Pesticide Residues Controls in Soil And Plants for Sustainable Farming in Lombardy

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Introduction

The European Community regulation 817/2004 gives applicative details to the former EU Community regulation 1257/99 to sustain a development of farming without use of certain pesticides. These pesticides have been characterized by an important acute and/or chronic toxicity and by a non optimal degradability of their residues in the environment.

The farmers who accept these regulations on a voluntary basis can obtain an economic support from the EU fund through their member state in order to change their plant protection strategies towards the use of alternative molecules. In addition each member state needs to activate controls to assess eventual misuse of active substances unauthorized by these regulations.

The Lombardy Region of Italy in cooperation with ARPA Lombardia (Regional Environmental Protection Agency) activated analytical controls of pesticide residues in plants and soils at the farms that chose to take part in the Regulation 817/2004 programme.

Materials and methods

The ARPA Laboratory to which the task has been assigned, adopted a multiresidue method (1-3) already used in monitoring pesticide residues in food and validated in the EUPT, FAPAS Proficiency Testing schemes. The original method was modified for rapid screening in order to process more samples in briefer times and to obtain evidence if or not a given treatment has occurred. Method performances (repeatabilities as CV% and recoveries) on soil and leaf matrices respectively are listed below:

Active subst.	Matrix	Target	Operator 1		Operator 2		Mean	
			Value	Z-score	Value	Z-score	Value	Z-score
Diazinon	Carrot [1]	50.4 ± 12.7	55.8	0.4	49.3	-0.09	62.6	0.2
Triazophos	Carrot [1]	253.1 ± 49.9	284.0	0.6	144.1	-2.2	214.0	-0.8
Iprodione	Carrot [1]	108.9 ± 24.3	165.4	2.3	146.0	1.5	155.7	1.9
Vinclozolin	Wine [1]	36.8 ± 9.7	29.2	-0.78	35.0	-0.18	32.1	-0.5
Myclobutanil	Wine [1]	25.9 ± 7.1	31.9	0.84	30.2	-0.60	31.0	-0.7
Propargite	Wine [1]	81.0 ± 18.9	89.4	0.44	83.1	-0.11	86.3	0.3
Chlorpyriphos	Grapes [1]	177.8 ± 36.8	149.9	-0.76	124.2	-1.4	137.1	-1.1
Procymidone	Grapes [1]	375.8 ± 69.5	303.5	-1.0	262.1	-1.6	283.8	-1.3
Bifenthrin	Grapes [1]	133.0 ± 28.8	71.1	-2.1	49.6	-2.9	60.3	-2.5
Dimethoate	Zucchino [2]	1030 ± 164	1190	1.0	1430	2.4	1310	1.7
Diphenylamine	Zucchino [2]	773 ± 128	1260	3.8	1070	2.3	1160	3.1
Deltametryn	Zucchino [2]	235 ± 47	407	3.6	377	3.0	392	3.3
Metosicloro	Zucchino [2]	135 ± 33	316	5.9	306	5.2	311	5.4
Vinclozolin	Zucchino [2]	120 ± 26	207	3.3	179	2.3	193	2.8
Metalaxyl	Zucchino [2]	526 ± 95	642	1.2	632	1.1	637	1.2
Acephate	Cucumber [4]	146 ± 44	144	0	148	0	146	0
Deltametryn	Cucumber [4]	109 ± 22	61	-2.2	62	-2.2	615	-2.15
Diazinon	Cucumber [4]	143 ± 29	167	0.8	150	0.2	159	0.55
Endosulfan	Cucumber [4]	76 ± 15	81	0.3	75	0	78	0.1
Imazalyl	Cucumber [4]	4232 ± 1270	4550	0.25	3090	-0.9	3820	-0.32
Metalaxyl	Cucumber [4]	516 ± 103	468	-0.5	461	-0.5	464.5	-0.5
Methamidophos	Cucumber [4]	627 ± 188	632	0	553	-0.4	593	-0.2
Methomyl	Cucumber [4]	199 ± 24	199	3.3	137	0.7	168	2
Permethrin	Cucumber [4]	540 ± 108	587	0.4	486	-0.5	537	0
Propoxur	Cucumber [4]	262 ± 52	281	0.2	267	0.1	274	0.23
Pirimiphos-Me	Cucumber [4]	50 ± 10	49	-0.1	46	-0.4	48	-0.04
Vinclozolin	Cucumber [4]	216 ± 43	210	-0.1	189	-0.6	200	-0.38
Ethion	Grapes [4]	44.3 ± 11.3	45.35	0.08	47.04	0.23	46.20	0.2
Phosalone	Grapes[4]	88.6 ± 20.4	88.20	-0.02	87.54	-0.06	87.87	-0.03
Iprodione	Grapes[4]	418.8 ± 76.2	404.29	-0.19	427.28	0.11	415.79	-0.04
Metamidophos[5]	Grapes[4]	15.7 ± 4.69	19.94	0.90	18.68	0.63	19.31	0.77
Chloropropham	Potato[4]	110.4 ± 24.6	91.98	-0.7	108.89	-0.1	100.43	-0.4
Chloropropham	Carrot[4]	184.3 ± 37.9	127.9	1.48	150.0	-0.90	138.9	-1.2
Chlorfenvinphos	Carrot[4]	22.0 ± 6.2	19.8	-0.35	22.4	0.06	21.1	-0.1
Iprodione[6]	Carrot[4]	57.6 ± 14.2	30.98	-1.9	27.0	-2.16	29.0	-2.0
Dicloran	Wine[4]	98.0 ± 22.2	75.31	-1.0	61.30	-1.6	68.30	-1.3
Fenarimol	Wine[4]	135.6 ± 29.3	137.18	0.05	114.10	-0.7	125.64	-0.3

