Technical paper

Pesticide Residues in Agricultural Products of the Slovene Origin Found in 2007

Helena Baša Česnik, Špela Velikonja Bolta and Ana Gregorčič

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

** Corresponding author: E-mail: helena.basa@kis.si*

Received: 26-03-2008

Abstract

In the year 2007, 210 apple, cereal, cherry, head cabbage, leek, lettuce, peach, potato, strawberry and tomato samples from Slovene producers were analysed for pesticide residues. The samples were analysed for the presence of 118 different active compounds using four analytical methods. In four samples (1.9%) exceeded maximum residue levels (MRL-s) were determined, which is better than the results obtained at the monitoring of pesticide residues in the products of plant origin in the European union, Norway, Iceland and Liechtenstein in 2005 (4.9%). Trends which can be observed through the years are the following: the highest number of active compounds are found in fruit, lower MRL exceedances were observed during the years, and the number of active substances found in one sample has increased.

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

1. Introduction

Pesticide residues found in agricultural products produced by Slovene market producers were determined until the placement of the products on the market, i.e. after harvesting, in accordance with the Law on Plant Protection Products and Regulation on Residues of Plant Protection Products Found in and on Agricultural Commodities and Products.[1–2]

Monitoring of pesticide residues in agricultural products of Slovene market producers until the placement of the products on the market allows determination and control of a correct use of plant protection products conforming to the good agricultural practice applied in the conventional, integrated and ecological production, and determination of origin and cause of the residues found. Due to the random selection of producers it is possible to evaluate the situation and effectiveness of the previous measures.

The results are used for:

– determination of harmonisation with the legally prescribed maximal residue level (MRL),
– determination of harmonisation of conventional, integrated and ecological production with good agricultural practice,
– determination of origin or cause of residues determined and
– risk assessment of samples which exceeded MRLs.

Due to the characteristic type of foods consumed by Slovenes (the Slovene Food Basket has not yet been made), pesticide residues are determined each year in the samples of apples, lettuce and potatoes while the choice of other agricultural products is adjusted to the guidelines indicated in the recommendations issued by European Union.[3]

Beside apple, lettuce and potato samples, agricultural inspectors took samples of cereals, cherries, head cabbage, leek, peaches, strawberries and tomatoes in 2007. 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 storehouses 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 the prescribed way of use of the plant protection products is therefore of key importance.

2. Experimental

Samples were analysed for the content of selected active substances.

In 2007, residues of 118 different compounds were determined using four different methods:

1. *Multiresidual GC/MS method* for the determination of 71 compounds: acephate, aldrin, azinphos-methyl, azoxystrobin, bifenthrin, boscalid, bromopropylate, bupirimate, captan, carbaryl, carbofuran, chlorothalonil, chlorpropham, chlorpyriphos, chlorpyriphos-methyl, cyhalotrin-lambda, cypermethrin, cyprodinil, DDT, deltamethrin, diazinon, dichlofluanid, dichlorvos, dimethoate, diphenylamine, endosulfan, endrin, fenamidone, fenitrothion, fenthion, fludioxonil, folpet, HCH-α, heptachlor, heptenophos, imazalil, iprodione, kresoxim-methyl, lindane, malathion, mecarbam, metalaxyl, methamidophos, methidathion, myclobutanil, omethoate, oxydemeton-methyl, parathion, penconazole, permethrin, phorate, phosalone, pirimicarb, pirimiphos-methyl, procymidone, propargite, propyzamide, pyridaphenthion, pyrimethanil, quinalphos, quinoxyfen, spiroxamine, tebuconazole, thiabendazole, tolclofos-methyl, tolylfluanid, triadimefon, triadimenol, triazophos, trifloxystrobin and vinclozolin.[4, 5]
2. *GC/MS method* for the determination of dithiocarbamate group: maneb, mankozeb, metiram, propineb and zineb, the sum is expressed as carbon disulfide.[5, 6]
3. *HPLC method* for the determination of benzimidazoles: tiabendazol and the sum of benomil and carbendazim (only in cereals).[5, 7]
4. *Multiresidual LC/MS/MS method* for the determination of 45 compounds: acetamiprid, aldicarb, amidosulfuron, benalaxyl, bentazon, bitertanol, clofentezine, cymoxanil, cyromazine, difenoconazole, dimethomorph, epoxiconazole, ethofumesate, famoxadone, fenazaquin, fenhexamid, fenpropidin, fenpropimorf, fenpyroximate, flufenacet, fluroxypyr, fluquinconazole, hexythiazox, imidacloprid, iprovalicarb, lufenuron, methiocarb, methomyl, metosulam, pendimethalin, phoxim, prochloraz, propamocarb, propiconazole, pymetrozine, pyridate, spinosad, spirodiclofen, tebufenozide, terbuthylazine, thiacloprid, thiamethoxam, thiophanate-methyl, trichlorfon, zoxamide.[8–10]

Limits of detection of all active substances determined are presented in Table 1.

The trueness of methods is verified by participation in the French inter-laboratory proficiency testing scheme BIPEA (Bureau interprofessionnel d´etudes analytiques) and CRL European Proficiency Test 09.

