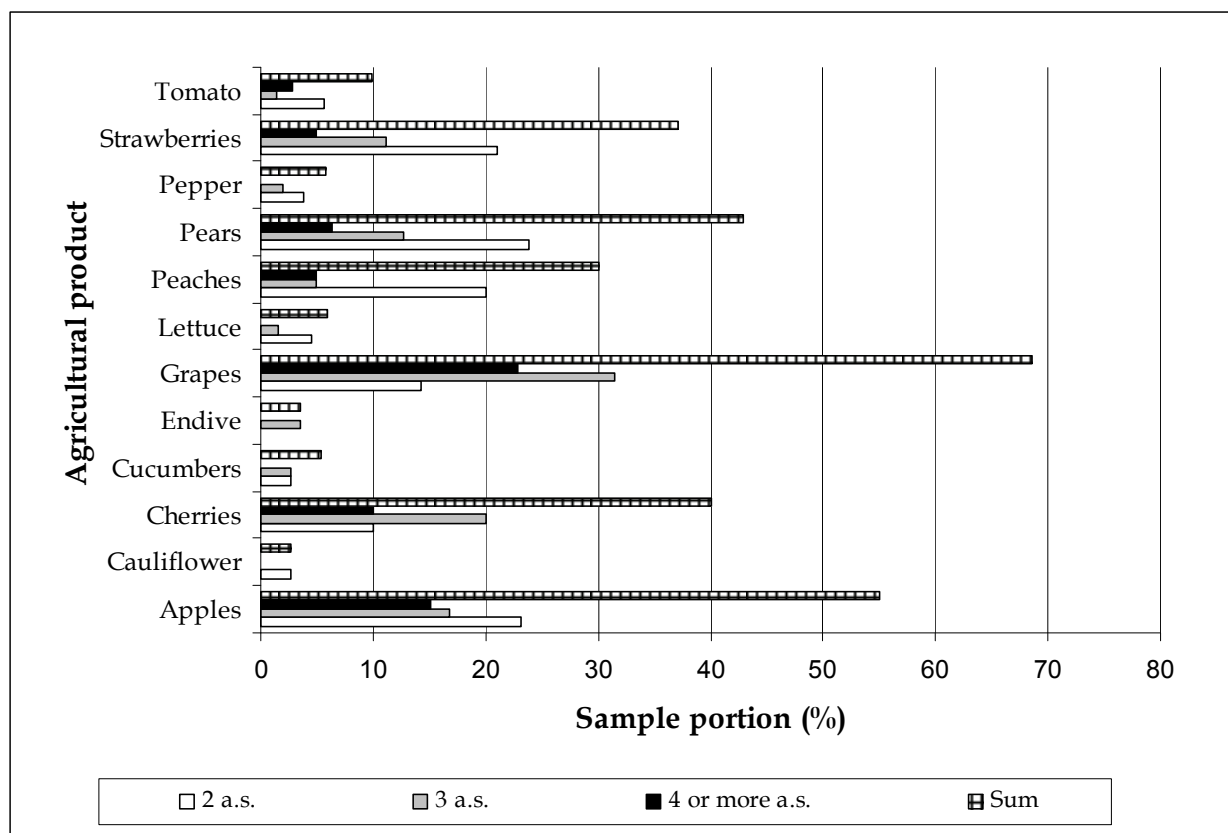


Fig. 5. Annual results for potato from 2001 to 2009

2002 (66.7%). The highest MRL exceedances in apple samples were found in 2005 (5.9%), exceedances were also found in 2002, 2004 and 2006. The highest percentage of lettuce samples with determined but not exceeding PPP residues was found in 2004 (57.1%) and the lowest in 2005 (5.9%). The highest MRL exceedances in lettuce samples were found in 2001 (13.3%), exceedances were also found in 2002, 2007 and 2008. MRL exceedances in potato samples were found in 2001 (20.0%), 2002 (40.0%), 2003 (37.1%) and 2004 (8.2%). From 2005 to 2009 MRL exceedances in potato samples were not found.

Multiple residues were found in 274 out of 1504 samples (18.2%). Residues of two active substances were determined in 125 samples (8.3%), residues of three active substances were determined in 86 samples (5.7%) and residues of four or more active substances were determined in 63 samples (4.2%). Multiple residues were mainly found in fruit samples, i.e. in grape samples (68.6%), in apple samples (55.1%), in pear samples (42.9%), in cherry samples (40.0), in strawberry samples (37.0%) and in peach samples (30.0%). According to our study the grapes were treated with different active substances, the sample in 2006 contained residues of nine active substances. In vegetable samples multiple residues were found in less than 10% of the matrix analysed. In some vegetable samples (beans, carrot, eggplant, head cabbage, leek, peas, potatoes, spinach and string beans) and in cereal samples multiple residues were not found. Results are presented in Figure 6 and in Table 6. Details about samples containing 5 or more active substances are presented in Table 7. Most of the pesticides, presented in Table 7, were insecticides or fungicides, some acaricides were also found.



