

Monitoring of Pesticide Residues On Cucumber, Tomatoes, And Strawberries In Gaza Governortes, Palestine

By

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ABSTARCT

Three techniques of gas chromatography (GC) either with flame photometric-detector (FPD), electron capture detector (ECD), or with mass-spectrometry (MS) were applied for identification and quantification of pesticide residues (45 samples) on cucumber, tomatoes, and strawberries in fifteen locations in Gaza Governorates, Palestine. GC-FPD analysis showed the presence of four different OP pesticides: parathion-methyl, chlorpyrifos, pyrazophos, and methamidophos. All OP levels were very low and below maximum residue limits (MRL's). GC-ECD detected penconazole, triadimenol, α and β -endosulfan, endosulfan sulfate and vinclozolin, hexaconazole, iprodione, chlorothalonil and dechlorfuanid at levels below the MRL's.

Using the GC-MS technique, the chlorinated insecticide α and β -endosulfan was detected only on cucumber at Beit Hanoun and Khan Younis Center, while the OP insecticide chlorpyrifos was detected only on strawberry at Khan Younis East and Rafah West. The carbamate insecticide/nematicide carbofuran was only detected on cucumber at Shejaia.

The chitin inhibitor chlorfluazuron, was detected on tomatoes at Jabalia, and on strawberry at Beit Hanoun and Khan Younis Center. The fungicide triadimenol I & II were detected on cucumber and strawberry at Beit Hanoun and Khan Younis West respectively while on tomatoes at respectively while on tomatoes at five locations. On the other hand, the fungicide penconazole was detected on cucumber, at three locations, while on strawberry only at two locations. The fungicide captafol- metabolite was detected only strawberry at six locations, while the fungicide Iprodione was only detected on strawberry at four locations. All GC-MS pesticide residues detected on tomato were below the MRL's except chlorfluazuron while on strawberry were below the MRL's except penconazole, chlorfluazuron and pyrimethanil but on cucumber were slightly higher than the MRL's.

Generally, tomatoes showed the least number and level of the pesticide residues by all the GC-techniques. On the other hand, strawberries showed greater number and levels on pesticide residues particularly by the GC-MS technique. These results indicate that the protective period to elapse before harvesting should be increased especially on strawberry. The results also can help in risk assessment of consumers exposure to the expected pesticide residues.

INTRODUCTION

Pesticides are applied worldwide to a broad variety of crops both for field and post-harvest protection. Increasing public concern in recent years about possible health risks from pesticide residues in the diet, has deeply modified strategy for crop protection, with emphasis on food quality and safety, and the widespread concern for the health of society has led to strict regulation of MRL's and total dietary intakes of pesticide residues in food commodities (Codex Alimentarius Commission, 1993).

Standard multiresidue procedures for fruits and vegetables are described by many monitoring agencies in their screening programs (US Food and Drug Administration, 1994) and are officially accepted in many countries. Holland and Malcolm (1992) in their review article report the official methodologies currently adopted in some European and oversea

countries.

Chromatographic methods are the most suitable for residue analysis (Barcelo, 1993, Cairns & Sherma, 1992, Grosser *et al.*, 1993 and Tekel & Kovacicova, 1993) in gas chromatography (GC) using long, narrow-bore capillary columns equipped with selective and sensitive detection methods such as electron-capture detection (ECD) (Nakamura *et al.*, 1994 and Tsumura *et al.*, 1994), nitrogen-phosphorus detection (NPD) (del al Colina, 1993 and Sanchez-Brunete, 1994) and flame-photometric detection (FPD) (Aguera *et al.*, 1993 and Miyahara *et al.*, 1994) according to different classes of pesticides. An emerging strategy in multiresidue methodology is the search for universal detection systems, e.g., in GC coupled with mass-selective detectors (Tuinstra *et al.*, 1991, Fillion *et al.*, 1995, Sanni *et al.*, 1995 and Tuinstra *et al.*, 1995). A modern trend in multiresidue methodology is moving to the development of reliable procedures capable of determining accurate manner. (GC-ECD is the favored technique for the determination of majority of pesticides. Confirmation of identity of pesticide residues may be performed by GC-MS (Fernandez-Alba *et al.*, 1994, Psathaki *et al.*, 1994, Salau *et al.*, 1994 and Viana *et al.*, 1994).