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

Table 1: Limits of detection for active substances analysed in 2007

Pesticide	LOD lettuce (mg/kg)	LOD strawberries (mg/kg)	LOD cherries (mg/kg)	LOD peaches (mg/kg)	LOD cereals (mg/kg)	LOD tomato (mg/kg)	LOD apples (mg/kg)	LOD potatoes (mg/kg)	LOD leek (mg/kg)	LOD cabbage (mg/kg)
acephate	0.02	0.01	0.01	0.02	0.01	0.02	0.02	0.02	0.02	0.02
acetamiprid	0.1	0.01	0.05	0.01	0.01	0.01	0.01	0.01	0.01	0.01
aldicarb	0.01	0.01	0.01	0.01	0.03	0.01	0.01	0.02	0.01	0.02
aldrin	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
amidosulfuron	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.05	0.01	0.03
azinphos-methyl	0.01	0.01	0.01	0.02	0.01	0.01	0.01	0.01	0.01	0.02
azoxystrobin	0.02	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
benalaxyl	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
benomyl, carbendazim	–	–	–	–	0.01	–	–	–	–	–
bentazone	0.03	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.03
bifenthrin	0.01	0.01	0.01	0.02	0.02	0.02	0.01	0.01	0.01	0.01
bitertanol	0.01	0.01	0.01	0.03	0.01	0.01	0.01	0.01	0.01	0.01
boscalid	0.01	0.01	0.01	0.02	0.02	0.02	0.05	0.01	0.01	0.01
bromopropylate	0.01	0.01	0.01	0.02	0.02	0.01	0.01	0.02	0.05	0.05
bupirimate	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
captan	0.16	0.05	0.16	0.02	0.02	0.16	0.05	0.04	0.05	0.02
carbaryl	0.05	0.05	0.05	0.05	0.03	0.05	0.05	0.05	0.05	0.05
carbofuran	0.01	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02
chlorothalonil	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
chlorpropham	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.04
chlorpyriphos	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.04
chlorpyriphos-methyl	0.01	0.01	0.02	0.02	0.02	0.04	0.01	0.01	0.01	0.04
clofentezine	0.02	0.03	0.02	0.01	0.02	0.03	0.01	0.02	0.01	0.01
cyhalotrin-lambda	0.01	0.01	0.02	0.03	0.02	0.03	0.01	0.01	0.01	0.02
cymoxanil	0.03	0.01	0.01	0.03	0.03	0.01	0.01	0.01	0.01	0.01

Pesticide	LOD lettuce (mg/kg)	LOD strawberries (mg/kg)	LOD cherries (mg/kg)	LOD peaches (mg/kg)	LOD cereals (mg/kg)	LOD tomato (mg/kg)	LOD apples (mg/kg)	LOD potatoes (mg/kg)	LOD leek (mg/kg)	LOD cabbage (mg/kg)
cypermethrin	0.02	0.03	0.04	0.03	0.03	0.05	0.05	0.04	0.03	0.04
cyprodinil	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
cyromazine	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
DDT	0.05	0.05	0.05	0.05	0.05	0.05	0.01	0.01	0.01	0.02
deltamethrin	0.04	0.02	0.03	0.05	0.05	0.05	0.04	0.01	0.02	0.02
diazinon	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
dichlofluanid	0.03	0.02	0.02	0.02	0.05	0.01	0.05	0.03	0.05	0.03
dichlorvos	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
difenoconazole	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
dimethoate	0.04	0.01	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02
dimethomorph	0.03	0.03	0.03	0.01	0.01	0.01	0.01	0.01	0.01	0.01
diphenylamine	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
dithiocarbamates	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
endosulfan	0.04	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
endrin	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
epoxiconazole	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.03
ethofumesate	0.01	0.05	0.01	0.01	0.01	0.01	0.03	0.03	0.01	0.01
famoxadone	0.02	0.01	0.01	0.02	0.01	0.01	0.01	0.01	0.02	0.01
fenamidone	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
fenazaquin	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
fenhexamid	0.03	0.03	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
fenitrothion	0.01	0.01	0.01	0.01	0.02	0.01	0.01	0.01	0.01	0.01
fenpropidin	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
fenpropimorph	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
fenpyroximate	0.01	0.01	0.01	0.01	0.01	0.03	0.01	0.01	0.01	0.01
fenthion	0.01	0.01	0.01	0.01	0.02	0.01	0.05	0.01	0.01	0.01
fludioxonil	0.05	0.02	0.04	0.05	0.05	0.05	0.05	0.02	0.02	0.05
flufenacet	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
fluquinconazole	0.03	0.03	0.01	0.01	0.01	0.01	0.05	0.03	0.01	0.01
fluroxypyr	0.03	0.03	0.01	0.03	0.01	0.01	0.01	0.01	0.03	0.01
folpet	1	0.02	0.01	0.02	0.02	0.02	0.01	0.02	0.02	0.02
HCH-alpha	0.01	0.01	0.01	0.01	0.02	0.01	0.01	0.01	0.01	0.01
heptachlor	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
heptenophos	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.02	0.01	0.02
hexythiazox	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
imazalil	0.02	0.02	0.02	0.02	0.02	0.05	1	0.02	0.02	0.02
imidacloprid	0.01	0.01	0.01	0.03	0.01	0.01	0.01	0.01	0.01	0.01
iprodione	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
iprovalicarb	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
kresoxim-methyl	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
lindane (HCH-gamma)	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
lufenuron	0.01	0.01	0.01	0.01	0.01	0.03	0.01	0.01	0.01	0.01
malathion	0.02	0.04	0.02	0.05	0.03	0.04	0.05	0.05	0.02	0.05
mecarbam	0.03	0.02	0.05	0.05	0.05	0.05	0.05	0.02	0.03	0.03
metalaxyl	0.03	0.01	0.01	0.01	0.02	0.01	0.04	0.01	0.02	0.05
methamidophos	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
methidathion	0.02	0.02	0.02	0.05	0.02	0.02	0.02	0.02	0.02	0.02
methiocarb	0.03	0.01	0.03	0.01	0.05	0.05	0.05	0.03	0.05	0.05
methomyl	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
metosulam	0.03	0.03	0.01	0.01	0.01	0.01	0.03	0.01	0.01	0.01
myclobutanil	0.02	0.03	0.02	0.04	0.02	0.04	0.01	0.02	0.02	0.02
omethoate	0.02	0.01	0.01	0.01	0.01	0.01	0.02	0.02	0.01	0.03
oxydemeton-methyl	0.04	0.01	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.03
parathion	0.03	0.05	0.02	0.03	0.03	0.02	0.04	0.02	0.02	0.05
penconazole	0.01	0.01	0.01	0.03	0.04	0.03	0.01	0.01	0.01	0.01
pendimethalin	0.01	0.01	0.01	0.01	0.01	0.01	0.03	0.03	0.01	0.01
permethrin	0.02	0.03	0.04	0.05	0.05	0.05	0.05	0.02	0.02	0.02
phorate	0.01	0.02	0.02	0.01	0.04	0.02	0.01	0.01	0.01	0.01

