POLISH MONITORING OF PESTICIDE RESIDUES IN CROPS

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ABSTRACT

Polish monitoring of pesticide residues in crops conducted during the 6-year period 1996-2001 encompassed 34 crops and 91 pesticides including their derivatives. 13 406 samples of domestic crops were analysed. Overall, 63 compounds were found in 21,4% of the controlled samples. The residues were mainly detected in the greenhouse vegetable (27,1%) and fruit (26,6%) samples. Field vegetables and arable crops were less contaminated by residues. Respectively, 13,4% and 4,4% of samples of these crops contained residues. The residues occurred in the samples of raspberries (50,6%), field tomatoes (43,0%), greenhouse tomatoes (40,8%), strawberries (38,3%) and currants (33,0%) most often. The most frequently found pesticides were the dithiocarbamate fungicides, chlorothalonil, procimidone, tolylfluanid, dichlofluanid, endosulfan, carbendazim and linuron. Their residues were present in more than 10% of samples of some crops. Violations of Polish MRLs were found in 0,9% of samples.

Key words: arable crops, fruits, pesticide residues, vegetables

IZVLEČEK

MONITORING OSTANKOV FITOFARMACEVTSKIH SREDSTEV V KMETIJSKIH PRIDELKIH NA POLJSKEM

Monitoring za ostanke fitofarmacevtskih sredstev v pridelkih je bil l. 1971 izdelan na Inštitutu za varstvo rastlin - Plant Protection Institute (PPI) v sodelovanju z UNDP/FAO. Monitoring se izvaja od l. 1995, pod nadzorom Glavnega inšpektorata za varstvo rastlin - Main Inspectorate of Plant Protection (MIPP). V monitoring je vključenih 6 laboratorijev omenjenega inštituta. Program monitoringa vključuje fitofarmacevtska sredstva, ki jih pridelovalci na Poljskem največ uporabljajo in pridelke, ki so za prehrano bistvenega pomena, s poudarkom na pridelkih iz intenzivne pridelave (iz rastlinjakov in sadovnjakov). Na področju vse države letno naključno vzamejo približno 2200 vzorcev pridelkov. Vzorce zbirajo strokovnjaki iz območnih enot inšpektorata. Vzorce analizirajo takoj, ko je mogoče, najpozneje v 3-4 tednih. Rezultate analiz na ostanke zbirajo deželni inšpektorati provinc - Province Plant Protection Inspectorates (PPPI). V primeru, da ostanki presegajo najvišjo dovoljeno mejo (MRL), so laboratoriji dolžni o tem takoj obvestiti PPPI in MIPP. Končno poročilo o monitoringu konec leta oddajo na MIPP.
Od 1996-2001 je bilo zbranih 13 406 vzorcev pridelkov iz domače pridelave. Monitoring je obsegal 31 vrst pridelkov in 89 fitofarmacevtskih sredstev. 21 % analiziranih vzorcev je vsebovalo ostanke fitofarmacevtskih sredstev. Najdenih je bilo 60 aktivnih snovi. Ostanke so našli predvsem v zelenjavi iz rastlinjakov (27 %) in sadju (27 %), redko pa v zelenjavi s polja (13 %) in drugih pridelkih, npr. koruzi in krompirju (4 %). Največkrat so ostanke našli v vzorcih malin (51 %), paradižnika iz rastlinjakov in s polja (41 in 43 %), jagodah (38 %) in ribezu (33 %). Ostanki enega fitofarmacevtskega sredstva so bili najdeni v manj kot 10 % vzorcev posameznih pridelkov. Le ostanke ditiokarbamatov, klortalonila, procimidona, tolilfluanida, diklofluanida, endosulfana, MBC in linurona so večkrat našli v vzorcih iste vrste pridelkov. Glede na veljavne predpise na Poljskem, je bila vsebnost ostankov pesticidov čez dovoljeno mejo v 0,8 % vzorcev, po EU direktivah pa je bilo kršitev več (2,2 %).