Approximately 200 citrus samples from markets of the Valencian community (Spain) were analyzed to establish their residue levels in organophosphorous pesticide residues during the 1994-1995 campaign. A total of 32.25% of the samples contained pesticide residues and 6.9% exceeded the European Union MRL's. The OP's residues found in the samples with above MRL's were: carbophenothrin, ethion, mentidathion, and methyl parathion. Lower level residues of these and the other pesticides studied (except diazinon) were frequently found. The estimated daily intake of the 12 OP insecticides were frequently found and the pesticide residues during the studied period was 0.000187 mg/kg body weight/day. This value is lower than the provisional tolerances daily intakes set by FAO and WHO (Torres *et al.*, 1997).

Lee *et al.*, (1996) reported that over the past 7 years, acute food poisoning arising from the consumption of methamidophos-tainted vegetables has occurred sporadically in Hong Kong. A simple and rapid gas chromatographic method was developed to determine methamidophos residues in food remnants. The residues were determined by gas

chromatography with flame photometric detection. Four of 13 food remnants of poisoned cases were found to contain high concentration of methamidopbas. Ahmed *et al.*, (1996) described the headspace gas-liquid chromatographic method for the determination of dithiocarbamate residues in fruits and vegetables with confirmation by conversion to ethylene thiourea.

Metwally *et al.*, (1997) used a high-performance liquid chromatographic method for the determination of cypermethrin in vegetables and its application to kinetic studies after greenhouse treatment. The method was utilized to study the disappearance kinetics of cypermethrin (CM) under field conditions on cucumber, eggplant, green pepper, and tomato. The high disappearance rate of the pesticides on cucumber is mainly due to the high growth rate of this fruit relative to the other fruits. The pre-harvest waiting period was calculated for such vegetable fruit at different application rates. At the regular application rate, the value ranged from 36 to 120 h depending on the type of the fruit, rate of disappearance of the pesticide and the maximum allowable limit.

According to Gil-Gracia *et al.*, (1997) levels of methomyl residues were studied on tomatoes and green beans (*Phaseolus vulgaris*) in an experimental greenhouse to establish the effect of the kind of greenhouse, application concentration, species grown and climatic condition on the degradation of the insecticide methomyl. The residue half life was significantly longer on *P.Vulgaris* than on tomatoes and was longer in winter. A preharvest time of about 5 days was suggested. Gelsomino *et al.*, (1997) studied the multiresidue analysis of pesticides in fruits and vegetables by gel permeation chromatography followed by gas chromatography with electron-capture and mass spectrometric detection.

Antonious *et al.*, (1998) studied the residues and fate of endosulfan on field-grown pepper and tomato. Analysis of samples was accomplished using gas chromatography-mass selective detection (GC-MSD). The results indicated the formation of endosulfan sulfate as a residue component on the plant tissues and also the relatively higher persistence of the β -endosulfan isomer as compared to the α -isomer on pepper fruits. The initial total residues were higher on leaves than on fruits. Total residues on tomato leaves revealed longer persistence (half life 4.5 days) compared to the total

residues on pepper leaves (half life 2 days) 3-14 days after spraying. It was concluded that the longer persistence of the total residues on tomato foliage should be considered of importance for timing the safe entry of tomato harvesters to the high mammalian toxicity of endosulfan.

The persistence and dissipation of the fungicide carbendazim residues in and on berries of grape following spraying of 250 or 500 g a.i. per hectare were reported by Mohapatra *et al.*, (1998). The residues persisted for over 15 days, and dissipated with a half life of 5 days. A waiting period of 2 and 5 days before consumption is recommended for the lower and the higher doses, respectively.

Miliadis and Malaton (1998) developed a multiresidue analysis of 39 pesticides as a rapid screening method for pesticide residues in vegetable samples. Gas chromatography with nitrogen-phosphorous detector, and electron capture detector, was employed for the separation and identification of 15 compounds sensitive to NPD and 24 sensitive to ECD. The estimated limits of detection for all studied compounds were between 0.001 and 0.01 mg/kg. Mac Donald and Meyer (1998) emphasized that a sensitive and reliable method for the determination of imidacloprid, triadimefon and triadimenol by GC-MS has been developed. Imidacloprid was converted to the heptafluorobutyl derivative, whereas triadimefon and triadimenol were determined directly. This method has been successfully applied to quantify residues in plant after treatment of white pine seedlings with a controlled release pellets containing imidacloprid and triadimefon for control of white pine weevil and white pine blister rust, respectively.