Pesticide	LOD lettuce (mg/kg)	LOD strawberries (mg/kg)	LOD cherries (mg/kg)	LOD peaches (mg/kg)	LOD cereals (mg/kg)	LOD tomato (mg/kg)	LOD apples (mg/kg)	LOD potatoes (mg/kg)	LOD leek (mg/kg)	LOD cabbage (mg/kg)
phosalone	0.01	0.01	0.01	0.02	0.01	0.02	0.01	0.01	0.01	0.05
phoxim	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
pirimicarb	0.01	0.01	0.01	0.02	0.02	0.01	0.01	0.01	0.01	0.02
pirimiphos-methyl	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
prochloraz	0.03	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
procymidone	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
propamocarb	0.03	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.03	0.05
propargite	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
propiconazole	0.03	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
propyzamide	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.02
pymetrozine	0.03	0.02	0.01	0.01	0.01	0.01	0.02	0.01	0.01	0.03
pyridaphenthion	0.02	0.03	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.04
pyridate	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
pyrimethanil	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
quinalphos	0.01	0.01	0.05	0.05	0.05	0.05	0.01	0.01	0.01	0.01
quinoxyfen	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.02
spinosad	1	1	0.5	0.01	0.01	0.1	0.1	0.01	0.1	0.5
spirodiclofen	0.03	0.01	0.01	0.01	0.01	0.01	0.01	0.03	0.01	0.03
spiroxamine	0.03	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
tebuconazole	0.02	0.02	0.02	0.03	0.02	0.03	0.03	0.02	0.02	0.02
tebufenozide	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.03	0.01	0.01
terbuthylazine	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
thiabendazole	0.02	0.04	0.03	0.04	0.03	0.04	0.02	0.02	0.01	0.03
thiacloprid	0.03	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.01
thiamethoxam	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
thiophanate-methyl	0.03	0.01	0.01	0.01	0.01	0.01	0.01	0.03	0.02	0.03
tolclofos-methyl	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
tolylfluanid	0.01	0.01	0.02	0.04	0.04	0.04	0.01	0.01	0.01	0.02
triadimefon	0.01	0.03	0.02	0.03	0.02	0.03	0.01	0.02	0.01	0.05
triadimenol	0.03	0.03	0.04	0.05	0.05	0.05	0.01	0.02	0.02	0.05
triazophos	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
trichlorfon	0.01	0.03	0.03	0.01	0.01	0.03	0.01	0.01	0.01	0.01
trifloxystrobin	0.01	0.01	0.01	0.01	0.02	0.02	0.02	0.02	0.01	0.01
vinclozolin	0.03	0.01	0.01	0.02	0.02	0.03	0.02	0.01	0.02	0.04
zoxamide	0.02	0.02	0.02	0.02	0.02	0.01	0.01	0.02	0.02	0.01

3. Results and Discussion

210 samples of agricultural products presented in Table 2 were analysed in 2007.

43 **apple** samples were analysed: residues exceeding MRLs were not determined, 35 samples (81.4%) contained residues lower than MRLs, residues were not found in 8 samples (18.6%).

10 **cereal** samples (oats and rye) were analysed: residues were not found in 10 samples (100.0%).

10 **cherry** samples were analysed: residues exceeding MRLs were not determined, 8 samples (80.0%) contained residues lower than MRLs, residues were not found in 2 samples (20.0%).

