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RESIDUES AND DEGRADATION OF PIRIMIPHOS-METHYL UNDER SOME ENVIRONMENTAL CONDITIONS AND FOOD PROCESSING

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ABSTRACT

The present investigation was carried out to study the persistence of the insecticide pirimiphos-methyl (Actellic 50% EC) on apple and peach fruits as well as grape leaves under the Egyptian field conditions. The recommended application rate 150ml/100L water was used, the role of food processing were also studied by using washing and blanching processes. The role of photodecomposition rate was estimated by exposure of pirimiphos-methyl to the short UV-rays (254nm) as well as direct sunlight in open field and different temperatures and pH buffered degrees in the rate of photodecomposition of pirimiphos-methyl , also degradation products were studied by GC-MS.

Results indicated that the residues half-life ($t_{0.5}$) values for pirimiphos-methyl were 2.56, 2.68 and 1.91 days in apple, peach fruits and grape leaves, respectively. Residues of pirimiphos-methyl were reduced by washing process to 29.28, 34.49 and 35.65% at zero time in apple, peach and grape samples, respectively. Blanching process of grape leaves removed 64.77% at zero time.

Photodegradation by direct sunlight was more effective than UV-rays in accelerating the degradation rate of pirimiphos-methyl. Data indicated that alkaline or acidic media are more effective than natural media in the degradation of pirimiphos-methyl in all treatments. Data reveal that the degradation of pirimiphos-methyl was faster at high temperature. Four Photodegradation products were identified using GC-MS.

Keywords: Pirimiphos-methyl; Apple; Peach; Grape leaves; Residue levels; Photochemical; Degradation products; Food processing; PHI.

INTRODUCTION

Pesticides have been applied worldwide to a broad variety of crops either in the field or post-harvest protection. The use of synthesis pesticides is known to have a significant positive impact on crop yields and, therefore these are used in increasing amounts. This is confirmed by the registered pesticide import statistics showing that traditional subsistence farmers apply increasing amounts of pesticides in their production systems. But the effective pesticide use must be seen in a wider context than just the efficient pest control, and must take into account the effect of the pesticide accumulation in the environment, and the impact of pesticide residues on human health (Domotorova *et al.*, 2006).

Transformation of pesticides in the environment is a highly complex process affected by different factors. Both biological and physico-chemical factors may play a role in the degradation, whose ratio depends on the actual environmental conditions (Kiss *et al.*, 2007).

In Egypt fruits usually attacked by many insect pests such as several insects, spider mites, aphids and powdery mildew thought-out the growing season causing reduction in productivity. If an insecticide is to be accepted to control insect pests on crops, it must be effective in controlling these pests, persisting, not long enough to cause residue problems in the harvested plants, and have a very low mammalian toxicity. Pirimiphos-methyl was used to control pests as a recommendation from Anonymous (2001). Our study aims to reveal specific details on the persistence and behavior of pirimiphos-methyl insecticide on and in apple and peach fruits as well as grape leaves under the Egyptian field conditions and determining pre-harvest interval (PHI). The effect of washing and blanching processes on the removal of the residues from treated fruits and leaves were studied. Effect of some factors such as direct sunlight, ultraviolet rays and different temperature 30, 40 and 50°C on the degradation rate of pirimiphos-methyl in different buffer solutions (pH 5, 7, and 9).

Identification of the degradation products were determined by GC-MS.

MATERIALS AND METHODS

Field Experiment and sampling:

Three popular fruit crops were used in this study, apple (*Malus sylvestris*) and peach (*Prunus persica*) grown in Shiwa village, Aga center, Dakahlia governorate, Egypt. Trees were sprayed with pirimiphos-methyl on June 3rd 2007. Grapes (*Tomasson sideless*) grown in El-Dair village, Aga center, Dakahlia governorate, Egypt. Trees were sprayed on June 18th 2007.

The experimental area was divided according to the complete randomized block design including three replicates, the northern plots were left as control. The insecticides formulation were diluted with water and applied using a knapsack sprayer equipped with one nozzle at the recommend rates according to the specification of anonymous (2001).

Three representative samples of grown fruits weighed 1.5kg, were randomly taken from the plants of each treatment at the harvest season one hour after insecticide treatments and then 1, 3, 6, 10 and 15 days for residues determination. The collected samples were transferred to the laboratory, divided to sub samples and kept at -20°C until pesticide residues analysis.