Molinari *et al.*, (1998), developed a multiresidue method for the analysis of 14 organophosphorous pesticides in vegetables before processing. The extracted samples were analyzed by gas chromatography with a nitrogen phosphorous detector. Recoveries performed on samples of beans, fresh beans, spinach, peas and zucchini at 3 fortification levels were over 77% for all pesticides except demeton-s-methyl (70%) and omethoate (52%). Waliszewski *et al.*, (1998) described a simple analytical method for determining fluvalinate residues in honey, analysis was carried out by gas chromatography-electron capture detector. Burchat *et al.*, (1998) investigated the distribution of nine pesticides between the juice and pulp of carrots and tomatoes after home processing.

Recently, Miliadis *et al.*, (1999) described a high-performance liquid chromatographic determination of benzoylurea insecticide residues in grapes and wine using liquid and solid-phase extraction. The method was applied to the determination of flufenoxuron; residues in grapes from treated fields and in produced wine. Sanz-Asensio *et al.*, (1999) studied the behavior of acephate and its metabolite methamidophos. The results showed that acephate penetrates into the fruit, where, it is transformed to methamidophos. This transformation was not seen on the external apple surface.

Navickiene *et al.*, (1999) described a simple and efficient method for the determination of fenpropathrin in oranges, pears, apples and strawberries. Gas chromatographic analysis with electron capture detection was applied on the extracted samples. The fortification levels of (0.5, 1.0, 2.0 mg/kg) were selected according to the MRL's established for fenpropathrin by Brazilian legislation. Garland *et al.*, (1999) stated that an analytical method, using gas chromatography combined with detection by high-resolution mass-spectrometry, was developed to allow for the simultaneous monitoring of both pesticides in peppermint leaves and oil. Field trials; were established to determine the rate of dissipation of tebuconazole and propiconazole in peppermint crops. Pang *et al.*, (1999) reported that fourteen laboratories from 6 countries and regions participated in an international collaborative study to evaluate a multiresidue gas chromatographic method for determining 8 synthetic pyrethroid pesticides in grains, fruits and vegetables.

Sadlo (1999) studied the quantitative relationship of application rate and pesticide residues in greenhouse tomatoes. The average residue level (R) of any pesticide in ripe tomatoes remained in quantitative relation to its dose (D), expressed by the following regression equation: $R = 0.24 D$ (mg/kg), where the numerical factor, 0.24, represents the average residue in mg/kg after application of 1 kg active ingredient per hectare with relative standard deviation of 23%. Quantitative association between these 2 factors enables evaluation of greenhouse tomato growers with respect to their observation of Good Agricultural Practice rules and the Plant Protection Act, obligatory in Poland since 1996, and thus may be a reliable basis for the registration of new agrochemicals.

Fillion *et al.*, (2000) described a multiresidue method for the determination of residues of 251 pesticides in fruits and vegetables by gas chromatography/mass spectrometry and liquid chromatography with fluorescence detection, while Fernandez-Alba *et al.*, (2000) described the determination of imidacloprid and benzimidazole residues in fruits and vegetables by liquid chromatography-mass spectrometry after ethyl acetate multiresidue extraction.

Ripley *et al.*, (2000) indicated that for the 5 years period 1991 to 1995, 1536 vegetable and 805 fruit samples from Ontario, Canada, were analyzed. The purpose of this study was to determine if pesticides were present on Ontario-produced fruits and vegetables, and if so, to determine if residues violated MRL's. Overall, 31.5% of the samples had no detectable pesticide residues, whereas 68.5% contained one or more residues. Most of the residues were present at very low concentrations; 48% of the detections were 0.1 parts per million (ppm), and 86% were < 1 ppm. However, violations of MRL's were observed in only 3.2% of the vegetable samples and 3.1% of the fruit samples. In addition, 4.8% of the samples contained a "technical" violation, that is, there was no specified MRL's for the pesticide commodity combination and the residues exceeded 0.1 ppm.

The present study was planned to monitor the levels of pesticide residues on the cucumber, tomatoes, and strawberries in samples collected from different localities in Gaza Governorates, Palestine. The pesticide residues were detected, identified and quantified using gas chromatography techniques with flame photometric detector (FPD) and electron capture detector (ECD). Confirmation of the type of residue was carried out using gas chromatography-mass spectrometry (GC-MS) techniques.

MATERIALS AND METHODS

Samples:

Fourty five fruit samples of cucumber, tomatoes and strawberries were collected from the harvest at fifteen different localities (Jabalia, Beit Lahia, Beit Hanoun, Shejaia, Gaza Center, Sheikh Rcdwan, Deer El-Balah,

Nusairat, Berej-Maghazi, Khan Younis East, Khan Younis Center, Khan Younis West, Rafah East, Rafah Center, and Rafah West) in Gaza Governorates (Northren. Gaza, Middle, Khan Younis and Rafah), Palestine (PNA) during the season 1998/1999. The samples were kept in paper bags in a refrigerator until use for multiresidue analysis of pesticides.