21 **head cabbage** samples were analysed: residues were not found in 21 samples (100.0%).

9 **leek** samples were analysed: residues were not found in 9 samples (100.0%).

25 **lettuce** samples were analysed: one sample (4.0%) exceeded MRLs, four samples (16.0%) contained

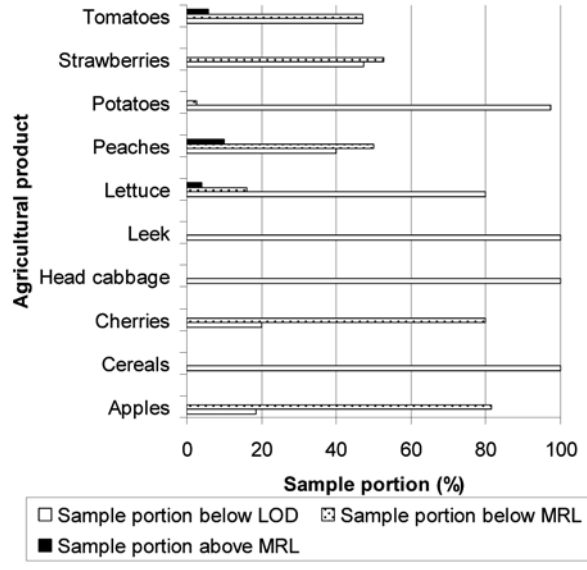


Figure 1: Pesticide residues in different agricultural products in 2007

Table 2: List of agricultural products, analysed in 2007, and distribution of sample locations among individual production areas

Area	Agricultural product										Sum
	Apples	Cereals	Cherries	Head cabbage	Leek	Lettuce	Peaches	Potatoes	Strawberries	Tomatoes	
Celje	3	0	0	2	1	4	0	3	2	2	17
Koper	3	0	3	1	1	3	4	0	0	4	19
Kranj	1	0	0	3	1	2	0	14	1	1	23
Ljubljana	3	1	2	5	3	5	2	6	4	4	35
Maribor	14	4	0	3	1	4	2	6	3	4	41
Murska Sobota	4	5	0	4	0	3	0	3	3	1	23
Nova Gorica	2	0	5	1	1	1	10	0	0	1	21
Novo mesto	13	0	0	2	1	3	2	4	6	0	31
Sum	**43**	**10**	**10**	**21**	**9**	**25**	**20**	**36**	**19**	**17**	**210**

residues lower than MRLs, residues were not found in 20 samples (80.0%).

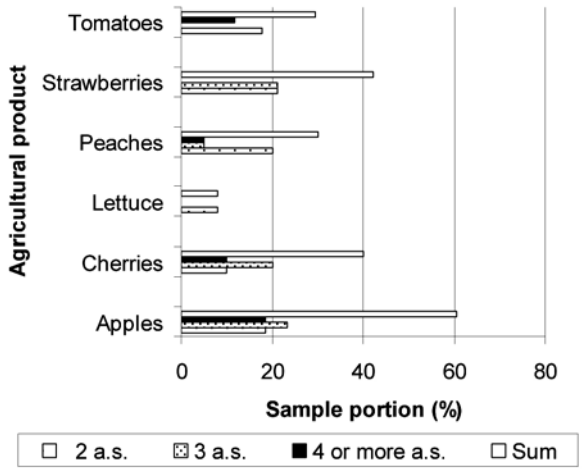
20 **peach** samples were analysed: two samples (10.0%) exceeded MRLs, 10 samples (50.0%) contained residues lower than MRLs, residues were not found in 8 samples (40.0%).

36 **potato** samples were analysed: residues exceeding MRLs were not determined, one sample (2.8%) contained residues lower than MRLs, residues were not found in 35 samples (97.2%).

19 **strawberry** samples were analysed: residues exceeding MRLs were not determined, 10 samples (52.6%) contained residues lower than MRLs, residues were not found in 9 samples (47.4%).

17 **tomato** samples were analysed: one sample (5.9%) exceeded MRLs, 8 samples (47.1%) contained residues lower than MRLs, residues were not found in 8 samples (47.1%).

51 samples (24.3%) out of 210 samples contained **multiple residues**. Residues of two active substances were determined in 8 out of 43 apple samples (18.6%), 1 out of 10 cherry samples (10.0%), 2 out of 25 lettuce samples (8.0%), 4 out of 20 peach samples (20.0%), 4 out of 19 strawberry samples (21.1%) and 3 out of 17 tomato samples (17.6%). Residues of three active substances were determined in 10 out of 43 apple samples (23.3%), 2 out of 10 cherry samples (20.0%), 1 out of 20 peach samples (5.0%) and 4 out of 19 strawberry samples (21.1%). Residues of more than three active substances were determined in 8 out of 43 apple samples (18.6%), 1 out of 10 cherry samples (10.0%), 1 out of 20 peach samples (5.0%), and 2 out of 17 tomato samples (11.8%).



a.s. stands for active substances

Figure 2: Distribution of samples with multiple residues in 2007

The contribution of samples with multiple residues was 60.5% (26 samples) for apples, 40.0% (4 samples) for cherries, 8.0% (2 samples) for lettuce, 30.0% (6 samples) for peaches, 42.1% (8 samples) for strawberries and 29.4% (5 samples) for tomatoes.