Active subst.	Matrix	Target	Operator 1		Operator 2		Mean	
			Value	Z-score	Value	Z-score	Value	Z-score
Carbaryl	Apple[4]	203.3 ± 41.3	253	1.2	413[E]	5.1	333	3.1
Phosalone	Apple [4]	481.8 ± 86.04	272	-2.4	158[D]	-3.8	215	-3.1
Chlorpyriphos	Apple[4]	44.3 ± 9.74	29	-1.5	17[R]	-2.8	23	-2.2
Carbaryl[3]	Apple[4]	203.3 ± 41.3	253	1.2	294	2.2	273	1.7
Phosalone[3]	Apple[4]	481.8 ± 86.04	272	-2.4	466	-0.2	369	-1.2
Chlorpyriphos[3]	Apple[4]	44.3 ± 9.74	29	-1.5	38	-0.6	34	-1.1
Methamidophos	Melon[4]	40.6 ± 8.94	25.6	-1.7	26.0	-1.7	25.8	-1.7
Omethoate	Melon[4]	45.6 ± 10.0	48.3	0.27	58.9	1.05	53.6	0.8
Chloropropham	Ly.potato A[4]	29 ± 7.97	36/45	0.9/2.0	30/38	0.1/1.1	37.3	1.0
Diphenylamine	Ly.potato A[4]	25 ± 7.01	30/30	0.7/0.7	26/25	0.1/0	27.7	0.4
4,4' DDT	Ly.potato A[4]	250 ± 49.2	259/197	0.18/-1.1	208/214	-0.8/-0.7	220	-0.6
Chloropropham	Ly.potato B[4]	29 ± 7.97	32/36	0.4/0.9	37/36	1.0/0.9	35.2	0.8
Diphenylamine	Ly.potato B[4]	21 ± 6.01	18/24	-0.5/0.5	20/23	-0.2/0.3	21.2	0
Dimethoate	Ly.potato B[4]	730 ± 123.6	700/561	-0.2/-1.4	727/636	0/-0.8	656	-0.7
Vinclozolin	Ly.potato B[4]	930 ± 150.7	836/770	-0.6/-1.0	897/797	-0.2/-0.9	825	-0.7
Chloropropham	Ly.potato C[4]	28 ± 7.73	31/45	0.4/2.2	35/36	0.9/1.0	36.7	1.1
Diphenylamine	Ly.potato C[4]	37 ± 9.75	35/39	-0.2/0.2	40/41	0.3/0.4	38.7	0.2
Dimethoate	Ly.potato C[4]	350 ± 64.4	292/243	-0.9/-1.7	360/284	0.2/-1.0	295	-0.8
Vinclozolin	Ly.potato C[4]	440 ± 79.6	410/417	-0.4/-0.3	470/424	0.4/-0.2	430	-0.12