Solvents and Chemical Reagents:

The used solvents and chemical reagents were of gas chromatography grade purity and were provided by Sigma Co.

Sample Processing and Extraction:

Fifteen gram samples of each fruit type were weighed and transferred to a homogenizer where it was mixed with 30 ml acetone, and was homogenized for one minute, then the homogenete was extracted and portioned according to (Mills et al., 1963) and Pesticide Analytical Manual Vol. 1 (1994). Then the homogenate was centrifuged at 4000 r.p.m for 10 minutes at room temperature. Aliquots each of 25 ml of the supernatant were subjected to evaporation under nitrogen then 1 ml of the mixture of (90% isooctane + acetone 10%) then the solution was well mixed in a vortex. The resulting solution was, injected in the Gas chromatograph identification and quntifications of each residue.

Analytical Equipments:

Gas chromatography with electron capture detector (ECD)) and/or flame photometric detector (FPD) manufactured by Shimadzu Co. was used. The Shimadzu apparatus, equipped with the ECD) was used for detection and quantification of the halogen containing pesticides. The FPD detector was for identification of the other compounds mainly the organophosphorous compound.

Confirmation of the detected residues was carried using the GC-MS Shimadzu. The analytical procedure was applied according to GC methods, in the US Food and Drug Administration, Pesticide Analytical Manual. Multiresidue Methods (1994) as well as the methods described by Mills *et*

al., (1963). Reference samples were used as standards for both calibration and confirmation purposes. The maximum residue limits (MRL's) were adopted from Codex Alimentarius Commission, Joint FAO/WHO Food Standard Programme (1998) as well as Israeli Directory of Pesticides, Ministry of Agriculture and Rural Development (1998), because until now there is no Palestinian Directory of Pesticides.

RESULTS AND DISCUSSION*

GC-FPD Pesticide Residues on Cucumber, Tomato, and Strawberry:

The gas chromatography flame photometric detector analysis of the fruit samples for pesticide residues on cucumber, tomato and strawberry in fifteen different localities in Southern Governorates in Palestine was carried out and the data are presented in Tables 1, 2, and 3. Residues of the following organophosphorus insecticides were detected and quantified: - methyl-parathion, chlorpyrifos, methamidophos, and pyrazophos. Parathion-methyl was detected on cucumber while pyrazophos and methamidophos were detected only on strawberry. On the other hand, chlorpyrifos was detected on cucumber, tomato and strawberry. All the detected pesticide residues were very low and below the maximum residue limits.

GC-ECD Pesticide Residues on Cucumber, Tomato and Strawberry:

The results of gas chromatography with electron capture detector (Tables 1, 2 and 3) revealed that residues of several compounds were detected particularly on cucumber especially in Beit Hanoun, where residues, of five pesticides were recorded (Table 1). However, all the detected levels of all pesticides in the fifteen localities on cucumber were very low and below the MRL's. Penconzale was detected at six localities, while endosulfan and its isomers or metabolites were detected at four localities, which is similar to Triadimenol.

The situation on tomatoes (Table 2) showed that no pesticide residues were detected on Beit Hanoun, Beit Lahia, Jabalia, Shejaia, Gaza

Table (1-a): GC-FPD, GC-ECD and GC-MS Pesticide Residues on Cucumber in Gaza Governorates, PNA.

Governorate	Detected Pesticides	T _R . (min.)	Residue mg/kg	MRL's Mg/kg
GC-FPD				
Northern Gov.				
Jabalia	N.D	-	-	-
Beit Lahia	N.D	-	-	-
Beit Hanoun	N.D	-	-	-
Gaza Gov.				
Shejaia	N.D	-	-	-
Center	N.D	-	-	-
Sheikh Redwan	N.D	-	-	-
Middle Gov.				
Deer El-Balah	Parathion/methyl	22.49	0.0009	N.F.
Nusairat	N.D.	-	-	-
Berej-Maghazi	N.D.	-	-	-
Khan Yunis Gov.				
East(Abassan)	Chlorpyrifos	28.52	0.013	0.10
Center	N.D.	-	-	-
West	N.D.	-	-	-
Rafah Gov.				
East(Shaboura)	N.D.	-	-	-
Center	N.D.	-	-	-
West	N.D.	-	-	-

N.D. : No Detected Pesticide Residue

N.F. : Not found

Table (1-b): GC-FPD, GC-ECD and GC-MS Pesticide Residues on Cucumber in Gaza Governorates, PNA.