a.s. stands for active substances

Fig. 6. Distribution of samples with multiple residues from 2001 to 2009

Commodity	No. of samples 2 a.s.	Portion (%)	No. of samples 3 a.s.	Portion (%)	No. of samples 4 or more a.s.	Portion (%)	No. of samples sum multiple	Portion (%)
Apples	66	23.2	48	16.8	43	15.1	157	55.1
Beans	0	0.0	0	0.0	0	0.0	0	0.0
Carrot	0	0.0	0	0.0	0	0.0	0	0.0
Cauliflower	1	2.6	0	0.0	0	0.0	1	2.6
Cereals	0	0.0	0	0.0	0	0.0	0	0.0
Cherries	1	10.0	2	20.0	1	10.0	4	40.0
Cucumbers	1	2.7	1	2.7	0	0.0	2	5.4
Eggplant	0	0.0	0	0.0	0	0.0	0	0.0
Endive	0	0.0	1	3.6	0	0.0	1	3.6
Grapes	5	14.3	11	31.4	8	22.9	24	68.6
Head cabbage	0	0.0	0	0.0	0	0.0	0	0.0
Leek	0	0.0	0	0.0	0	0.0	0	0.0
Lettuce	9	4.5	3	1.5	0	0.0	12	5.9
Peaches	4	20.0	1	5.0	1	5.0	6	30.0
Pears	15	23.8	8	12.7	4	6.3	27	42.9
Peas	0	0.0	0	0.0	0	0.0	0	0.0
Pepper	2	3.8	1	1.9	0	0.0	3	5.8
Potatoes	0	0.0	0	0.0	0	0.0	0	0.0
Spinach	0	0.0	0	0.0	0	0.0	0	0.0
Strawberries	17	21.0	9	11.1	4	4.9	30	37.0
String beans	0	0.0	0	0.0	0	0.0	0	0.0
Tomatoes	4	5.6	1	1.4	2	2.8	7	9.9

a.s. stands for active substances

Table 6. Samples with multiple residues from 2001 to 2009

Active substances found from 2001 to 2009 are presented in Figure 7 and in Table 8. Dithiocarbamates were most frequently found (in 21.7% of all samples), followed by phosalone (in 7.9% of all samples) and diazinone (in 5.3% of all samples).

Dithiocarbamates (maneb group) were found each year and were expressed as carbon disulfide. Cauliflower and head cabbage naturally contain substances that during preparation liberate carbon disulfide and give the same responses as dithiocarbamates. Diazinon and phosalone were found each year from 2001 to 2007 but not in 2008 and 2009, captan was found each year except in 2003 and in 2009, fludioxonil each year except in 2005 and in 2008, folpet each year except in 2002 in 2008 and in 2009 and procymidone each year except in 2007 and in 2009.

Active substances exceeding MRLs in the period from 2001 to 2009 are presented in Figure 8 and in Table 9. Dithiocarbamates were most frequently exceeding (in 2.53% of all samples), followed by cyprodinil (in 0.47% of all samples) and tolylfluanid (in 0.40% of all samples). Dithiocarbamates (maneb group) were exceeding in 2001, 2002, 2003, 2004 and in 2008, tolylfluanid in 2004, 2005 and in 2006, chlorothalonil in 2005 and in 2007, dimethoate in 2001 and in 2002, fludioxonil in 2003 and in 2006 (Table 9).

The samples were taken randomly in **8 different production areas** in Slovenia. During the period from 2001 to 2009 the highest average percentage of active substances was found in the region of Nova Gorica (49.9%). In this region mainly fruit is produced. The lowest average percentage of active substances was found in the region of Kranj (22.3%). From 2001 to 2009 a reduced percentage of active substances was noticed in this region in spite of the increased number of active substances sought. Results are presented in Table 10.

Regional inspection showed that the highest average percentage of active substances exceeding MRLs, from 2001 to 2009, was in the regions of Maribor (6.7%) and Kranj (6.7%). In Kranj MRL exceedances occurred only in potato samples and did not occur after 2004. The lowest average percentage of active substances exceeding MRLs was in the region of Nova Gorica (0.5%) in spite of the fact that the same region had the highest average percentage of active substances found. Results are presented in Table 11.

Commodity	Test year	Multiple PPP residues from 1 sample (mgkg ⁻¹)		
Apple	2004	Captan 0.10 (F)	Diazinon 0.02 (I)	Maneb group 0.06 (F)
		Phosalone 0.14 (I)	Tolyfluanid 0.02 (F)	
Apple	2004	Captan 0.21 (F)	Chlorpyrifos-methyl 0.01 (I)	Diazinon 0.03 (I)
		Folpet 0.06 (F)	Tolyfluanid 0.09 (F)	
Apple	2004	Captan 0.17 (F)	Cyprodinil 0.02 (F)	Diazinon 0.02 (I)
		Maneb group 0.06 (F)	Phosalone 0.17 (I)	Tolyfluanid 0.18 (F)
Apple	2004	Captan 0.21 (F)	Cyprodinil 0.02 (F)	Diazinon 0.04 (I)
		Folpet 0.06 (F)	Maneb group 0.61 (F)	Phosalone 0.15 (I)
		Pyrimethanil 0.03 (F)	Tolyfluanid 0.17 (F)	
Apple	2005	Chlorpyrifos 0.04 (I)	Chlorpyrifos-methyl 0.03 (I)	Cyprodinil 0.02 (F)
		Diazinon 0.02 (I)	Maneb group 0.09 (F)	Pirimicarb 0.05 (I)
Apple	2005	Captan 0.36 (F)	Chlorpyrifos 0.09 (I)	Cyprodinil 0.01 (F)
		Diazinon 0.15 (I)	Maneb group 0.27 (F)	Tolyfluanid 0.73 (F)
Apple	2006	Captan 0.17 (F)	Maneb group 0.80 (F)	Pyrimethanil 0.02 (F)
		Spirodiclofen 0.02 (A)	Thiacloprid 0.01 (I)	
Apple	2006	Captan 0.34 (F)	Diazinon 0.06 (I)	Maneb group 0.23 (F)
		Tebufenozide 0.01 (I)	Tolyfluanid 0.24 (F)	
Apple	2006	Captan 0.16 (F)	Chlorpyrifos 0.17 (I)	Diazinon 0.14 (I)
		Maneb group 0.21 (F)	Phosalone 0.01 (I)	Spirodiclofen 0.06 (A)
		Tolyfluanid 0.05 (F)		
Apple	2006	Captan 0.26 (F)	Diazinon 0.01 (I)	Maneb group 0.15 (F)
		Phosalone 0.02 (I)	Spirodiclofen 0.02 (A)	