Ključne besede: poljščine, sadje, ostanki fitofarmacevtskih sredstev, vrtnine

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1 INTRODUCTION

The Polish system of monitoring of pesticide residues in foodstuff of plant origin have been established in the Institute of Plant Protection (IPP) in 1971 as a result of the co-operation agreement between the Polish Government and the FAO/UNDP organization. These organizations equipped the IPP laboratories with analytical instrumentation, trained their staff in recognized foreign laboratories and helped to design the first national monitoring programme for pesticide residues.
At present, the network of six IPP laboratories conducts these studies. The laboratories are located in Poznan, Białystok, Rzeszow, Sosnicowice, Torun and Trzebnica. Their activities are coordinated by the IPP Department of Pesticide Residue Research in Poznan. The purpose of the studies is to determine if the pesticide residues are present in and on Polish-produced fruits, vegetables, and arable crops if so, to determine if residues violated maximum residue limits (MRLs) permitted under the Polish regulations[2]. Overall, 2000 samples of domestic crops are controlled every year. The monitoring is especially concentrated on those crops where residues are likely to be found (greenhouse vegetables and fruits).

2 MATERIALS AND METHODS

In the years 1996-2001, totally 13 406 samples of mature crops were analysed. 4412 greenhouse vegetable, 3222 field vegetable, 4464 fruit and 1308 arable crop samples were randomly taken from the production sites on the territory of the whole country by the extension officers of the regional plant protection inspectorates. The monitoring covered 34 crops and 91 pesticides including their derivatives. The frequency of monitoring depended on importance of the commodity in the diet and the likelihood of finding residues. The monitoring programme was slightly changed from year to year. A distinct analytical programme was performed for each commodity. Table 1 shows the number of samples analysed for each commodity. The sought pesticides are listed in table 2.

The unwashed edible portion of the sample was analysed as received, expect that any adhering soil was removed with light rubbing. Loose outer leaves of onions, cabbage, and lettuce were also removed. The samples were analysed by using internationally recommended and validated methods, first of all multiresidue methods that could simultaneously detect a large number of pesticides. The multi-residue method based on extraction with acetone, partition to dichloromethane and solid phase extraction (SPE) clean up was mainly used. The determination of residues was performed by capillary column gas chromatography with NPD/ECD and high performance liquid chromatography with UV/DAD. Alternative GC columns and detectors, especially mass selective detector (MSD), were used for confirmation of the results. Several compounds were analysed by individual methods, i.e. benomyl group determined as carbendazim and linuron. The dithiocarbamates were determined by distillation of CS_2 and measured by a spectrophotometer.
Samples were analysed in six IPP laboratories. The laboratories implement the quality system compliant with ISO/IEC 17025. Since 1996 regularly, they participate with positive results in home (National Institute of Hygiene) and international (EU, FAPAS) proficiency tests on pesticide residues. The studies were conducted according to the rules described in “Quality control procedures for pesticide residues analyses. Guidelines for residues monitoring in the European Union. Second edition. Document No. SANCO/1303/2000”.

[2] Decree of the Minister of Health and Welfare from 15.04.1997

Table 1: Analysed crops

Crop	Number of analysed samples							% of samples	
	1996	1997	1998	1999	2000	2001	Totally	A*	B**
Greenhouse vegetables	759	769	737	682	765	700	4412	32,9	
Cucumber	204	263	220	194	218	202	1301		29,5
Radish		8	4				12		0,3
Lettuce	138	101	112	102	110	111	674		15,3
Mushroom	19	65	67	59	78	58	346		7,8
Pepper, sweet	67	69	64	54	42	34	330		7,5
Tomato	331	263	270	273	317	295	1749		39,6
Field vegetables	668	473	492	557	495	537	3222	24,0	
Asparagus		8	11	11	10	7	47		1,5
Broccoli				2			2		0,1
Carrot	104	102	90	118	116	127	657		20,4
Cauliflower	24		17	20	20	37	118		3,7
Celery	53	14	1				68		2,1
Chinese cabbage				5		2	7		0,2
Cucumber	199	84	118	105	115	121	742		23,0
Dill		1					1		<0,1
Green peas	20	1					21		0,7
Head cabbage	83	140	117	159	118	107	724		22,5
Leek	19						19		0,6
Lettuce						3	3		0,1
Onion	25	46	71	59	70	66	337		10,5
Parsley	27	5	3			1	36		1,1
Red beet	51	35	20	19	14	8	147		4,6
String bean		8	1				9		0,3
Tomato	63	29	43	59	32	58	284		8,8
Fruits	825	732	758	719	707	723	4464	33,3	
Apple	283	294	290	292	289	287	1735		38,9
Cherry	53	81	114	82	98	102	530		11,9
Currant	149	53	47	67	48	42	406		9,1
Gooseberry		1					1		<0,1
Pear		4	2				6		0,1
Plum		53	61	41		12	167		3,7
Raspberry		25	15	15	15	15	85		1,9
Strawberry	340	221	229	222	257	265	1534		34,4
Arable crops	204	240	218	245	236	165	1308	9,8	
Cereals	41	41	37	27	21	17	184		14,1
Potato	163	199	181	213	215	148	1119		85,5
Sugar beets				5			5		0,4