Food processing treatment:

Washing process of apple and peach fruits as well as grape leaves were studied by washing the samples with running tap water for three minutes and left to dry on clean paper for 15 minutes at laboratory temperature, then divided to sub samples and kept at -20°C until pesticide residues analysis. Blanching process of grape leaves were carried out using a jar filled with boiling water for 2 – 3 minutes then drained and kept freezed until analysis. Control samples were taken from untreated plots.

Residues analysis:

The method described by Pihlström *et al.* (2007) was used for extraction of pirimiphos-methyl residues by using ethyl acetate from apple and peach fruits and grape leaves samples. The florisil column

clean up procedure of Mills *et al.* (1972) was used in cleaning up the sample extract.

Determination of pirimiphos-methyl residues:

Quantitative analysis of pirimiphos-methyl residues were performed by the gas chromatograph (GC), Hp 6890 serial equipped with flame photometric detector (FPD) operated in the phosphorus mode (529 nm filter). The extracted samples were dissolved in ethyl acetate and injected under the following conditions, capillary column DB-5MS (30 m x 0.32 mm i.d. x 0.25 μ m film thickness). Detector temperature was 250°C, injector temperature was 245°C, and the column temperatures were programmed 190°C and hold 2min., and rises to 240°C, at a rate of 6°C/ min., and hold 5 minutes. Nitrogen carrier gas flow was 3ml min⁻¹, hydrogen flow was 75ml/min and air flow was 100ml/min using splitless mode for injection.

Degradation of pirimiphos-:

Photodegradation experiments were carried out according to USEPA, (1982); Zabic and Ruzo (1980) and Nelson and Termes (1992) by using aqueous potassium phosphate buffer pH 5, 7 and 9. Pesticide solutions were prepared in water to obtain a final concentration were of 1000 μ g/ml as working solution. A set of experiment for photodegradation studies were carried out as follow:

Photochemical degradation:

UV-irradiation:

Samples solutions were irradiated in 10 ml Quartz tube to short UV-irradiation at 254nm at a distance of 30Cm at room temperature for 0, 1, 2, 5, 9, 14 and 23 days.

Direct sunlight:

Samples solutions were exposed to the direct sunlight in may 2008, pirimiphos methyl samples were taken after 0,1, 3, 6, 12, 24 and 48 hours. dominant atmospheric temperature during the exposure time was 36 \pm 2°C.

Thermal degradation:

Samples solution were exposed to different temperature degrees 30, 40 and 50°C for 0, 1, 2, 5, 9, 14 and 23 days in electric oven provided with temperature regulating system and dark conditions.

A set of samples solution left in dark at room temperature at pH 7 were used as blank.

The method described by EPA (1992) were used for extraction pirimiphos-methyl from buffer solution using dichloromethane.

The degradation rate and the half-life values ($t_{0.5}$) of pirimiphos-methyl were calculated mathematically according to Moye *et al.* (1987).

GC-MS Identification of pirimiphos-methyl degradation products:

Degradation products of pirimiphos-methyl were injected in GC-MS analysis which performed with an Agilent 6890 gas chromatograph equipped with an Agilent mass spectrometric detector, with a direct capillary interface and fused silica capillary column HP-5MS (30 m X 0.32 mm i.d. X 0.25 μm film thickness). Pesticide samples were injected under this conditions, Helium was used as carrier gas at approximately 1.0 ml/min., Splitless mode was used in injection. The solvent delay was 3 min. and the injection size was 1.0 μl . The GC temperature program was started at 80°C hold 3 min then elevated to 260°C at rate of 8°C/min. The detector and injector temperature were set at 280 and 250 °C, respectively. Wiley7Nist05 and pesticides mass spectral data base was used in the identification of the separated peaks.

RESULTS AND DISCUSSION

Pirimiphos-methyl residues:

Data in Table (1) and Fig. (1) showed the residue level and loss rates of pirimiphos-methyl on and in unwashed apple and peach fruits as well as grape leaves at different intervals after pirimiphos-methyl application. The residue amounts were decreased with time elapsed and percent loss (%) was increased to reach 90.09, 83.51 and 98.88 % in apple and peach fruits and also grape leaves after 10 days of pirimiphos-methyl application, respectively. The residues half-life values ($t_{0.5}$) of pirimiphos-methyl as calculated mathematically were 2.56, 2.68 and 1.91 days for apple fruits, peach fruits and grape leaves, respectively. The obtained results are in agreement with El-Lakwah *et al.* (1998), who reported that the loss rate of pirimiphos-methyl was continued to prolonged the time to 94.1 and 96.6% after 14 days after treatment on peach fruits and grape leaves, respectively. The

maximum residue limit (MRL) of pirimiphos-methyl on apple fruits, peach fruits and grape leaves recorded by the European Union (2008) were 0.05ppm, so the pre-harvest interval value (PHI) for pirimiphos-methyl was 13, 16 and 15days on apple and peach fruits as well as grape leaves to be safe for human consumption.