Apple	2006	Chlorpyriphos 0.07 (I)	Diazinon 0.02 (I)	Diphenylamine 0.02 (F)
		Maneb group 0.26 (F)	Phosalone 0.01 (I)	
Apple	2006	Captan 0.16 (F)	Chlorpyriphos 0.07 (I)	Cyprodinil 0.02 (F)
		Maneb group 0.12 (F)	Pyrimethanil 0.04 (F)	
Apple	2007	Captan 0.16 (F)	Cyprodinil 0.02 (F)	Diazinon 0.04 (I)
		Maneb group 0.10 (F)	Phosalone 0.57 (I)	
Apple	2007	Acetamiprid 0.02 (I)	Captan 0.51 (F)	Chlorpyriphos 0.07 (I)
		Pyrimethanil 0.03 (F)	Spirodiclofen 0.02 (A)	
Apple	2007	Diazinon 0.04 (I)	Maneb group 0.17 (F)	Phosalone 0.13 (I)
		Pyrimethanil 0.01 (F)	Trifloxystrobin 0.03 (F)	
Apple	2008	Boscalid 0.02 (F)	Maneb group 0.12 (F)	Methoxyfenozide 0.01 (I)
		Pyraclostrobin 0.01 (F)	Pyrimethanil 0.02 (F)	
Apple	2008	Acetamiprid 0.01 (I)	Boscalid 0.06 (F)	Captan 0.44 (F)
		Maneb group 0.96 (F)	Pyraclostrobin 0.02 (F)	Pyrimethanil 0.02 (F)
Grape	2006	Azoxystrobin 0.04 (F)	Chlorpyriphos 0.04 (I)	Cyprodinil 0.10 (F)
		Fenazaquin 0.03 (A)	Fenhexamid 0.33 (F)	Fludioxonil 0.03 (F)
		Folpet 0.09 (F)	Maneb group 0.10 (F)	Metalaxyl 0.05 (F)
Grape	2006	Cyprodinil 0.02 (F)	Folpet 0.42 (F)	Maneb group 0.12 (F)
		Phosalone 0.02 (I)	Pyrimethanil 0.53 (F)	Zoxamide 0.07 (F)
Grape	2006	Chlorothalonil 0.17 (F)	Cyprodinil 0.25 (F)	Fenhexamid 0.05 (F)
		Folpet 0.20 (F)	Tebufenozide 0.01 (I)	
Grape	2006	Chlorothalonil 0.39 (F)	Cyprodinil 0.01 (F)	Folpet 0.84 (F)
		Metalaxyl 0.18 (F)	Myclobutanil 0.02 (F)	
Pear	2005	Captan 0.09 (F)	Chlorpyriphos-methyl 0.03 (I)	Maneb group 0.07 (F)
		Phosalone 0.13 (I)	Tolyfluanid 0.28 (F)	
Pear	2005	Chlorpyriphos-methyl 0.01 (I)	Diazinon 0.04 (I)	Maneb group 0.43 (F)
		Procymidone 0.04 (F)	Tolyfluanid 0.17 (F)	
Pear	2008	Boscalid 0.36 (F)	Difenoconazole 0.01 (F)	Fluquinconazole 0.03 (F)
		Lufenuron 0.09 (I)	Maneb group 0.36 (F)	Pyraclostrobin 0.13 (F)
		Thiacloprid 0.09 (I)		
Strawberry	2004	Cyprodinil 0.03 (F)	Fludioxonil 0.01 (F)	Maneb group 0.37 (F)
		Metalaxyl 0.04 (F)	Pyrimethanil 0.27 (F)	
Strawberry	2004	Azoxystrobin 0.04 (F)	Bromopropylate 0.04 (A)	Cyprodinil 0.10 (F)
		Fludioxonil 0.11 (F)	Maneb group 0.14 (F)	Pyrimethanil 0.20 (F)
Strawberry	2006	Cyprodinil 0.20 (F)	Fludioxonil 0.13 (F)	Maneb group 0.25 (F)
		Metalaxyl 0.02 (F)	Tolyfluanid 0.01 (F)	

A-acaricide, F-fungicide, I-insecticide

Table 7. Agricultural products containing 5 or more active substances per sample from 2001 to 2009