Governorate	Detected Pesticides	t _R (min.)	Residue mg/kg	MR L's Mg/kg
GC-ECD				
Northern Gov.				
Jabalia	Penconazole	18.52	0.002	0.1
	Endosulfan-Sulf.	23.55	0.004	0.5
Beit Lahia	Permethrin	37.86	0.098	0.5
Beit Hanoun	Penconazole	18.52	0.003	0.1
	Triadimenol	18.80	0.004	0.1
	α -Endosulfan	19.65	0.005	0.5
	β -Endosulfan	21.89	0.009	0.5
	Endosulfan-Sulf.	23.55	0.003	0.5
Gaza Gov.				
Shejaia	Penconazole	18.52	0.001	0.1
	Endosulfan-Sulf.	23.55	0.0006	0.5
Center	Triadimenol	21.34	0.023	0.1
Sheikh Redwan	N.D.	-	-	-
Middle Gov.				
Deer El-Balah	Triadimenol	18.8	0.063	0.1
	Penconazole	18.52	0.044	0.1
Nusairat	Vinclozolin	12.69	0.004	0.10
Berej-Maghazi	N.D.	-	-	-
Khan Yunis Gov.				
East (Abassan)	Triadimenol	15.8	0.082	0.1
Center	N.D.	-	-	-
West	α -Endosulfan	22.26	0.001	0.5
	β -Endosulfan	24.82	0.004	0.5
Rafah Gov.				
East (Shaboura)	Chlorthalonil	16.68	0.001	5.0
	Penconazole	20.84	0.014	0.1
	Iprodione	30.61	0.183	5.0
Center	N.D.	-	-	-
West	Chlorthalonil	16.68	0.005	5.0
	Dichlofluanid	19.06	0.006	5.0
	Penconazole	20.84	0.03	0.1

N.D. : No Detected Pesticide Residue

N.F. : Not found

Table (1-c): GC-FPD, GC-ECD and GC-MS Pesticide Residues Cucumber in Gaza Governorates, PNA.

Governorate	Detected Pesticides	t _R . (min.)	Residue mg/kg	MR L's mg/kg
GC-MS				
Northern Gov.				
Jabalia	Penconazole	11.44	0.16	0.1
Beit Lahia	N.D.	-	-	-
Beit Hanoun	α-Endosulfan	11.93	0.94	0.5
	β- Endosulfan	12.68	0.85	0.5
	Triadimenol I	11.58	0.13	0.1
	Triadimenol II	11.69	0.15	0.1
Gaza Gov.				
Shejaia	Penconazole	11.44	0.11	0.1
	Carbofuran	5.46	0.11	0.1
Center	N.D.	-	-	-
Sheikh Redwan	N.D.	-	-	-
Middle Gov.				
Deer El-Balah	Penconazole	11.44	0.237	0.1
Nusairat	N.D.	-	-	-
Berej-Maghazi	N.D.	-	-	-
Khan Yunis Gov.				
East(Abassan)	Triadimenol	11.58	0.31	0.1
	α-Endosulfan	12.15	0.147	0.5
	β- Endosulfan	12.93	0.168	0.5
Center	N.D.	-	-	-
West	N.D.	-	-	-
Rafah Gov.				
East(Shaboura)	N.D.	-	-	-
Center	N.D.	-	-	-
West	N.D.	-	-	-

N.D. : No Detected Pesticide Residue

N.F. : Not found

Table (2-a): GC-FPD, GC-ECD and GC-MS Pesticide Residues on Tomato in Gaza Governorates, PNA.

Governorate	Detected Pesticides	T _R . (min.)	Residue mg/km	MR L's mg/kg
GC-FPD				
Northern Gov.				
Jabalia	N.D.	-	-	-
Beit Lahia	N.D.	-	-	-
Beit Hanoun	N.D.	-	-	-
Gaza Gov.				
Shejaia	N.D.	-	-	-
Center	N.D.	-	-	-
Sheikh Redwan	N.D.	-	-	-
Middle Gov.				
Deer El-Balah	Chlorpyrifos	14.2	0.006	0.5
Nusairat	N.D.	-	-	-
Berej-Maghazi	N.D.	-	-	-
Khan Yunis Gov.				
East(Abassan)	N.D.	-	-	-
Center	N.D.	-	-	-
West	N.D.	-	-	-
Rafah Gov.				
East(Shaboura)	N.D.	-	-	-
Center	N.D.	-	-	-
West	N.D.	-	-	-

N.D. : No Detected Pesticide Residue

N.F. : Not found

Table (2-c): GC-FPD, GC-ECD and GC-MS Pesticide Residues on Tomato in Gaza Governorates, PNA.