[1] Test material FAPAS 1998/99 proficiency testing
[2] Test material ARPA ANPA1998 proficiency testing
[3] Test material EUPT 1999 proficiency testing
[4] Test material FAPAS 1999 proficiency testing
[5] Test material FAPAS 2000 proficiency testing
[6] Test material (lyophilised potatoes) Region of Lombardy (I)/ International Center for Pesticide Safety 2000 proficiency testing; values corrected for recovery and expressed in mg/Kg of lyophilised potato. Chloropropham and diphenylamine were already present in the vegetable.
[A] Revealed from the method but underestimated and not reported from the operators. Values recalculated after.
[B] Datum obtained by ,qantitation with MS instead of ECD, because of some interferences occurring at the ECD detection at such level
[C] Error in Operator 2 who analised a scarcely homogeneous thawed apple sample portion. See discussion.
[D] Values obtained from Operator 2 after re-analysing a well re-mixed portion of thawed apple sample.

active molecule (detector) leaf matrix	CV%
LINDANE (ECD)	>50%
CHLOROTHALONIL (ECD)	>50%
FENITROTHION (NPD)	7%
CHLORPYRIPHOS (NPD)	5%
CAPTAN (ECD)	30%
FOLPET (ECD)	33%
PROCYMIDONE(ECD)	16%
BIFENTRIN (ECD)	16%
AZINPHOS METHYL (NPD)	7%
PHOSALONE (NPD)	7%
lambda CYHALOTRIN (ECD)	15%
AZINFOS ETHYL (NPD)	7%
PERMETHRIN (ECD)	15%
CIFLUTRIN (ECD)	14%
CYPERMETHRINA (ECD)	14%
FENVALERATE (ECD)	14%
tau-FLUVALINATE (ECD)	15%
DELTAMETHRIN (ECD)	16%
ACEPHATE (NPD+ECD)	24%
OMETHOATE (NPD)	12%
TERBUTHYLAZINE DESETHYL (NPD)	12%
DIMETHOATE (NPD)	12%
TERBUTHYLAZINE (NPD)	11%
MALATHION (NPD)	16%
TOLYLFLUANIDE (NPD+ECD)	25%
METIDATHION (NPD)	12%
TRICYCLAZOLE (NPD)	17%
DINOCAP (ECD)	13%

active molecule (detector) soil matrix	CV%
LINDANE (ECD)	23%
CHLOROTHALONIL (ECD)	46%
FENITROTHION (NPD)	9%
CHLORPYRIPHOS (NPD)	9%
CAPTAN (ECD)	27%
FOLPET (ECD)	22%
PROCYMIDONE(ECD)	20%
BIFENTRIN (ECD)	21%
AZINPHOS METHYL (NPD)	12%
PHOSALONE (NPD)	12%
lambda CYHALOTRIN (ECD)	22%
AZINFOS ETHYL (NPD)	12%
PERMETHRIN (ECD)	19%
CIFLUTRIN (ECD)	21%
CYPERMETHRINA (ECD)	21%
FENVALERATE (ECD)	21%
tau-FLUVALINATE (ECD)	21%
DELTAMETHRIN (ECD)	22%
ACEPHATE (NPD+ECD)	25%
OMETHOATE (NPD)	18%
TERBUTHYLAZINE DESETHYL (NPD)	13%
DIMETHOATE (NPD)	12%
TERBUTHYLAZINE (NPD)	13%
MALATHION (NPD)	12%
TOLYLFLUANIDE (NPD+ECD)	11%
METIDATHION (NPD)	10%
TRICYCLAZOLE (NPD)	17%
DINOCAP (ECD)	18%