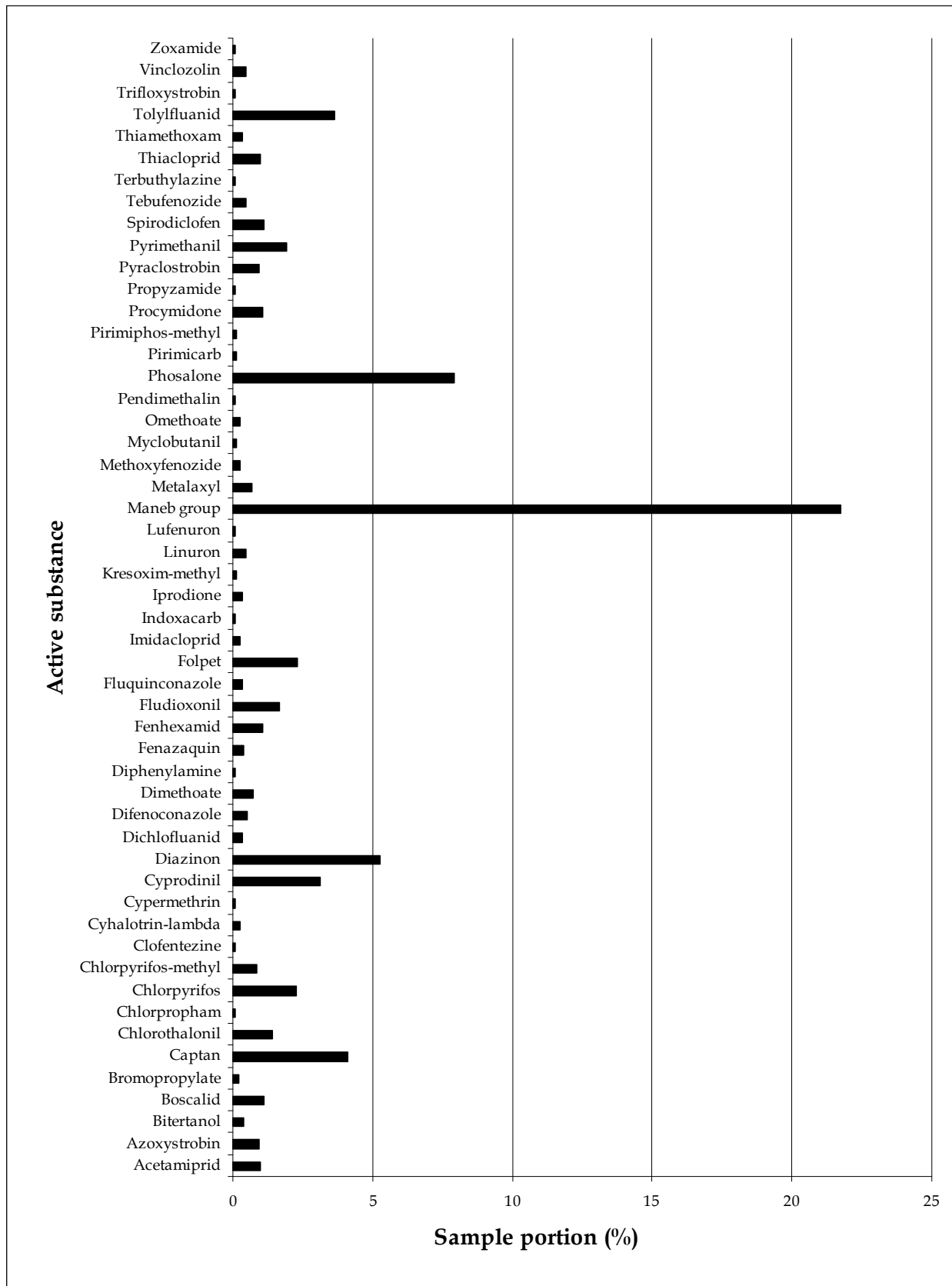


Fig. 7. Sample portion of active substances found in the period from 2001 to 2009

Active substance	Sample portion (%)								
	2001	2002	2003	2004	2005	2006	2007	2008	2009
Acetamiprid	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	1.9	6.6	n.d.
Azoxystrobin	n.a.	n.a.	0.3	0.8	n.d.	2.2	2.4	n.d.	0.6
Bitertanol	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	2.9	n.d.	n.d.
Boscalid	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	1.4	8.4	n.d.
Bromopropylate	n.a.	n.a.	0.6	0.3	n.d.	n.d.	n.d.	n.d.	n.d.
Captan	2.6	2.0	n.d.	5.8	7.0	4.4	5.7	3.6	n.d.
Chlorothalonil	n.a.	n.a.	n.d.	0.3	2.6	5.0	3.3	n.d.	0.6
Chlorpropham	n.a.	n.a.	n.a.	n.a.	0.9	n.d.	n.d.	n.d.	n.d.
Chlorpyrifos	n.d.	n.d.	n.d.	n.d.	3.5	4.4	7.6	3.6	n.d.
Chlorpyrifos-methyl	n.d.	1.3	0.6	1.7	2.6	n.d.	n.d.	n.d.	n.d.
Clofentezine	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.d.	0.6	n.d.
Cyhalotrin-lambda	0.7	n.d.	n.d.	0.3	n.d.	n.d.	1.0	n.d.	n.d.
Cypermethrin	n.a.	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	0.6	n.d.
Cyprodinil	n.a.	n.a.	n.a.	3.3	2.6	10.5	4.8	n.d.	1.8
Diazinon	4.0	4.7	3.3	6.4	10.4	5.0	4.8	n.d.	n.d.
Dichlofluanid	n.a.	n.a.	0.6	0.6	n.d.	0.6	n.d.	n.d.	n.d.
Difenoconazole	n.a.	n.a.	n.a.	n.a.	n.a.	1.1	1.9	1.2	n.d.
Dimethoate	1.3	3.3	0.3	n.d.	n.d.	n.d.	1.4	n.d.	n.d.
Diphenylamine	n.a.	n.a.	n.a.	n.d.	n.d.	0.6	n.d.	n.d.	n.d.
Fenazaquin	n.a.	n.a.	n.a.	n.a.	n.a.	2.8	n.d.	0.6	n.d.
Fenhexamid	n.a.	n.a.	n.a.	n.a.	n.a.	3.3	4.8	n.d.	n.d.
Fludioxonil	0.7	0.7	1.4	2.5	n.d.	2.8	0.5	n.d.	1.8
Fluquinconazole	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.d.	3.0	n.d.
Folpet	0.7	n.d.	2.2	1.4	0.9	10.5	0.5	n.d.	n.d.
Imidacloprid	n.a.	n.a.	n.a.	n.a.	n.a.	1.1	1.0	n.d.	n.d.
Indoxacarb	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.d.	0.6
Iprodione	2.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.2
Kresoxim-methyl	n.a.	n.a.	n.a.	n.d.	n.d.	0.6	n.d.	n.d.	n.d.
Linuron	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	1.2	n.d.
Lufenuron	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	1.4	1.8	0.6
Maneb group	17.2	42.0	15.0	15.5	20.9	22.7	10.5	12.7	11.8
Metalaxyl	n.d.	1.3	n.d.	0.3	n.d.	2.2	0.5	1.2	n.d.
Methoxyfenozide	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	2.4	n.d.
Myclobutanil	n.a.	n.a.	n.a.	n.d.	n.d.	1.1	n.d.	n.d.	n.d.
Omethoate	n.a.	n.a.	n.d.	n.d.	n.d.	n.d.	1.9	n.d.	n.d.

