RESIDUE ANALYSIS OF PESTICIDES COMMONLY USED BY LEBANESE FARMERS ON STRAWBERRIES

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ABSTRACT

Strawberry plantations are vulnerable to attacks by insect pests and pathogens especially when grown under greenhouses. Pesticides are therefore used extensively to save the crops. A pesticide residue survey was conducted in strawberry production areas in Lebanon. Extracted residues were quantified by GC – ECD. Results show variation in residue levels, with some locations exceeding permissible levels.

Keywords : pesticide residues, strawberry, Lebanon

INTRODUCTION

Pesticides play an important role in the production of fruits and vegetables grown in greenhouses or in the open field. FAO/OMS (1993) has published maximum permissible residue levels (MRLs) for pesticides in different commodities. In Lebanon, the total area of strawberries cultivated in greenhouses or in the open field is 136 hectars. According to local farmers different pesticides are used within this small area without adhering to recommended guidelines and practices (Kfoury and El-Amil, unpublished). The risk of *Pythium* sp. or *Phytophtora* sp. attacks, causing root rot, or by *Botrytis cinerea* causing fruit rot, require chemical interventions (Hennion and Veschambre, 1997) in order to control these diseases. The same applies for the control of spider mites and thrips, which are equaly dangerous. Thus, the evaluation of the sanitary status of the marketed strawberry fruits is essential. This paper discusses the residue levels of six pesticides in strawberries grown at different locations in Lebanon.

MATERIALS AND METHODS

Analytical approach

The solvents used were : hexane, acetonitrile, petroleum ether, and diethylic ether (Residue analysis grade, BDH, Britain); the salts used were : sodium chloride (May and Baker) and sodium sulfate anhydre (Merck, Germany). The standards used: fenarimol, bromopropylat, cypermethrin, dimethoate, metalaxyl, procymidon (All 99 % pure, Pestanal), were obtained from Riedel de Haïn (Seelze, Germany), and dissolved in hexane (0.2 mg/ml). Samples were analysed by a gas chromatograph (Shimadzu, GC – 17A) equipped with an electron capture detector (ECD 63Ni), a fused silica capillary column (Supelco, 15m × 0.53mm ID and 0.50μm film thickness) containing 100% methylpolisiloxane as stationary phase, and an integrator, HP3395, and a column chromatograph (Supelco, visiprep ™) for the solid phase extraction. A definite thermic program of GC – ECD was adopted. A Hamilton syringe was used for the injections. The temperatures of the apparatus were as follows : injector temperature : 290°C; detector temperature : 310°C; column temperature : 165°C splitless time 2 min. The initial oven temperature was 150°C for 2min, 10°C/min up to 265°C and then held at 265°C for 5 min ; Thus, the duration of injection was 20 min. The carrier gas was nitrogen at 1 ml/min.

Sampling and storage

Samples were collected from each strawberry field at different times during the season: February 14 till July 20. The sampling was conducted along the coastal area from the north to the south (40 - 100m. altitude); in mountainous zones at an altitude of 1400m.; and in the Bekaa plain (600 - 850m. altitude) (Table 1). Samples were frozen in polyethylene bags at -20°C until used for analysis.

Extraction, purification and analysis

The extraction method is that recommanded by the AOAC (Method 970.52, 1995). After defrosting, each sample (50g) was homogenized and shaken mechanically (in a mixer) with acetonitrile (100ml) for 3min, then sodium chloride (10g) was added. After that, the mixture was filtered in the presence of sodium sulfate (2g). Petroleum ether (50ml) was added to the mixture. Then, the phase containing the pesticide residue was collected by passing it through a florisil column (silicate of synthetic magnesium – Supelco, LC18, SPE, 6ml). It was then washed twice through a florisil column with a mixture of petroleum ether (85%) and diethyl ether (15%).Flow rate was 1ml/min. The elute was then collected and evaporated with nitrogen gas. Finally, 2ml of hexane was added to the residues from which triplicate samples of 1μl each were injected.

Recovery study and reproducibilty of the extraction method

The recovery study was accomplished by injecting the strawberry fruits free of pesticides, with different standards at different concentrations (0.2, 1, or 5mg/kg). The standard injection was realized individually or whole at the same time : the recovery rate was 83% or 85%, respectively. After dosage, the difference between two replicates of the

extraction method was less than 20% (as recommended by AOAC), and the difference between three dosages of the same extraction was less than 10% (between 3-4%) (see Results).