Governorate	Detected Pesticides	t _R (min.)	Residue mg/km	MRL's mg/kg
GC-MS				
Northern Gov.				
Jabalia	Chlorfluazuron	12.0	0.36	0.20
Beit Lahia	N.D.	-	-	-
Beit Hanoun	N.D.	-	-	-
Gaza Gov.				
Shejaia	N.D.	-	-	-
Center	N.D.	-	-	-
Sheikh Redwan	Triadimenol I	11.76	0.093	0.5
	Triadimenol II	11.97	0.142	0.5
Middle Gov.				
Deer El-Balah	N.D.	-	-	-
Nusairat	N.D.	-	-	-
Berej-Maghazi	Triadimenol I	11.76	0.118	0.5
	Triadimenol II	11.85	0.118	0.5
Khan Yunis Gov.				
East (Abassan)	Triadimenol I	11.76	0.74	0.5
	Triadimenol II	11.85	0.342	0.5
Center	Triadimenol I	11.76	0.096	0.5
	Triadimenol II	11.96	0.120	0.5
West	N.D.	-	-	-
Rafah Gov.				
East (Shaboura)	Triadimenol I	11.76	0.116	0.5
	Triadimenol II	11.85	0.139	0.5
Center	N.D.	-	-	-
West	N.D.	-	-	-

N.D. : No Detected Pesticide Residue

N.F. : Not found

Table (3-a): GC-FPD, GC-ECD and GC-MS Pesticide Residues on Strawberry in Gaza Governorates, PNA.

Governorate	Detected Pesticides	T _R . (min.)	Residue mg/km	MR L's mg/kg
GC-FPD				
Northern Gov.				
Jabalia	Methamidophos	9.79	0.007	0.05
Beit Lahia	N.D	-	-	-
Beit Hanoun	Pyrazophos	39.24	0.013	0.20
Gaza Gov.				
Shejaia	Chlorpyrifos	14.2	0.013	0.10
Center	N.D.	-	-	-
Sheikh Redwan	N.D.	-	-	-
Middle Gov.				
Deer El-Balah	Chlorpyrifos	14.2	0.02	0.10
Nusairat	Chlorpyrifos	14.2	0.018	0.10
Berej-Maghazi	N.D.	-	-	-
Khan Yunis Gov.				
East(Abassan)	Chlorpyrifos	14.2	0.02	0.10
Center	N.D.	-	-	-
West	N.D.	-	-	-
Rafah Gov.				
East(Shaboura)	N.D.	-	-	-
Center	N.D.	-	-	-
West	Chlorpyrifos	14.2	0.007	0.10

N.D. : No Detected Pesticide Residue

N.F. : Not found

Table (3-b): GC-FPD, GC-ECD and GC-MS Pesticide Residues on Strawberry in Gaza Governorates, PNA.

Governorate	Detected Pesticides	tg. (min.)	Residue mg/5m	MRL's Mg/kg
GC-ECD				
Northern Gov.				
Jabalia	N.D.	-	-	-
Beit Lahia	Chlorthalonil	14.77	0.009	5.0
Beit Hanoun	Penconazole	18.50	0.09	0.1
	Hexaconazol	20.29	0.003	0.01
Gaza Gov.				
Shejaia	Iprodione	20.95	0.507	10.0
Center	Chlorthalonil	14.77	0.017	5.0
Sheikh Redwan	Chlorthalonil	14.77	0.004	5.0
	Penconazole	18.50	0.008	0.1
Middle Gov.				
Deer El-Balah	Chlorthalonil	11.98	0.01	5.0
	Iprodione	20.95	0.59	10.0
Nusairat	Iprodione	20.95	0.62	10.0
Berej-Maghazi	N.D.	-	-	-
Khan Yunis Gov.				
East(Abassan)	Iprodione	20.95	0.46	10.0
Center	N.D.	-	-	-
West	N.D.	-	-	-
Rafah Gov.				
East(Shaboura)	N.D.	-	-	-
Center	Dichlofluanid	13.19	0.036	10.0
	α -Endosulfan	15.01	0.003	0.5
	β - Endosulfan	16.61	0.015	0.5
West	N.D.	-	-	-

N.D. : No Detected Pesticide Residue

N.F. : Not found

Table (3-c): GC-FPD, GC-ECD and GC-MS Pesticide Residues o Strawberry in Gaza Governorates, PNA.