Pendimethalin	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.d.	0.6	n.d.
Phosalone	4.0	17.3	4.4	5.3	7.8	10.5	11.4	n.d.	n.d.
Pirimicarb	n.a.	n.a.	n.a.	n.a.	0.9	n.d.	n.d.	0.6	n.d.
Pirimiphos-methyl	0.7	0.7	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Procymidone	2.0	2.7	0.6	0.6	0.9	1.7	n.d.	0.6	n.d.
Propyzamide	n.a.	n.a.	n.d.	n.d.	n.d.	n.d.	0.5	n.d.	n.d.
Pyraclostrobin	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	8.4	n.d.
Pyrimethanil	n.a.	n.a.	n.a.	1.7	n.d.	6.6	2.9	3.0	n.d.
Spirodiclofen	n.a.	n.a.	n.a.	n.a.	n.a.	3.3	3.8	1.8	n.d.
Tebufenozide	n.a.	n.a.	n.a.	n.a.	n.a.	2.2	n.d.	1.8	n.d.
Terbutylazine	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	0.5	n.d.	n.d.
Thiacloprid	n.a.	n.a.	n.a.	n.a.	n.a.	1.7	2.9	3.6	n.d.
Thiamethoxam	n.a.	n.a.	n.a.	n.a.	n.a.	n.d.	0.5	0.6	1.8
Tolyfluanid	n.a.	n.a.	n.d.	7.2	13.9	7.2	n.d.	n.d.	n.d.
Trifloxystrobin	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	0.5	n.d.	n.d.
Vinclozolin	4.6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Zoxamide	n.a.	n.a.	n.a.	n.a.	n.a.	0.6	n.d.	n.d.	n.d.

n.a. means not analysed

n.d. means not detected

Table 8. Annual sample portions of active substances found in the years from 2001 to 2009

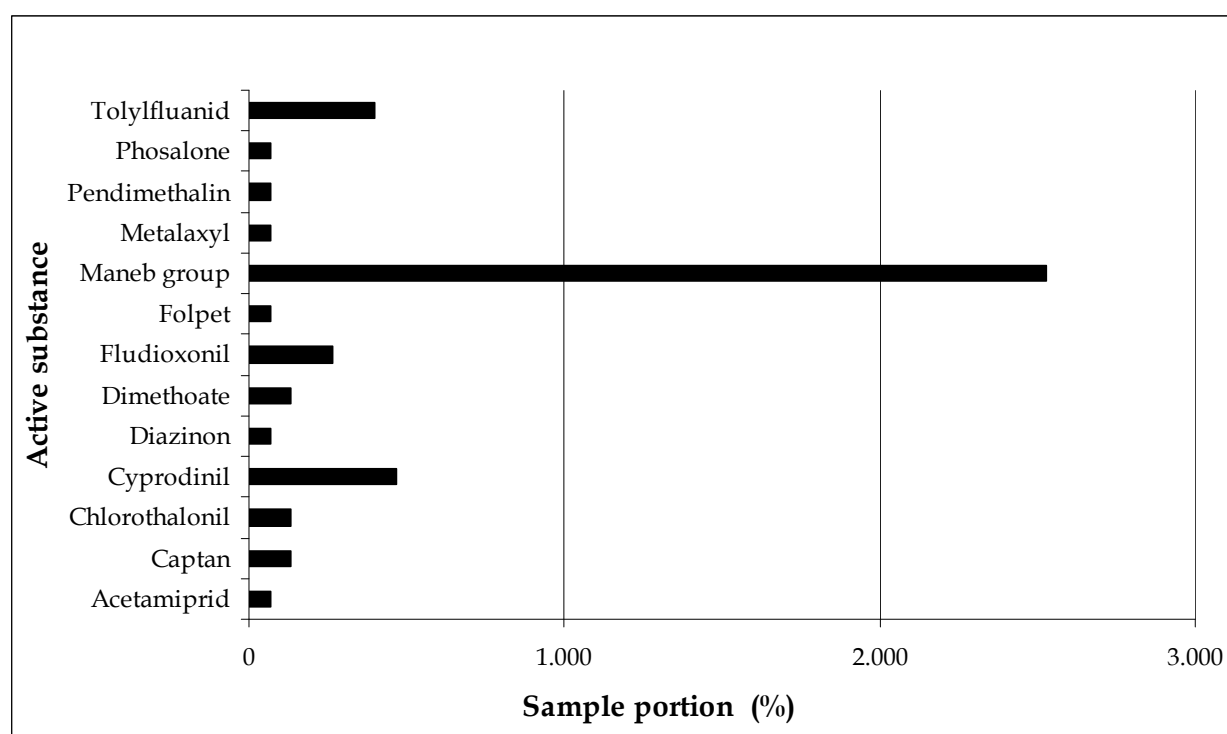


Fig. 8. Sample portion of active substances exceeding MRLs in the period from 2001 to 2009