The increased rates of detection of plant protection product residues can be partly explained by the enhanced analytical capabilities of the laboratory. This development is reflected by the continuously increasing numbers of active substances sought in the analytical screens. In spite of this, in 2007, the highest number of different residues in one sample was 5, while in 2006, the highest number was 9.

Residues of one active substance were found in potato samples while no residues were found in cereals, head cabbage and leek. The results are shown in Figure 2.

In 2007, apple, cereal, cherry, head cabbage, leek, lettuce, peach, potato, strawberry and tomato samples contained the following **active substances**: fludioxonil, folpet, metalaxyl, propyzamide, terbuthylazine, thiamethoxam and trifloxystrobin each in one sample (0.5%), cyhalotrin-lambda and imidacloprid each in 2 samples (1.0%), boscalid, dimethoate and lufenuron each in 3 samples (1.4%), acetamiprid, difenoconazole and omethoate each in 4 samples (1.9%), azoxystrobin in 5 samples (2.4%), bitertanol, pyrimethanil and thiacloprid each in 6 samples (2.9%), chlorothalonil in 7 samples (3.3%), spirodiclofen in 8 samples (3.8%), cyprodinil, diazinon and fenhexamid each in 10 samples (4.8%), captan in 12 samples (5.7%), chlorpyrifos in 16 samples (7.6%), maneb group in 22 samples (10.5%) and phosalone in 24 samples (11.4%). The results are given in Table 3 and Fig. 3.

Active substances exceeding MRLs were the following: acetamiprid, chlorothalonil and folpet in one sample (0.5%) and captan in 2 samples (1.0%). The re-

Table 3: Number of active substances found in each matrix analysed in 2007 and portion of each active substance found

Active substance	Apples	Cereals	Cherries	Head cabbage	Leek	Lettuce	Peaches	Potatoes	Strawberries	Tomatoes	Sum	Sample portion (%)
Acetamiprid	**1**	0	0	0	0	0	0	0	0	**3**	**4**	**1.9**
Azoxystrobin	0	0	0	0	0	0	0	0	**1**	**4**	**5**	**2.4**
Bitertanol	**2**	0	**4**	0	0	0	0	0	0	0	**6**	**2.9**
Boscalid	**3**	0	0	0	0	0	0	0	0	0	**3**	**1.4**
Captan	**10**	0	0	0	0	0	**2**	0	0	0	**12**	**5.7**
Chlorothalonil	0	0	0	0	0	**1**	0	0	**4**	**2**	**7**	**3.3**
Chlorpyrifos	**15**	0	0	0	0	0	**1**	0	0	0	**16**	**7.6**
Cyhalotrin-lambda	0	0	0	0	0	0	0	0	0	**2**	**2**	**1.0**
Cyprodinil	**2**	0	0	0	0	0	0	0	**8**	0	**10**	**4.8**
Diazinon	**10**	0	0	0	0	0	0	0	0	0	**10**	**4.8**
Difenoconazole	0	0	0	0	0	**1**	0	0	**1**	**2**	**4**	**1.9**
Dimethoate	0	0	**3**	0	0	0	0	0	0	0	**3**	**1.4**
Fenhexamid	0	0	0	0	0	0	**4**	0	**3**	**3**	**10**	**4.8**
Fludioxonil	0	0	0	0	0	0	0	0	**1**	0	**1**	**0.5**
Folpet	0	0	0	0	0	0	**1**	0	0	0	**1**	**0.5**
Imidacloprid	0	0	0	0	0	0	0	0	0	**2**	**2**	**1.0**
Lufenuron	**2**	0	0	0	0	0	**1**	0	0	0	**3**	**1.4**
Maneb group	**12**	0	**3**	0	0	**1**	**4**	**1**	**1**	0	**22**	**10.5**
Metalaxyl	0	0	0	0	0	0	0	0	**1**	0	**1**	**0.5**
Omethoate	0	0	**4**	0	0	0	0	0	0	0	**4**	**1.9**
Phosalone	**19**	0	**1**	0	0	0	**4**	0	0	0	**24**	**11.4**
Propyzamide	0	0	0	0	0	**1**	0	0	0	0	**1**	**0.5**
Pyrimethanil	**4**	0	0	0	0	0	0	0	**2**	0	**6**	**2.9**
Spirodiclofen	**8**	0	0	0	0	0	0	0	0	0	**8**	**3.8**
Terbuthylazine	0	0	0	0	0	**1**	0	0	0	0	**1**	**0.5**
Thiacloprid	**1**	0	**1**	0	0	**1**	**3**	0	0	0	**6**	**2.9**
Thiamethoxam	0	0	0	0	0	**1**	0	0	0	0	**1**	**0.5**
Trifloxystrobin	**1**	0	0	0	0	0	0	0	0	0	**1**	**0.5**

Table 4: Number of active substances exceeding maximum residue levels in 2007 in each analysed matrix and portion of each exceeded active substance