* - % of crop groups in total quantity of analysed samples
**- % of individual crops in crop groups

Successively, the reports on the residues studies were sent to Province Plant Protection Inspectorates and The Main Inspectorate of Plant Protection. They were used to enforce the proper use of plant protection products in Poland. Information on the detection of MRLs violations were immediately transmitted to the inspectorates mentioned above.

Table 2: Pesticides and derivatives sought

Insecticides - 48 compounds	bifenthrin*, bromopropylate*, buprofezin, chlorfenvinphos*, chlorpyrifos* ,chlorpyrifos-methyl*, cyfluthrin, cypermethrin*, deltamethrin*, diazinon*, dichlorfos*, diflubenzuron, dimethoate*, α-endosulfan*, β-endosulfan *, endosulfan sulphate*, esfenwalerate, fenitrotion*, fenpropathrin*, fenthion, fenwalerate, formothion, heptenophos, , izofenphos, malathion*, methidathion, methomyl*, parathion-methyl, metoxychlor*, o,p'-DDT, p,p'- DDD*, p,p'-DDE*, p,p'-DDT, permethrin, phosalone*, pirimicarb*, pirimiphos-methyl*, propoxur*, thiometon, tetradifon*, trichlorfon, α-cypermethrin*, α-HCH*, β-HCH*, δ-HCH*, HCB, γ-HCH*, λ-cyhalothrin*
Fungicides - 31 compounds	Dithiocarbamates expressed as CS_2* (maneb, mancozeb, metiram, propineb, thiram, zineb), benomyl group determined as carbendazim* (benomyl, carbendazim, thiofanate-methyl), azoxystrobin*, bitertanol*, bupirimate, captan*, chlorothalonil*, cyprodinil, dichlofluanid*, dithianon*, difenoconazole*, dimethomorph, fenarimol*, flusilazole*, iprodione*, metalaxyl*, pyrimethanil*, prochloraz*, procimidone*, pyrazophos, tolylfluanid*, triadimefon*, trifloxystrobin*vinclozolin*
Herbicides - 12 compounds	atrazine*, chloridazon, flurochloridone, lenacil, linuron*, metribuzin, napropamide, pendimethalin, prometryn, propachlor, simazine, trifluralin*

* detected compound

3 RESULT AND DISCUSSION

Totally, 78,6 % of the analysed samples had no detectable residues. 63 out of 91 sought compounds were found in and on 21,4% of the samples (Fig.1, tab.2). The residues were detected in 27,1% of the greenhouse vegetable and 26,6% of the fruit samples. Only 13,4% of the field vegetable and 4,4 % of the arable crop samples contained the residues. The decrease in frequency of the residues occurrence in fruit and vegetable samples was observed in the third year of studies. In the last four years percentage of findings in these groups of crops was similar.