Active substance	Sample portion (%)								
	2001	2002	2003	2004	2005	2006	2007	2008	2009
Acetamiprid	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	0.5	n.e.	n.d.
Captan	n.e.	n.e.	n.d.	n.e.	n.e.	n.e.	1.0	n.e.	n.d.
Chlorothalonil	n.a.	n.a.	n.d.	n.e.	0.9	n.e.	0.5	n.d.	n.e.
Cyprodinil	n.a.	n.a.	n.a.	n.e.	n.e.	0.3	n.e.	n.d.	n.e.
Diazinon	n.e.	n.e.	n.e.	n.e.	0.9	n.e.	n.e.	n.d.	n.d.
Dimethoate	0.7	0.7	n.e.	n.d.	n.d.	n.d.	n.e.	n.d.	n.d.
Fludioxonil	n.e.	n.e.	2.0	n.e.	n.d.	0.6	n.e.	n.d.	n.e.
Folpet	n.e.	n.d.	n.e.	n.e.	n.e.	n.e.	0.5	n.d.	n.d.
Maneb group	4.6	8.0	8.7	2.4	n.e.	n.e.	n.e.	0.6	n.e.
Metalaxyl	n.d.	0.7	n.d.	n.e.	n.d.	n.e.	n.e.	n.e.	n.d.
Pendimethalin	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.d.	0.6	n.d.
Phosalone	n.e.	0.7	n.e.	n.e.	n.e.	n.e.	n.e.	n.d.	n.d.
Tolyfluanid	n.a.	n.a.	n.d.	1.4	0.9	1.1	n.d.	n.d.	n.d.

n.a. means not analysed

n.d. means not detected

n.e. means not exceeding

Table 9. Annual sample portions of active substances exceeding MRLs in the years from 2001 to 2009

Region / Year	Sample portion of active substances found (%)									
	2001	2002	2003	2004	2005	2006	2007	2008	2009	Average
Celje	35.7	55.0	52.2	48.8	33.3	31.3	23.5	14.3	22.2	35.1
Koper	21.4	58.3	52.9	41.2	50.0	53.3	52.6	40.0	33.3	44.8
Kranj	47.6	41.2	22.2	36.4	20.0	10.5	8.7	10.5	4.0	22.3
Ljubljana	22.2	53.6	29.2	41.7	20.0	39.1	25.7	20.7	23.1	30.6
Maribor	20.8	59.3	46.7	55.9	31.8	56.8	41.5	41.0	18.5	41.4
Murska Sobota	15.0	40.0	23.5	55.0	40.0	37.0	30.4	0.0	0.0	26.8
Nova Gorica	22.2	75.0	50.0	63.6	50.0	78.6	57.1	42.9	9.5	49.9
Novo mesto	29.0	50.0	66.7	40.0	36.4	53.3	61.3	35.5	15.8	43.1

Table 10. Active substances found in the years from 2001 to 2009 for different regions

Region / Year	Sample portion of active substances exceeding MRLs (%)									
	2001	2002	2003	2004	2005	2006	2007	2008	2009	Average
Celje	0.0	10.0	13.0	0.0	0.0	6.3	0.0	4.8	0.0	3.8
Koper	0.0	16.7	0.0	0.0	0.0	0.0	5.3	0.0	0.0	2.4
Kranj	23.8	11.8	11.1	13.6	0.0	0.0	0.0	0.0	0.0	6.7
Ljubljana	0.0	10.7	12.5	2.8	10.0	4.3	0.0	0.0	0.0	4.5
Maribor	8.3	7.4	20.0	5.9	3.1	10.8	2.4	2.6	0.0	6.7
Murska Sobota	0.0	0.0	5.9	10.0	0.0	3.7	0.0	0.0	0.0	2.2
Nova Gorica	0.0	0.0	0.0	0.0	0.0	0.0	4.8	0.0	0.0	0.5
Novo mesto	3.2	16.7	11.1	0.0	0.0	6.7	3.2	0.0	0.0	4.5

Table 11. Active substances exceeding MRLs in the years from 2001 to 2009 for different regions

4. Comparison of Slovenia with the European Union, Norway, Iceland and Liechtenstein

In the European Union, Norway, Iceland and Liechtenstein 58003 of samples were tested in monitoring from 2001 to 2006, i.e. 4829 cereal samples (oat, rice, rye, wheat), 20978 fruit samples and 32196 vegetable samples

(http://ec.europa.eu/food/fvo/specialreports/pesticides_index_en.htm). The sampling is presented in Table 12.

Sample portions below reporting level (RL), sample portions below or equal to MRLs and sample portions above MRLs are presented in Figure 9, Figure 10 and Table 13.

PPP residues were not found in 33734 samples (58.2%), in 22782 samples (39.3%) PPP residues were lower or equal to MRLs and PPP residues were above MRLs in 1487 samples (2.6%).