Food processing:

Food is a basic necessity for life but when food is contaminated with toxic pesticides, it is associated with severe effects on the human health. Hence it is pertinent to explore strategies that address this situation of food safety especially for the developing countries where pesticide contamination is widespread due to indiscriminate usage and a major part of population lives below poverty line. It is therefore of significance to evaluate simple, cost effective strategies to enhance food safety from harmful pesticides for poor populace. Food processing at domestic and industrial level would offer a suitable means to tackle the current scenario of unsafe food.

Effect of washing with tap water on pirimiphos-methyl residues:

Washing is the most common form of processing which is a preliminary step in both household and commercial preparation. The results in Table (1) showed the reduction of residues levels and the percent of removal of pirimiphos-methyl insecticides from apple fruits, peach fruits and grape leaves treatment. Data showed that pirimiphos-methyl residues at zero time reduced by washing process to 29.28, 34.49 and 35.65% in apple fruits, peach and grape leaves, respectively, which decreased by 50.00, 55.22 and 71.99% in apple fruits, peach fruits and grape leaves, respectively after one day. Radwan *et al.* (2004), stated that washing the treated fruits with tap water led to 52-58% removal of the initial residues of pirimiphos-methyl from the tested fruits. Hegazy *et al.* (2006), indicated that washing with tap water removed about 10-30% of organophosphorus insecticide residues after one hour from application, respectively.

Effect of blanching process of treated grape leaves on pirimiphos-methyl residues:

The results in Table (1) show the reduction of residues levels and the increasing of removal percent of pirimiphos-methyl from grape leaves treatment after one hour (64.77%) and one day (89.30%) due to blanching process. The obtained results by Hegazy *et al.*

(2006), showed blanching process removed 40-50% of organophosphorus insecticide residues after one hour from application. The obtained results disagreement with El-Lakwah *et al.* (1998), who reported boiling grape leaves removed 9.5% of pirimiphos-methyl residues after one hour of treatment.

The above results emphasizes the fact that the advantages associated with the application of pesticides in enhancing the agricultural productivity must be weighed against the possible health hazard arising from the toxic pesticide residues in food. First and foremost the application of pesticides should be in compliance with good agricultural practices, using only the required amounts.

Further the current shift in world opinion from 'chemical farming' towards 'organic farming' is a sustainable approach to minimize the damage posed by widespread contamination of environment by pesticides. However, the challenge lies in achieving food safety in developing countries where the indiscriminate application of pesticides results in the presence of residues in food commodities. It is important concern of food safety through suitable processing techniques and appropriate storage period that enhance food safety even in developing countries especially for the poor populace which cannot afford the expensive organic food. In this background common and simple processing techniques acquire significance for reducing the harmful pesticide residues in food.

Pesticide residues in food are influenced by storage; handling and processing which is post-harvest of raw agricultural commodities but prior to consumption of prepared foodstuffs. Extensive literature review demonstrates that in most cases processing leads to large reductions in residue levels in the prepared food, particularly through washing, peeling and cooking operations. Washing with water are necessary to decrease the intake of pesticide residues. blanching of food products helps to eliminate most of the pesticide residues.

Removal of residues in food by processing is affected by type of food, insecticide type and nature as well as severity of processing procedure used (Kaushik *et al.* 2009).

Table (1): residues and loss rates of pirimiphos-methyl (50%EC) on apple and peach fruits as well as grape leaves.