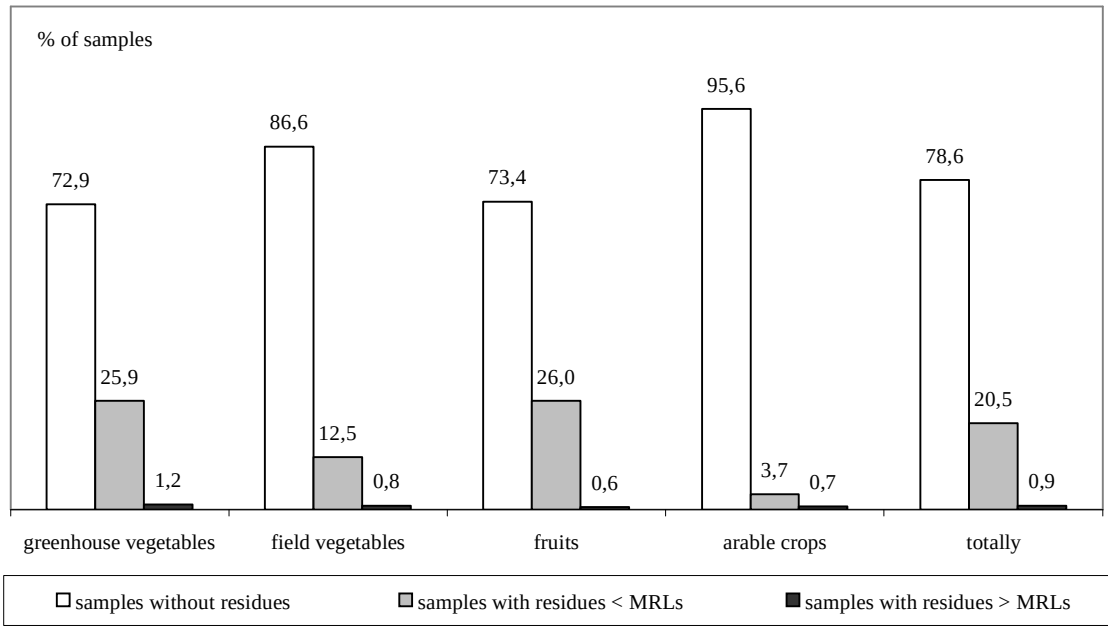

Fig.1: Pesticide residues in crops (1996-2001)

The samples of 26 crops were contaminated by pesticides residues. No residues were found in 8 crops. Most often, the residues were detected in the raspberry, field tomato, greenhouse tomato, strawberry and currant samples. The information on the occurrence of residues both in the individual crops and groups of crops is shown in table 3.

Table 3: Pesticide residues in groups of crops and individual crops

Crop	% of samples with residues						
	1996	1997	1998	1999	2000	2001	1996-2001
Greenhouse vegetables	36,6	41,2	23,6	19,6	17,5	22,7	27,1
Tomato	52,9	60,1	38,5	34,4	24,6	35,6	40,8
Pepper, sweet	9,0	65,2	29,7	16,7	7,1	23,5	27,3
Lettuce	26,1	45,5	12,5	19,6	21,8	18,9	23,9
Mushroom	68,4	16,9	10,4	6,8	28,2	20,7	19,9
Cucumber	23,5	21,7	13,6	3,6	3,2	6,4	12,5
Radish		0	0				0
Field vegetables	19,9	15,4	16,1	5,9	10,5	11,4	13,4
Greek peas	90,0	0					85,7
Tomato	47,6	27,6	62,8	30,5	50,0	39,7	43,0
Carrot	14,4	21,6	30,0	9,3	17,2	15,7	17,5
Leek	15,8						15,8
Cucumber	20,1	15,5	11,0	1,0	11,3	9,1	12,3
Celery	3,8	42,9	0				11,8
Cauliflower	37,5		11,8	5,0	5,0	0	11,0
Head cabbage	18,1	15,0	8,5	0	0	2,8	6,8
Parsley	0	20,0	0			0	2,8
Onion	4,0	2,2	0	1,7	2,9	6,1	2,7
Asparagus		0	0	9,1	0	0	2,1
Red beets	0	2,9	0	0	0	0	0,7
Broccoli				0			0
Chinese cabbage				0		0	0
Dill		0					0
Lettuce						0	0
String bean		0	0				0
Fruits	31,8	38,9	22,6	18,5	22,5	24,3	26,6
Gooseberry		100,0					100,0
Raspberry		64,0	40,0	53,3	53,3	33,3	50,6
Strawberry	54,4	55,2	16,6	26,6	31,1	38,9	38,3
Currant	21,5	24,5	21,3	35,8	64,6	57,1	33,0
Plum		11,3	45,9	12,2		0	23,4
Apple	14,1	40,5	19,3	9,6	8,3	4,3	17,8
Cherry	9,4	9,9	28,9	11,0	16,3	2,9	14,0
Pear		0	0				0
Arable crops	4,9	16,3	2,3	0,8	0	0,6	4,4
Potato	4,9	17,6	2,8	0,9	0	0,7	4,6
Cereals	4,9	9,8	0	0	0	0	3,3
Sugar beets				0			0

The residues of 33 out of 48 sought insecticides and their derivatives, 27 out of 31 sought fungicides and 3 out of 12 sought herbicides were detected (tab. 2). The residues of the dithiocarbamate fungicides, chlorotalonil, procimidone, tolylfluanid, dichlofluanid, endosulfan, benomyl group and linuron were most frequently found. More than 10% of the

samples of some crops contained the residues of these pesticides. The pesticide residues detected in more than 5% of samples of the same crop are presented in tab. 4.