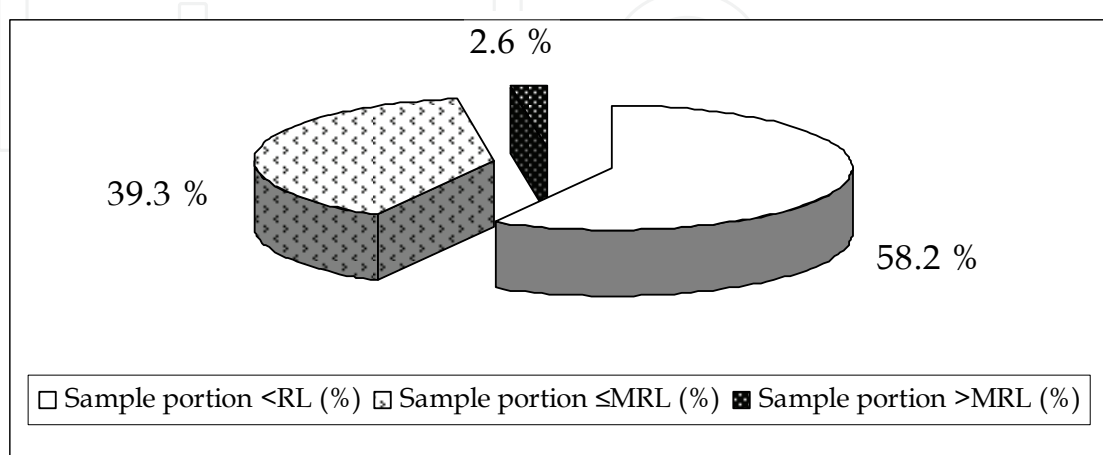


Fig. 9. Results of monitoring from 2001 to 2006 in the European Union, Norway, Iceland and Liechtenstein

Commodity	2001	2002	2003	2004	2005	2006	Sum
Apples	2641	/	/	3133	/	/	5774
Beans	/	896	/	/	1122	/	2018
Carrot	/	1457	/	/	1759	/	3216
Cauliflower	/	/	631	/	/	1014	1645
Cereals	/	/	1656	795	847	1531	4829
Cherries	/	/	/	/	/	/	/
Cucumbers	/	/	1150	/	1555	/	2705
Eggplant	/	/	706	/	/	960	1666
Endive	/	/	/	/	/	/	/
Grapes	1721	/	2163	/	/	2479	6363
Head cabbage	/	/	/	918	/	/	918
Leek	/	/	/	769	/	/	769
Lettuce	1838	/	/	2301	/	/	4139
Peaches/Nectarines	/	1190	/	/	/	/	1190
Pears	/	1330	/	/	2001	/	3331
Peas	/	/	519	/	/	853	1372
Pepper	/	/	1754	/	/	2248	4002
Potatoes	/	1502	/	/	1909	/	3411
Spinach	/	644	/	/	1010	/	1654
Strawberries	1652	/	/	2668	/	/	4320
String beans	/	/	/	/	/	/	/
Tomatoes	2016	/	/	2665	/	/	4681
Sum	9868	7019	8579	13249	10203	9085	58003

Table 12. Sampling of agricultural products in the years from 2001 to 2006 in the European Union, Norway, Iceland and Liechtenstein

The highest portion of determined but not exceeding PPP residues, (residues lower or equal to MRLs), was found in pear samples (68.8%), grape samples (62.2%), strawberry samples (58.6%), apple samples (53.5%) and peach/ nectarine samples (45.5%). Fruit samples contained also exceeding PPP residues (residues above MRLs), i.e. grape samples (3.5%), peach/nectarine samples (3.1%), strawberry samples (3.0%), apple samples (1.5%) and pear samples (1.1%). The highest portion of PPP residues was found in fruit, just like in Slovenia. The highest portion of PPP residues exceeding MRLs were found in spinach samples (8.9%) and bean samples (7.7%). The matrixes with exceeding MRLs were different from commodities in Slovenia.