TABLE 1

Locations of the Strawberry Production Areas and Varieties Surveyed in Lebanon. Five Random Samples Were Collected from Each Strawberry Field Surveyed

Regions	Nb of Fields visited	Total area *1000m2					
			Oso (Local)	Oso (imported)	Motto	Camarosa	Douglas
North							
Akkar	12	191	120	29	28	4	10
Jbeil-Jounie	6	34	0	24	2	8	0
Beirut	7	46	0	44	1	1	0
Chouefat	25	504	30	199	142	133	0
Jiye	30	220	0	25.5	194.5	0	0
Damour	5	30	0	11.5	15.5	3	0
South	3	14	0	10	4	0	0
Mount-Jbeil							
Lassa	13	72					72
Ghabat	11	41					41
Afka	15	81					81
Amaz	1	5					5
Yanouh	7	30					30
Mazraa Kfer-Debian	2	5		5			
Bekaa							
Jdita	7	41	21		20		
Kaa	5						
Deir El Ahmar	1						
Chaat	2	15	10				
Total	152	1359	181	348	407	149	239
%			14	25	30	11	17

N.B. Other varieties used at Kaa, Deir El-Ahmar and Chaat were Selva, Seascape and Chandler (25000 m2, 5000m2 and 5000m2, respectively, which are 3% of total).

Limit of determination with ECD

Different trials were conducted to define the limits of determination (LOD) or the minimal quantity of residues identified by the detector in spiked fruits. The following levels of 0.003, 0.001, 0.07, 0.08, 0.02, and 0.1 mg/kg for cypermethrin, bromopropylat, dimethoate, fenarimol, procymidon, and metalaxyl were obtained respectively. The retention times of different standards are illustrated in Figure 1.

Figure 1. Retention times of different standards used.

RESULTS AND DISCUSSION

Dimethoate (MRL = 1mg/kg). Fig. 2.

This insecticide was detected early in the season (March 4) in the samples from Jbeil, Jiye, and Choueifat, in concentrations equal to 1.053, 0.913, and 0.776mg/kg respectively *i.e*. close or higher than the MRL. Between May and June, the samples from Choueifat contained residue levels close to the MRL. In Beirut, the samples collected between April and May contained high concentrations : 1.490 and 1.107mg/kg respectively (higher than the MRL). The samples collected from May to July (end of the season) from the northern region, were contaminated with high doses close or higher than the MRL (1.091 and 1.188mg/kg respectively). In Mount-Jbeil, only the samples collected on May 11 showed a residue level of 1.12mg/kg (higher than the MRL). In the Bekaa plain, the samples collected in June showed a residue level higher than the MRL (1.236mg/kg).

Bromopropylat (MRL = 0.05mg/kg). Fig. 2.

In Choueifat, the samples collected between March 25 and May 20, contained higher doses than the MRL. In Jiye, only the samples of April 20 were contaminated with residues in concentration (0.135mg/kg) higher than the MRL. In Beirut, the samples of May 15 contained residues in concentration (0.202mg/kg) higher than the MRL. In Jbeil and in Northern region, only traces of bromopropylat were detected, whereas in the Bekaa plain, it was not at all detected. In Mount-Jbeil, only the samples of May 11 contained doses (0.132mg/kg) higher than the MRL.

Procymidon (MRL = 2mg/kg). Fig. 2.

This fungicide, recently used on strawberries, was detected in doses less than the MRL in all the regions and during the whole period of the study.

Metalaxyl (MRL = 0.5mg/kg). Fig.2.

This fungicide was detected only in the samples from Choueifat collected on June 20 at a concentration (0.958mg/kg) higher than the MRL.

Fenarimol (MRL = 0.2mg/kg). Fig. 2.

This fungicide was detected in almost all the samples from Choueifat with concentrations higher than the MRL. In Jiye, it was detected from the end of March till the end of the season, with residue levels higher (0.220mg/kg) or very close (0.191mg/kg) to the MRL. In Beirut, the samples collected between the end of March and May 20, contained fenarimol levels higher than the MRL; whereas in Jbeil, residue levels detected between March 25 and June 7 were higher than the MRL. In the Bekaa plain, this fungicide was not used, whereas in Mount-Jbeil it was detected at concentrations less than the MRL. In the northern region, only the samples collected in June 20 showed residue levels slightly (0.2178mg/kg) higher than the MRL.