Governorate	Detected Pesticides	t _R (min.)	Residue mg/kg	MRL's mg/kg
GC-MS				
Northern Gov.				
Jabalia	Capatafol metab	7.16	0.71	20.0
Beit Lahia	Capatafol metab	7.16	4.24	20.0
	Captan	11.54	1.22	20.0
Beit Hanoun	Penconazole	11.44	0.20	0.10
	Chlorfluazuron	12.0	0.397	0.10
Gaza Gov.				
Shejaia	Iprodione	12.74	0.80	10.0
Center	Chlorthalonil	9.88	0.203	5.0
Sheikh Redwan	Capatafol metab	6.89	2.61	20.0
Middle Gov.				
Deer El-Balah	Iprodione	12.74	0.56	10.0
Nusairat	Capatafol metab	7.16	1.92	20.0
	Iprodione	12.74	0.56	10.0
Berej-Maghazi	N.D.	-	-	-
Khan Yunis Gov.				
East(Abassan)	Iprodione	12.74	0.490	10.0
	Chlorpyrifos	10.96	0.038	0.10
	Capatafol metab	7.16	1.60	20.0
Center	Penconazole	11.42	0.218	0.1
	Chlorfluazuron	11.98	0.072	0.1
West	Triadimenol I	11.29	0.113	0.1
	Triadimenol II	11.39	0.136	0.1
	Pyrimethanil	9.37	0.45	0.2
Rafah Gov.				
East(Shaboura)	Capatafol metab	6.90	2.10	20.0
Center	Triadimenol	11.30	0.116	0.1
	Pyrimethanil	9.37	0.43	0.20
West	Chlorpyrifos	10.7	0.023	0.1

N.D. : No Detected Pesticide Residue

N.F. : Not found

center, Nušairat and Rafah West tomato samples. While endosulfan was detected on tomato samples at Sheikh Redwan, Deer El-Balah, Berej-Maghazi and Khan Younis East. Triadimenol was also detected on Berej-Maghazi, Khan Younis, East and Center and Rafah East tomato samples. All levels were below MRL's.

Table (3) indicates the detected residues on the strawberry samples using the GC-ECD technique. Jabalia, Berej-Maghazi, Khan Younis Center and West and Rafah East and West samples were free of any detected residues. Iprodione was the more common residue on strawberry samples of Shejaia, Nusairat, Dear El-Balah and Khan Younis East. On the other hand, Beit Hanoun detected residues were penconazole and hexaconazole. Besides, chlorothalonil was detected on the samples of Beit Lahia, Gaza Center, Sheikh Redwan and Deer El-Balah. While α and β endosulfan and dichlofuanid were only detected on Rafah Center samples. However, the overall picture showed that all detected residues were below the MRL's., which means no expected health hazard.

GC-MS Detected and Confirmed Pesticide Residues on Three Vegetable Fruits.

Tables 1, 2, and 3 present the data of the detected pesticide residues by the GC-MS-technique in cucumber, tomato and strawberry samples respectively. Cucumber samples (Table 1), showed relatively high levels of endosulfan, triadimenol, penconazole, and carbofuran in six of the fifteen studied localities. All levels, slightly, exceeded the MRL's for the localities except Khan Younis Center.

Table (2) showed that tomato samples had only chlofluazuron residue at Jabalia, and Triadimenol I & II at Sheikh Redwan, Berej-Maghazi, Khan Younis East and Center and Rafah East. Triadimenol I & II levels were higher than the MRL's while chlofluazuron was slightly higher than the MRL's. However, the other nine localities did not show any detected residues.

Different types of residues were detected on the strawberry samples in all the localities except Berej-Maghazi (Table 3). The detected residues were captafol metabolites, captan, penconazole, chlorfluazuron, iprodion, chlorthalonil, chlorpyrifos, triadimenol 1 & 11 and pyrimethanil. All residue levels were below the MRL's except for penconazole, ehlofluazuron, and pyrimethanil which exceeded the MRL's with about 2 fold.

The short persistence of pesticide residues especially on tomatoes in the three gas chromatography detection techniques, (GC-FPD; GC-ECD; and GC-MS), agrees with the result of Gil-Gracia (1997). The high rate of degradation of most pesticide residues on cucumber can be attributed to the rapid physiological change during growth of cucumber as reported by Metwally *et al.* (1997). This can explain the tendency of no-or minute levels of residues on cucumber. The range of most detected pesticides levels in cucumber, tomatoes and strawberries coincides with Gil-Gracia (1997) Antonious *et al.*, (1998), Sadlo (2000) and Ripley *et al.*, (2000).