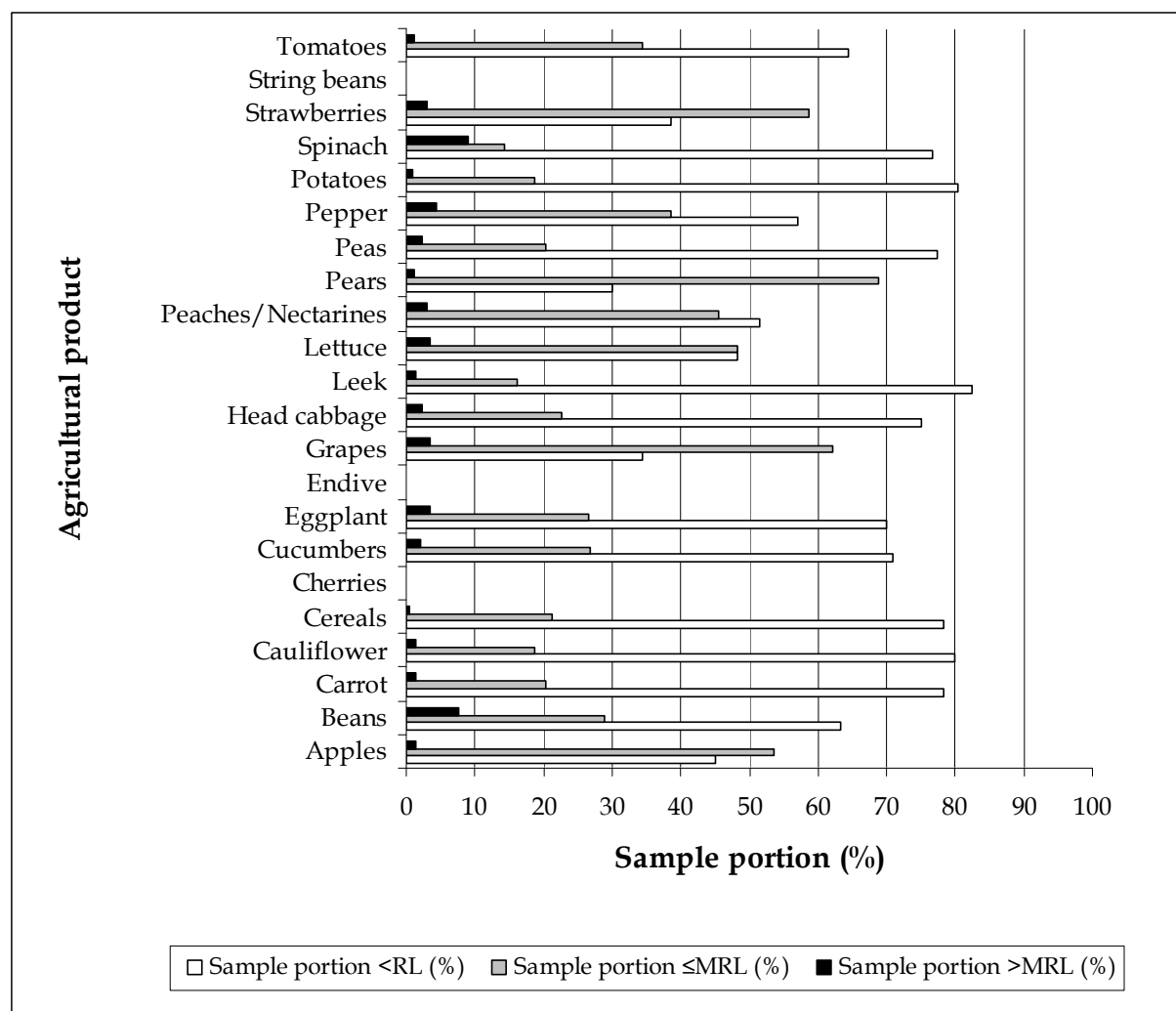


Fig. 10. Sample portions of PPP residues for each commodity from 2001 to 2006 in the European Union, Norway, Iceland and Liechtenstein

5. Conclusions

In Slovenia, during the monitoring from 2001 to 2009 the following samples were analysed:

- 102 cereal samples: PPP residues were not found in 101 samples (99.0%), 1 sample (1.0%) contained PPP residues lower or equal to MRLs, residues exceeding MRLs were not determined
- 494 fruit samples: 19 samples (3.8%) exceeded MRLs, 348 samples (70.4%) contained PPP residues lower or equal to MRLs, PPP residues were not found in 127 samples (25.7%)
- 908 vegetable samples: 46 samples (5.1%) exceeded MRLs, 144 samples (15.9%) contained PPP residues lower or equal to MRLs, PPP residues were not found in 718 samples (79.1%)

In the European Union, Norway, Iceland and Liechtenstein during the monitoring from 2001 to 2006 the following samples were analysed:

- 4829 cereal samples: 21 samples (0.4%) exceeded MRLs, 1024 samples (21.2%) contained PPP residues lower or equal to MRLs, PPP residues were not found in 3784 samples (78.4%)

Commodity	Sample portion <RL (%)	Sample portion ≤MRL (%)	Sample portion >MRL (%)
Apples	45.0	53.5	1.5
Beans	63.4	28.9	7.7
Carrot	78.4	20.2	1.4
Cauliflower	79.9	18.8	1.3
Cereals	78.4	21.2	0.4
Cherries	0.0	0.0	0.0
Cucumbers	70.9	26.9	2.2
Eggplant	69.9	26.5	3.5
Endive	0.0	0.0	0.0
Grapes	34.4	62.2	3.5
Head cabbage	75.1	22.7	2.3
Leek	82.4	16.3	1.3
Lettuce	48.2	48.2	3.6
Peaches/Nectarines	51.4	45.5	3.1
Pears	30.1	68.8	1.1
Peas	77.5	20.3	2.3
Pepper	57.0	38.6	4.4
Potatoes	80.4	18.7	0.9
Spinach	76.8	14.3	8.9
Strawberries	38.5	58.6	3.0
String beans	0.0	0.0	0.0
Tomatoes	64.4	34.4	1.2

Table 13. Sample portions of PPP residues for each commodity from 2001 to 2006 in the European Union, Norway, Iceland and Liechtenstein

- 20978 fruit samples: 506 samples (2.4%) exceeded MRLs, 12408 samples (59.1%) contained PPP residues lower or equal to MRLs, PPP residues were not found in 8064 samples (38.4%)
- 32196 vegetable samples: 960 samples (3.0%) exceeded MRLs, 9350 samples (29.0%) contained PPP residues lower or equal than MRLs, PPP residues were not found in 21886 samples (68.0%).

Levels of pesticide residues in agricultural products in Slovenia from 2001 to 2009 do not give any cause for alarm. In general the portion of exceedances is slightly higher (4.3%) than in the European Union, Norway, Iceland and Liechtenstein (2.6%) Exceedances in Slovenia have been reduced over the years. Otherwise in both monitoring results the highest portion of exceedances was found in vegetables and the lowest in cereals.

Healthy food in the Slovenian market can be achieved by frequent and accurate control of agricultural products. In future analytical work should be extended to other active

substances, determination of possible metabolites and improvement of sensitivity of testing methods, i.e. lowering limit of quantification.

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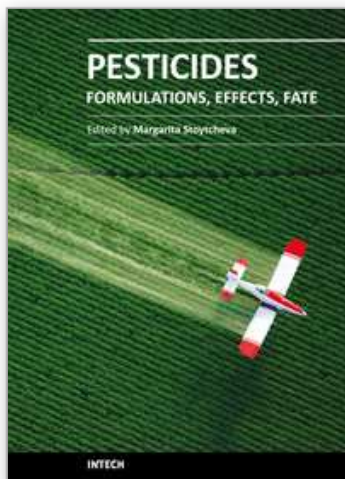
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Phone: +86-21-62489820
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