Table 4: Most frequently detected compounds (number of samples with residues > 5%, number of analysed samples > 100)

Compound	Commodity	Number of analysed samples	% of samples with residues
Benomyl group	Mushrooms	136	13
	Greenhouse tomato	175	11
	Apple	1177	6
	Currant	255	5
Captan	Apple	1613	7
Chlorothalonil	Field tomato	262	19
	Greenhouse tomato	1716	19
	Pepper, sweet	156	8
	Field cucumber	720	6
DDT	Carrot	657	7
Dichlofluanid	Strawberry	1534	15
	Greenhouse tomato	1749	7
Dithianon	Apple	214	5
Dithiocarbamates	Field tomato	284	32
	Plum	155	21
	Strawberry	857	20
	Currant	372	19
	Greenhouse lettuce	573	13
	Greenhouse tomato	1741	10
	Mushrooms	288	9
	Cherry	448	6
	Field cucumber	648	6
	Apple	217	5
Endosulfan	Currant	371	15
	Mushroom	288	5
Fenarimol	Cherry	407	7
Fenitrotion	Currant	179	7
Iprodione	Greenhouse tomato	1749	6
	Cherry	477	6
Linuron	Carrot	617	11
Phosalone	Apple	296	8
Procimidone	Pepper, sweet	301	23
	Greenhouse tomato	1716	12
	Strawberry	1534	8
	Greenhouse lettuce	383	8
Tolylfluanid	Strawberry	265	26
	Apple	129	5
Vinclozolin	Strawberry	1269	6

Overall most of the residues detected were well below Polish MRLs. Of all the residues detected, 0,9% were in violation of the MRLs. During six year period, the percent of violative residues dropped from 1,6% in 1996 to 0,1% in 2001. The violations of home MRLs were observed in only 1,3% of the greenhouse vegetable samples. The percent of exceedings in the other groups of crops was even lower and varied from 0,6% - 0,9% (Fig.1). The violative residues of 19 compounds were found in 16 crops. The residues of

dithiocarbamates, chlorothalonil, formothion and metalaxyl accounted for the majority of violations.