The present data in general shows that majority of the pesticide residues are below the MRL's. Thus, it can be concluded that future pesticide management policy in Palestine, should consider revision of the list of pesticides and to cancel the organochlorinated chemicals and the more persistent compounds. The data are also valuable in setting the safety period, which should elapse before harvesting and marketing of such vegetable fruits. The data are also essential for the monitoring type and for quantification of the high hazardous pesticide residues and their health risk assessment. Besides, regular monitoring of the pesticide residue levels in marketed fruits and vegetables should be extended periodically. Risk assessment according to the type and level of pesticide residues will be carried out with the concerned agencies.

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الملخص العربي

رصد متبقيات المبيدات على ثمار الخيار والطماطم والفراولة في قطاع غزة - بفلسطين

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تم استخدام التحليل الكروماتوجرافي بالغاز المزود بالكشاف FPD؛ ECD وكذلك المزوج مع التحليل الطيفي الكتلي GC-MS وذلك للتعرف على والتقدير الكمي لمتبقيات المبيدات في خمسة واربعين عينة من الخيار والطماطم والفراولة مأخوذة من خمسة عشر موقع في قطاع غزة بفلسطين. وقد اظهر التحليل الكروماتوجرافي GC-FPD - وجود متبقيات اربعة من المبيدات الفوسفورية وهي الميثيل براتيون - والكلوربيريفوس، وبيرازوفوس ، وكذلك ميثاميدوفوس. وقد كانت متبقيات تلك المركبات الفوسفورية كلها ذات مستوى منخفض ويقل عن الحدود القصوى المسموح بها. ومن ناحية اخرى فان التحليل الكروماتوجرافي GC-ECD. قد اظهر وجود متبقيات للمبيدات الاتية:- بنكونازول - ترايا ديمينول - الفاوبيتا اندوسلفان- وكبريتات الاندوسلفان فينكوزولين- هكساكونازول - ابروديون - كلوروثالونيل - وديكلوفلوانيد - على مستويات تقل عن الحدود القصوى المسموح بها MRL's. واخيرا فان استخدام GC-MS - قد أدى للتعرف على الفاوبيتا اندوسلفان-على ثمار الخيار في 'بيت حانون' ومنطقة وسط خان يونس-بينما تم التعرف على متبقيات المبيد الفوسفوري كلوبيريفوس على ثمار الفراولة فقط

في المنطقة الشرقية لخان يونس والمنطقة الغربية لرفح. اما المبيد الكارباماتي الحثري/ وضد النيماتودا - (كاربوفوران) فقد تم التعرف عليه فقط على ثمار الخيار في منطقة " شيجايا". اما المركب المثبط للكيوتين " كلور فلوازيرون" فقد تم التعرف عليه على ثمار الطماطم في منطقة "جبا لايا" وكذلك على ثمار الفراولة عند منطقة بين بيت حاثون والمنطقة الوسطى بخان يونس. أما المبيد الفطري ترايا ديمينول II,I فقد وجدت على ثمار الخيار والفراولة في "بيت حاثون" وغرب خان يونس" بينما ظهر على ثمار الطماطم في خمسة مناطق. ومن ناحية اخرى فقد ظهرت متبقيات المبيد الفطري بنكوثازول على ثمار الخيار في ثلاثة مناطق وعلى ثمار الفراولة في موقعين. كما ان المبيد الفطري كابيتافول واحد نواتج تحلله وقد تم التعرف عليه فقط على ثمار الفراولة في ستة مواقع بينما كان المبيد الفطري ايروديون قد تم التعرف عليه فقط على ثمار الفراولة في اربعة مواقع وقد كانت مستويات متبقيات المبيدات على ثمار الطماطم كانت اقل من الحدود القصوى المسموح بها فيما عدا مبيد البينكونازول، كلورفلوزارون وبيريميثانيل. بينما على ثمار الخيار كانت اعلى بقدر محدود عن الحدود القصوى المسموح بها. وعموما فان ثمار الطماطم قد اظهرت اقل عدد ومستوى من متبقيات المبيدات بواسطة كل طرق التحليل المستخدمة. ومن ناحية اخرى فان ثمار الفراولة قد اظهرت اعلى عدد ومستوى بين متبقيات المبيدات خاصة بطريقة GC-MS. وقد اظهرت النتائج ان فترة الامان التي يجب قضاؤها قبل الحصاد يجب ان تزداد عن الفراولة. كما ان النتائج تفيد في تقييم مخاطر التعرض للمبيدات.