Recoveries	
>70%	
40-70%	
<40%	

The clean-up step of the dichloromethanic through extract an NH_2 SPE column may be semplified omitting the subsequent elution with acetonitrile with exception in the case when Acephate, Captan and some other more polar active substances (4) are investigated.

For substances were very low recoveries were obtained only "free pesticide" are detectable: therefore the complete original multiresidue method has to be adopted to detect as much residue as possible

Results and Discussion

In the two years 2004 and 2005 about 350 samples of soil and leaves were collected - mainly from grapes, apples, pears, tomatoes, rice and maize crops. Only in few cases were pesticides detected and in relatively low concentrations, near to the levels allowed in the edible parts (fruits or vegetables) of the plants or the levels chracteristic for environmental contamination (Table 1 on the left). One surprise sample resulted in the finding of azinphos-methyl on apple. Legend: (l) = leaf (s) = soil (l+s) leaf or/and soil. Some of the allowed and widely utilized substances were detected in 10-20% of the samples (Table 2 on the right).

Active substance	Crop	Cases	Amount (mg/kg)
Lambda cyhalothrin	Apple (l)	1	0,02
Fenitrothion	Rice (l)	2	0,01/ 0,2
Azinphos-methyl	Apple (l)	1	21
Procymidone	Apple (l)	2	0,2 / 3

Active substance	% Samples	Crop	Mean / Median (mg/kg)	Range (mg/kg)
Fenitrothion	15%	Maize /(Rice) (l+s)	0.15	0.1 - 0.2
		Apple / Pear (l)	0.19 / 0.20	0.05 - 0.5
		Peach (l)	0.3 / 0.3	0.2 – 0.4
		Grape (l)	12 / 0.8	0.02 - 180
Chlorpyrifos	11 %	Maize / Rice (l+s)	0.03 / 0.02	0.01 – 0.05
		Apple / Pear (l)	1.9 / 0.9	0.1 - 8
		Grape (l)	4.3 / 1.7	0.02 - 23
Procymidone	10%	Maize / Rice (s)	0.01	0.01
		(Apple)/Pear (l)	3.3 / 2.6	0.2 / 12
		Peach (l)	0.06	0.01 – 0.2
		Grape (l)	6.7 / 0.2	0.01 – 90
Terbuthylazine+Terb.desethyl	4%	Maize / Rice (s)	0.15 / 0.11	0.01 – 0.8
Azinphos-methyl	1-2%	Apple / Pear (l)	8.8 / 5	0.5 - 20
Phosalone	1-2%	Apple / Pear (l)	5.5 / 0.5	0.2 - 22
Tolylfluanide	<0.5%	Grape (l)	1	1

Table 2 shows that the mean value for residues of the utilized substances indicatively range within 5-10 times the Maximum Residue Limit in the fruit (for active substances where the MRL is under 1 mg/kg) and 1-2 times the MRL (for active substances where the MRL is above 1-2 mg/kg). Leaves are characterized by a high surface/mass ratio, permitting them to capture and retain large amounts of each active molecule: therefore relatively high concentrations of pesticide residues should be expected, even in cases of environmental / cross contamination from neighbouring fields. Some authors (5) reported that the bioconcentration factor (BCF) for pesticides in leafs is related to the K_{ow} (octanol/water partition)/K_{aw} (air/water partition) ratio, where L is a constant related to the leaf lipid content:

$$BCF = L \times (K_{ow} / K_{aw})$$

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