Figure 2. Residue levels of six pesticides in strawberries detected at different times during the growing season. The pesticides monitored were: dimethoate (A), bromopropylate (B), procymidon (C), fenarimol (D), cypermethrine (E) and metalaxyl (F). Sampling time was : 1=4-12 March, 2=25 March-5 April, 3=20 April-1 May, 4=11-20 May, 5=31 May-7 June, 6= 20-30 June and 7=10-20 July.

Figure 2. (cont.)

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Cypermethrin (MRL = 0.5 mg/kg). Fig. 2.

The samples from Choueifat showed residue levels higher than the MRL, during the whole season. At Jiye, analysis of samples showed that this insecticide/acaricide was not used frequently : only between May 11 and June 7, with residue levels higher than the MRL (0.861 mg/kg and 0.541 mg/kg). In Beirut, it was detected at levels higher (0.681 mg/kg) or very close to the MRL (0.472 mg/kg and 0.478 mg/kg), during March (0.861 mg/kg), April (0.472 mg/kg) and June (0.478 mg/kg). Furtheremore, the collected samples from Jbeil, northern region, Bekaa and Mount-Jbeil did not show any trace of cypermethrin.

All six pesticides selected for analysis were detected at varying concentrations, reflecting on the spraying intensity in the different regions. The presence of metalaxyl (fungicide registered for use during vegetative growth and fruit development) in samples was limited since it was detected only at Choueifat, in the sample of June 20. The procymidon (fungicide sprayed during vegetative growth) has been detected in some regions, and especially Choueifat, but with concentrations below the MRL. Fenarimol (not approved for strawberries) has been frequently used in Choueifat where the detected residue levels exceeded the MRL during the whole season. The residue levels of this pesticide was lower in Beirut, Jiye, Jbeil, and the northern region. The frequent spraying of dimethoate is to be mentionned in the northern region, Choueifat and the Bekaa plain. It has been noticed that farmers in Jiye, and for economic reasons, would alternate spraying fungicides with insecticides/acaricides. Farmers of Mount-Jbeil, as far as the pesticides identified in this study were concerned, quantified, seem to be the most cautious since only two chemical products, bromopropylat and dimethoate were detected to exceed the MRL, and only during limited periods. It is necessary to mention, that the samples collected during the season could also contain other pesticides not detected in this study. Moreover, this study did not take into consideration the date of spraying and the level of the degradation products of pesticides, which depends on climatological conditions, applications, the dose, the interval between application and harvest, and the type of greenhouse (Martinez *et a*l., 1997). Furthermore, it was noticed that farmers sprayed some unauthorized products during vegetative growth and fruit development, such as fenamiphos and propamocarb (fungicides), *etc*., or non confirmed fungicides (fenarimol, nitrothal isopropyl, triadimenol, quinomethionate, *etc*.), or insecticides/acaricides (cypermethrine, dimethoate, methamidophos, methiocarb, methomyl). It would be interesting to identify and quantify these pesticides and their metabolites. Some of these chemicals are carcinogenic, such as phenylthiourea, others are thermostable, such as endosulfan and its metabolite the sulfate, which can be detected in the jams (Jones and Lambe, 1980).

Given the sanitary status of the lebanese strawberry, it would be useful and urgent for the authorities to intervene and introduce sound agricultural pratices (Regulation EEC N°3600/92,1992), in order to encourage the adoption of integrated pest management (IPM) programmes in greenhouses, because greenhouse studies from Holland, show that productivity is higher and the quality of the produce is improved when the crops are produced under an IPM program (Van-Oosten, 1992). In this respect, over the past 2 years Lebanese authorities have initiated concerted activities in order to introduce methyl bromide alternatives, and tests have been conducted in strawberry greenhouses with promising results.

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REFERENCES

FAO/OMS. 1993. *Codex Alimentarius*, 475 p.

Hennion B. et Veschambre D. 1997. *La fraise (2ème partie), Maîtrise de la production*. *CTIFL*. 299p.

Association of Official Analytical Chemists. 1995. *Official methods of analysis of AOAC International*, AOAC 16th edition, U S A.

Martinez Galera, M., Martinez Vidal, J.L., Egea Gonzalez, F.J. and Gil Garcia, M.D. 1997. A study of fenpropathrin residues in tomatoes and green beans grown in greenhouses. *Pesticide Science*, 50 : 127 – 134.

Jones, J.B., Lambe, R.C. 1980. Test for quantification of pesticide residues. *Fung. and Nemat. Tests*, 35(295) : 142 – 143.

Van-Oosten, H.J. 1992. IPM in protected crops : concerns, challenges and opportunities. *Pesticide Science*, 36 : 365–371.