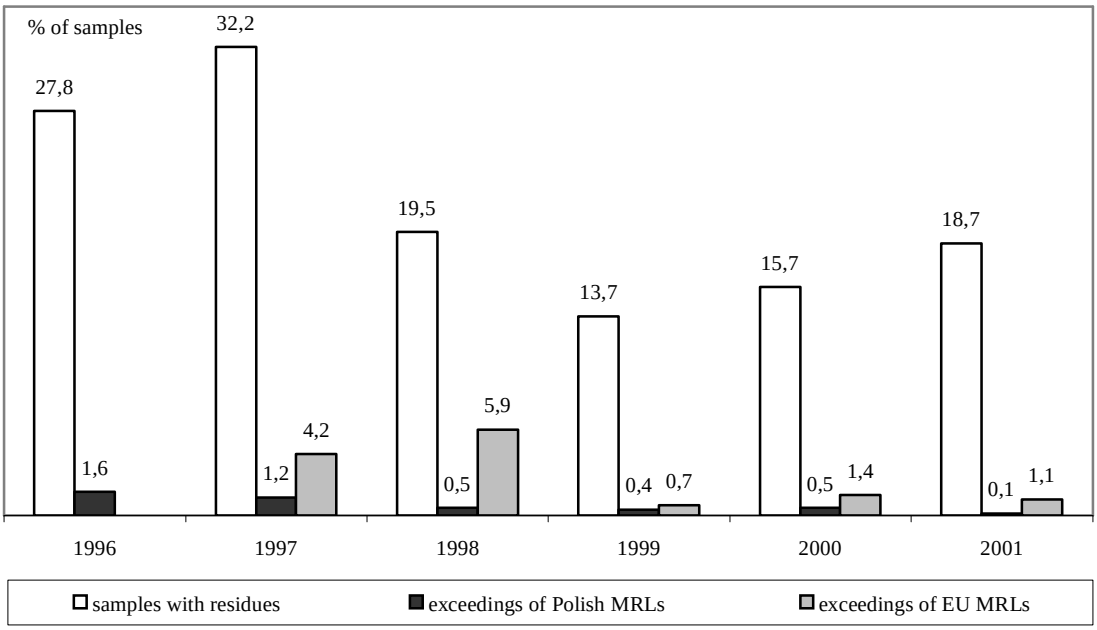

Fig 2: Violations of Polish and EU MRLs

The analysis of the achieved results in the 5 year period 1997-2001 revealed that in the light of EU regulations[3] more detected residues exceeded MRLs (Fig. 2). The percentage of violations of EU MRLs fluctuated from 0,7% (1999) to 5,9% (1998). The liberalization of EU MRLs for dithiocarbamates contributed to lessen existing differences between both regulations, but the significant differences in tolerances both for endosulfan and benomyl in currant still influence the rate of Polish and EU violations considerably. The violations of the EU MRLs were observed for 14 pesticides and 15 crops. The residues of the dithiocarbamate fungicides, metalaxyl, chlorothalonil, endodulfan, fenarimol, chloropiryfos, the benomyl group and methomyl exceeded the EU MRLs most often. Table 5 shows the comparative analysis of Polish and EU violations for the mentioned period.

The amounts of pesticide residues in Polish foodstuffs is still very low which reflects the low usage of plant protection products in Poland (0,6 kg a.i./ha). The decreasing tendency in frequency of pesticide residue occurrence and MRLs violations is supposed to be a result of the better knowledge of growers on the use of pesticide products, the improvement of application techniques (newer equipment and obligatory checks of sprayers), and the efficient enforcement of the rules of good agricultural practice by regional plant protection inspectors. The systematically expanding of integrated production in our country seems to contribute to that as well.
The results of conducted studies are the database on the pollution of Polish crops by pesticide residues, which is the only representative and reliable source of information on that. On the basis of these results the IPP cooperates, in charge of the Ministry of

[3] Council Directives 76/895/EEC, 86/362/EEC, 90/642/EEC

Agriculture, with international organizations such as Codex Alimentarius FAO/WHO and the HELCOM Commission.

Table 5: Violations of Polish and EU MRLs in controlled crops (1997-2001)

Compound	Crop	Number of analysed samples	Samples with residues			
			>Polish MRLs		>EU MRLs	
			Number	%	Number	%
Benomyl group	Currant	255			8	3,1
	Field cucumber	452			2	0,4
	Mushroom	155	2	1,3	2	1,3
Captan	Cherry	477	2	0,4	2	0,4
Chlorothalonil	Cherry	151	1	0,7	1	0,7
	Field cucumber	599	1	0,2	1	0,2
	Greenhouse lettuce	350	1	0,3	4	1,1
	Greenhouse tomato	1716	2	0,1		
	Head Cabbage	407			11	2,7
	Mushroom	327	2	0,6	2	0,6
	Pepper, sweet	118	6	5,1	5	4,2
	Celery	45			1	2,2
Chlorpyrifos	Carrot	553	2	0,4	2	0,4
	Cauliflower	90			3	3,3
	Head Cabbage	642	1	0,2	9	1,4
DDT	Carrot	657	1	0,2	1	0,2
Dichlofluanid	Greenhouse lettuce	589	1	0,2		
	Strawberry	1534	1	0,1		
Dithiocarbamates	Cherry	448	1	0,2	13	2,9
	Currant	257	4	1,6	7	2,7
	Field tomato	221	2	0,9	32	14,5
	Greenhouse cucumber	1290			1	0,1
	Greenhouse lettuce	763	6	0,8	6	0,8
	Greenhouse tomato	1418	12	0,8	63	4,4
	Mushroom	288			23	8,0
	Red beet	142			1	0,7
Endosulfan	Currant	256			21	8,2
	Mushroom	288			1	0,3
Fenarimol	Cherry	509			17	3,3
Iprodion	Greenhouse lettuce	636	1	0,2	1	0,2
λ-cyhalothrin	Cauliflower	74			1	1,4
Linuron	Carrot	617	1	0,2		
Metalaxyl	Greenhouse cucumber	850	6	0,7	29	3,4
	Greenhouse tomato	1252	3	0,2	4	0,3
	Greenhouse lettuce	170			1	0,6
Methomyl	Greenhouse tomato	374			12	3,2
Procimidone	Greenhouse lettuce	383	3	0,8	3	0,8
	Greenhouse tomato	1716	1	0,1		
	Mushroom	37			1	2,7