Active substance	Apples	Cereals	Cherries	Head cabbage	Leek	Lettuce	Peaches	Potatoes	Strawberries	Tomatoes	Sum	Sample portion (%)
Acetamiprid	0	0	0	0	0	0	0	0	0	**1**	**1**	**0.5**
Captan	0	0	0	0	0	0	**2**	0	0	0	**2**	**1.0**
Chlorothalonil	0	0	0	0	0	**1**	0	0	0	0	**1**	**0.5**
Folpet	0	0	0	0	0	0	**1**	0	0	0	**1**	**0.5**

sults are shown in Table 4. The acetamiprid content in tomato sample was 0.23 mg/kg (MRL is 0.10 mg/kg). The captan content in each peach sample was 0.04 mg/kg (MRL is 0.02 mg/kg). The chlorothalonil content in lettuce sample was 0.05 mg/kg (MRL is 0.01 mg/kg). The folpet content in peach sample was 0.03 mg/kg (MRL is 0.02 mg/kg). One peach sample exceeded MRLs for captan and folpet.

Active substances not registered in the Republic of Slovenia were found in lettuce (terbuthylazine, thiacloprid), peaches (captan, chlorpyriphos, folpet) and strawberries (pyrimethanil).[11]

Active substances not allowed in the integrated production in the Republic of Slovenia[12–14] and a**ctive substances not allowed in the ecological production** in the Republic of Slovenia were not found.

The comparison made in the years 2001 to 2007 for active substances found (Table 5) shows that only diazinon, maneb group and phosalone were determined each year. The increased rates of residue detections in the years 2001 to 2007 can be partly explained by enhanced analytical capabilities of the laboratory. This development is

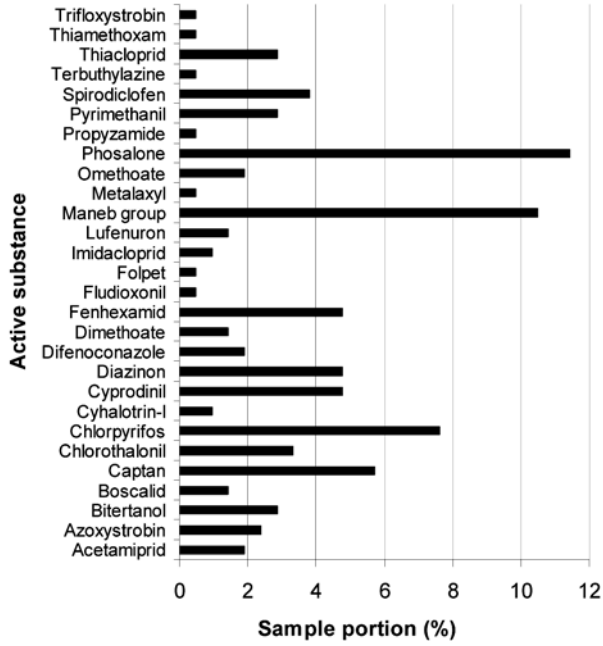


Figure 3: Samples with active substances found in 2007

Table 5: Portion of active substances found in the years 2001 to 2007

Active substance	Sample 2001	Portion 2002	(%) 2003	2004	2005	2006	2007
Acetamiprid	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	**1.9**
Azoxystrobin	n.a.	n.a.	**0.3**	**0.8**	n.d.	**2.2**	**2.4**
Bitertanol	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	**2.9**
Boscalid	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	**1.4**
Bromopropylate	n.a.	n.a.	**0.6**	**0.3**	n.d.	n.d.	n.d.
Captan	**2.6**	**2.0**	n.d.	**5.8**	**7.0**	**4.4**	**5.7**
Chlorothalonil	n.a.	n.a.	n.d.	**0.3**	**2.6**	**5.0**	**3.3**
Chlorpropham	n.a.	n.a.	n.a.	n.a.	**0.9**	n.d.	n.d.
Chlorpyrifos	n.d.	n.d.	n.d.	n.d.	**3.5**	**4.4**	**7.6**
Chlorpyrifos-methyl	n.d.	**1.3**	**0.6**	**1.7**	**2.6**	n.d.	n.d.
Cyhalotrin-lambda	**0.7**	n.d.	n.d.	**0.3**	n.d.	n.d.	**1.0**
Cyprodinil	n.a.	n.a.	n.a.	**3.3**	**2.6**	**10.5**	**4.8**
Diazinon	**4.0**	**4.7**	**3.3**	**6.4**	**10.4**	**5.0**	**4.8**
Dichlofluanid	n.a.	n.a.	**0.6**	**0.6**	n.d.	**0.6**	n.d.
Difenoconazole	n.a.	n.a.	n.a.	n.a.	n.a.	**1.1**	**1.9**
Dimethoate	**1.3**	**3.3**	**0.3**	n.d.	n.d.	n.d.	**1.4**
Diphenylamine	n.a.	n.a.	n.a.	n.d.	n.d.	**0.6**	n.d.
Fenazaquin	n.a.	n.a.	n.a.	n.a.	n.a.	**2.8**	n.d.
Fenhexamid	n.a.	n.a.	n.a.	n.a.	n.a.	**3.3**	**4.8**
Fludioxonil	**0.7**	**0.7**	**1.4**	**2.5**	n.d.	**2.8**	**0.5**
Folpet	**0.7**	n.d.	**2.2**	**1.4**	**0.9**	**10.5**	**0.5**
Imidacloprid	n.a.	n.a.	n.a.	n.a.	n.a.	**1.1**	**1.0**
Iprodione	**2.0**	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Lufenuron	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	**1.4**
Kresoxim-methyl	n.a.	n.a.	n.a.	n.d.	n.d.	**0.6**	n.d.
Maneb group	**17.2**	**42.0**	**15.0**	**15.5**	**20.9**	**22.7**	**10.5**
Metalaxyl	n.d.	**1.3**	n.d.	**0.3**	n.d.	**2.2**	**0.5**
Myclobutanil	n.a.	n.a.	n.a.	n.d.	n.d.	**1.1**	n.d.
Omethoate	n.a.	n.a.	n.d.	n.d.	n.d.	n.d.	**1.9**
Phosalone	**4.0**	**17.3**	**4.4**	**5.3**	**7.8**	**10.5**	**11.4**
Pirimicarb	n.a.	n.a.	n.a.	n.a.	**0.9**	n.d.	n.d.
Pirimiphos-methyl	**0.7**	**0.7**	n.d.	n.d.	n.d.	n.d.	n.d.