Time after application (days)	Apple fruits				Peach fruits				grape leaves					
	Unwashed		Washed		Unwashed		Washed		Unwashed		Washed		Blanching	
	Residues* (ppm)	% loss	Residues* (ppm)	% loss	Residues* (ppm)	% loss	Residues* (ppm)	% loss	Residues* (ppm)	% loss	Residues* (ppm)	% loss	Residues* (ppm)	% loss
0**	2.22	0.00	1.57	29.28	6.61	0.00	4.33	34.49	35.82	0.00	23.05	35.65	12.62	64.77
1	1.79	19.37	1.11	50.00	4.48	32.22	2.96	55.22	22.53	37.10	10.03	71.99	3.83	89.30
3	0.95	57.21	-	-	2.86	56.73	-	-	14.65	59.10	-	-	-	-
6	0.46	79.28	-	-	1.71	74.13	-	-	5.25	85.34	-	-	-	-
10	0.22	90.09	-	-	1.09	83.51	-	-	0.40	98.88	-	-	-	-
15	0.01	99.55	-	-	0.25	96.22	-	-	ND	ND	-	-	-	-
t _{0.5}	2.56				2.68				1.91					
PHI (days)	13				16				11					

* : Each value represents an average of three replicates.

** : Samples were taken one hour after application (zero time).

LOD : 0.01 ppm.

t_{0.5} : Half-life value.

PHI : pre harvest interval

ND : not detected

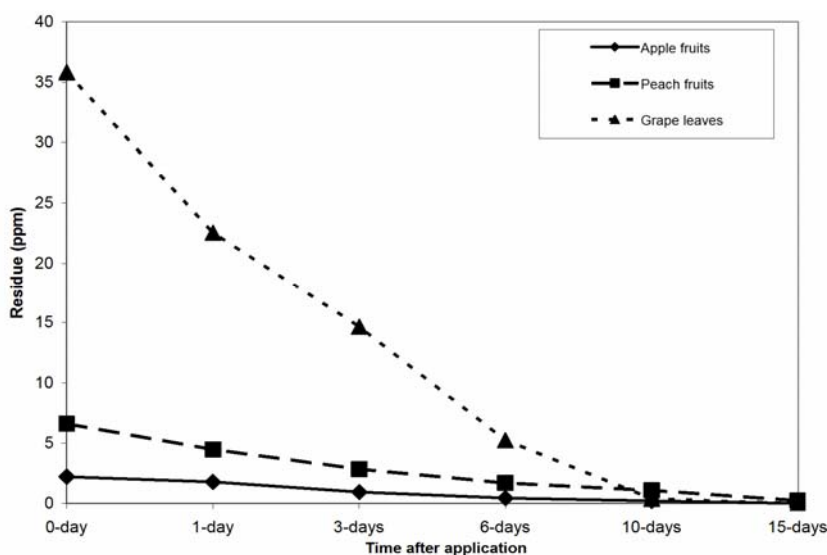


Fig.(1):Residues of Primifos-methyl on and in apple and peach fruits as well as grape leaves

Pirimiphos-methyl photodegradation:

Photochemical degradation at pH 5, 7 and 9:

Data in Table (2) demonstrate the influence of UV-irradiation at 254nm on the degradation rate of pirimiphos-methyl at different pH (5, 7, 9), the residues of pirimiphos-methyl were deteriorated after one day of UV-irradiation treatments by 23.73, 13.64 and 25.60% at pH 5, 7, 9 respectively. Continuous degradation was positively correlated with the exposure period that the long exposure period gave a high loss rate for all treatments. The degradation rate values were 62.04, 53.79 and 62.4% pH 5, 7 and 9 after 9 days of UV-irradiation treatments, respectively. No detected amount of pirimiphos-methyl at pH5 and 9 after 14 days of UV-irradiation treatments and after 23 days at pH7 the pesticide was also not detected.

The calculated half-life period ($t_{0.5}$) values in UV-irradiation treatment were 3.31, 5.37 and 3.11 days at pH 5, 7 and 9 respectively.

Data in Table (3) also showed the effect of exposure to sunlight in open field on the degradation of pirimiphos-methyl in aqueous solutions at pH 5, 7 and 9. The residues loss of pirimiphos-methyl one hour of exposure to direct sunlight was 19.21, 16.22 and 22.40% at pH 5, 7, 9 respectively. These percentage reached to 90.62, 85.48 and

91.45% at pH 5, 7 and 9 after 12 hours from direct exposure to sunlight respectively. No detected residues of pirimiphos-methyl were found after 24 and 48 hours in pH 5 and 9, respectively.