Active substance	Sample 2001	Portion 2002	(%) 2003	2004	2005	2006	2007
Procymidone	**2.0**	**2.7**	**0.6**	**0.6**	**0.9**	**1.7**	n.d.
Propyzamide	n.a.	n.a.	n.d.	n.d.	n.d.	n.d.	**0.5**
Pyrimethanil	n.a.	n.a.	n.a.	**1.7**	n.d.	**6.6**	**2.9**
Spirodiclofen	n.a.	n.a.	n.a.	n.a.	n.a.	**3.3**	**3.8**
Tebufenozide	n.a.	n.a.	n.a.	n.a.	n.a.	**2.2**	n.d.
Terbuthylazine	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	**0.5**
Thiacloprid	n.a.	n.a.	n.a.	n.a.	n.a.	**1.7**	**2.9**
Thiamethoxam	n.a.	n.a.	n.a.	n.a.	n.a.	n.d.	**0.5**
Tolylfluanid	n.a.	n.a.	n.d.	**7.2**	**13.9**	**7.2**	n.d.
Trifloxystrobin	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	**0.5**
Vinclozolin	**4.6**	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.a. means not analysed n.d. means not detected

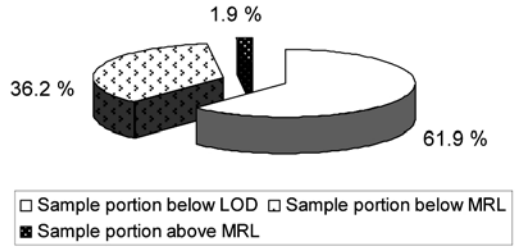


Figure 4: Results of monitoring in 2007

reflected by the continuously increasing numbers of active substances sought in the analytical screens.

In 2007, 130 samples (61.9%) out of 210 samples analysed did not contain any residue or their contents were below the limit of detection of the method, 76 samples (36.2%) contained residues lower or equal to MRLs and 4 samples (1.9%) contained residues above MRLs (Fig. 4).

The results of monitoring obtained from 2001 to 2006 are very similar to the results obtained in 2007 for the two groups: residues below limit of detection and residues below MRL. For the group of exceeded MRLs the percentage was reduced in 2007. From 2001 to 2006, 958 samples were analysed: 553 samples (57.7%) did not contain any residue or the contents were below the limit of detection of the method, 346 samples (36.1%) contained residues lower or equal to MRLs and 59 samples (6.2%) contained residues above MRLs.

A closer picture for apples, lettuce and potatoes (the only products sampled each year) during the period 2001 to 2007 is presented in Tables 6–8. In case of apples we can see, that the highest portion of samples contains pesticide residues, with the highest exceedances of 5.9% in 2005. In case of potatoes and lettuce the highest portions of samples are without residues. For lettuce, significant exceedances occurred only in 2001. For potatoes, significant exceedances occurred from 2001 to 2003.

Table 6: Pesticide residues in apples for the period 2001–2007

	Sample portion below LOD (%)	Sample portion below MRL (%)	Sample portion above 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

Table 7: Pesticide residues in lettuce for the period 2001–2007

	Sample portion below LOD (%)	Sample portion below MRL (%)	Sample portion above 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

Table 8: Pesticide residues in potatoes for the period 2001–2007

	Sample portion below LOD (%)	Sample portion below MRL (%)	Sample portion above 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

Table 9: Portion of active substances found in the years 2001 to 2007 for different sampling regions

	Sample portion of active substances found (%)							
Region / year	**2001**	**2002**	**2003**	**2004**	**2005**	**2006**	**2007**	**Average**
Celje	35.7	20.0	21.7	31.4	38.9	56.3	58.8	37.5
Koper	7.1	16.7	11.8	64.3	16.7	46.7	47.4	30.1
Kranj	19.0	23.5	22.2	33.3	40.0	5.3	17.4	23.0
Ljubljana	22.2	21.4	20.8	41.7	13.3	43.5	34.3	28.2
Maribor	29.2	14.8	13.3	43.5	45.5	48.6	39.0	33.4
Murska Sobota	20.0	30.0	29.4	57.1	50.0	40.7	52.2	39.9
Nova Gorica	33.3	33.3	50.0	100.0	87.5	78.6	47.6	61.5
Novo mesto	16.1	16.7	33.3	50.0	45.5	56.7	51.6	38.6

In 2001 to 2007 we found the highest percentage of active substances according to the amount of samples taken in the region of Nova Gorica. The reason lies probably in the fact that in this region mainly fruit is grown. The fruit usually contains the highest amount of different active substances. The results are presented in Table 9.

Through the years we observed:

– The highest number of active compounds are found in fruit. The farmers have to protect it against rot, mould and insects, otherwise the fruit would not grow.
– Farmers learned to use the plant protection products according to good agricultural practice, which results in lower MRL exceedances.
– The increasing number of active substances found in one sample is probably due to the increased number of active substances sought.

4. Conclusions

Levels of pesticide residues in agricultural products in Slovenia in 2007 do not give any cause for alarm. 61.9% samples examined did not contain any residues. Exceeding maximum residue levels were found in 1.9% samples of agricultural products. The risk assessment for all samples exceeding MRLs showed that the agricultural products did not represent any risk for health and were therefore safe for the consumers.

For comparison, the results of national monitoring, performed in the EU countries and in Norway, Iceland and Liechtenstein in 2005, are presented.[15] They have shown that 51% of all examined fresh (unprocessed) fruit, vegetable and cereals samples did not contain pesticide residues, 44% of fresh (unprocessed) samples contained residues lower or equal to MRLs and 4.9% of examined fresh (unprocessed) samples contained residues above MRLs.[15] The results for 2006 and 2007 are not available yet.

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.

6. References

1. Law on Plant Protection Products, Official Gazette of the Republic of Slovenia No. 98, 09.09.**2004**, pages 11885 – 11899.
2. Regulation on Pesticide Residues in/on Foodstuffs and Agricultural Products, Official Gazette of the Republic of Slovenia No. 84, 30.07.**2004**, pages 10210–10226.
3. Commission recommendation concerning a coordinated Community monitoring programme for 2006 to ensure compliance with maximum levels of pesticide residues in and on cereals and certain other products of plant origin and national monitoring programmes for 2007, EN SANCO/10235/2006 rev 3, Brussels, 18.10.**2006**
4. H. Baša Česnik, A. Gregorčič, *Research Reports Biotechnical Faculty University of Ljubljana, Agriculture, Zootechny*, **2003**, *82*, 167–180.
5. H. Baša Česnik, A. Gregorčič, Š. Velikonja Bolta, & V. Kmecl, *Food Addit. Contam.*, **2006**, *23*, 164–173.
6. H. Baša Česnik, A. Gregorčič, *Acta chim. slov.*, **2006**, *53*, 100–104.
7. General Inspectorate for Health Protection, Ministry of Public Health, Welfare and Sport, *Analytical methods for pesticide residues in foodstuffs*, Netherlands **1996**, part 2, 1–4.
8. R. Bossi, K. V. Vejrup, B. B. Mogensen, A. H. Asman, *J. Chromatogr. A*, **2002**, *957*, 27–36.
9. D. Ortelli, P. Edder, C. Corvi, *Anal. chim. Acta,* **2004**, *520*, 33–45.
10. S. J. Lehotay, A. de Kok, M. Hiemstra, P. Bodengraven, *J. AOAC Int.,* **2005**, *88*, 595–614.
11. *FITO-INFO, Informacijski sistem za varstvo rastlin*. Taken in 2007 from http://spletni2.furs.gov.si/FFS/REGSR/index.htm
12. *Tehnološka navodila za integrirano pridelavo zelenjave za leto 2007*, MAFF, **2007**, edited by Tomaž Džuban.
13. *Tehnološka navodila za integrirano pridelavo poljščin za leto 2007*, MAFF, **2007**, edited by Tomaž Džuban.

14. *Tehnološka navodila za integrirano pridelavo sadja za leto 2007*, MAFF, **2007**, edited by Tomaž Džuban.
15. *Monitoring of pesticide residues in products of plant origin in the European union, Norway, Iceland and Liechtenstein,* **2007**. Taken 14.03.2008 from http://ec.europa.eu/food/fvo/specialreports/pesticides_index_en.htm

Povzetek

V letu 2007 smo na ostanke pesticidov analizirali 210 vzorcev jabolk, žit, češenj, glavnatega zelja, pora, solate, breskev, krompirja, jagod in paradižnika slovenskih tržnih pridelovalcev. Vse vzorce smo analizirali s štirimi analitskimi metodami na prisotnost 118 različnih aktivnih spojin. V štirih vzorcih (1,9%) smo določili presežene maksimalno dovoljene količine ostankov, kar je boljše od rezultatov monitoringa ostankov pesticidov v rastlinskih proizvodih v Evropski skupnosti, Norveški, Islandiji in Lihtenštajnu v letu 2005 (4,9%). Trendi, ki smo jih opazili skozi leta so, da največ ostankov pesticidov ugotovimo v sadju, da določimo manj vzorcev s preseženimi MRL in, da število najdenih aktivnih snovi v enem vzorcu narašča.