Table (2): Effect of UV-irradiation on the degradation of pirimiphos-methyl at different pH

Time days	UV					
	pH 5		pH 7		pH 9	
	µg found*	% loss	µg found*	% loss	µg found*	% loss
0**	1000.00	0.00	1000.00	0.00	1000.00	0.00
1	762.70	23.73	863.60	13.64	744.00	25.60
2	563.54	43.65	685.52	31.45	541.07	45.89
5	420.49	57.95	509.74	49.03	404.24	59.58
9	379.60	62.04	462.12	53.79	375.97	62.40
14	ND	ND	446.81	55.32	ND	ND
23	ND	ND	ND	ND	ND	ND
$t_{0.5}$	3.31		5.64		3.11	

Table (3): Effect of direct sunlight on the degradation of pirimiphos-methyl at different pH.

Time hours	Sun light					
	pH 5		pH 7		pH 9	
	µg found*	% loss	µg found*	% loss	µg found*	% loss
0**	1000.00	0.00	1000.00	0.00	1000.00	0.00
1	807.91	19.21	837.85	16.22	776.01	22.40
3	495.71	50.43	526.97	47.30	444.13	55.59
6	234.80	76.52	274.16	72.58	212.76	78.72
12	93.77	90.62	145.24	85.48	85.53	91.45
24	ND	ND	100.80	89.92	ND	ND
48	ND	ND	3.64	99.64	ND	ND
$t_{0.5}$	3.13		4.24		2.81	

* : Each value represents an average of three replicates.

** : Samples were taken one hour after application (zero time).

LOD : 0.01 PPM.

$t_{0.5}$: Half-life value.

ND : not detected

The calculated half-life period ($t_{0.5}$) values were 3.13, 4.24 and 2.81 hours at pH 5, 7 and 9 respectively. Shokr (1997), reported that pirimiphos-methyl was most sensitive compound than fenitrothion and prothiofos when exposed to direct sunlight.

Generally, it was found that photodegradation was positively correlated with the period of exposure and chemical structure. Enhancement of photodecomposition by short UV-rays may be attributed to the interaction between the pesticide molecule and UV-rays produces many chemical changes via several types of reactions such as hydrolysis, oxidation and isomerization (Santoro *et al.*, 2000). The radiation energy produced from UV-rays and direct sunlight might be absorbed by a pesticide molecule principally at a given wavelength. The energy might increase the transitional, rotational, vibrational or electric energy which were absorbed to interact with the electrons of the molecule as mentioned, an electronically excited molecule would result. Energy might disappear or change from the molecule in many ways, one of which is chemical reaction (Plimmer, 1970). Generally, results showed that the exposure to direct sunlight was more effective than the exposure to UV-irradiation in the degradation of pirimiphos-methyl. The results also showed that in the direct sunlight the parent compound was completely disappeared within 24h under pH5 or 9 while it disappeared within 48h at pH7 at atmospheric temperature of $36\pm 2^{\circ}\text{C}$.

Thermal degradation at pH 5, 7 and 9 (dark conditions):

The effect of the exposure to different temperature degrees 30, 40 and 50°C on pirimiphos-methyl degradation manifested in Table (4). Results indicate the persistence of pirimiphos-methyl was highly influenced by temperature and period of exposure and its degradation was faster at high temperature. The loss percentage values of pirimiphos-methyl after one day of exposure were 4.86, 1.76 and 10.44% at 30°C , 21.46, 12.45 and 24.28% at 40°C , 31.45, 26.28 and 31.24 at 50°C at pH 5, 7, 9 respectively. These values reached to 56.86, 31.76 and 57.64% at 30°C , 61.92, 41.77 and 60.66% at 40°C , 62.98, 53.56 and 64.24% at 50°C at pH 5, 7, 9 after 9 days of experiments respectively. No residues of pirimiphos-methyl were detected after 23 days. The calculated half-life period ($t_{0.5}$) values were 7.21, 29.48 and 5.99 days at 30° , 3.6, 8.91 and 3.39 days at 40° , 2.65, 4.50 and 2.61 days at 50° for pH 5, 7 and 9 respectively. No

residues of pirimiphos-methyl were detected after 14 and 23 days at different pH. Hegazy *et al.* (1982), reported that the percent loss of pirimiphos-methyl were 17.68 and 41.03% at 35 and 45°C with in the first two days.

The results also showed that no effect of pH ranged between 5 and 9 on the degradation rate of pirimiphos-methyl at 30°C. The effect of pH under temperature higher than 30°C on other words, 40°C and above showed rate of pirimiphos-methyl degradation greater and disappeared after 14 days at pH 5 or 9 which takes longer time (23days) at pH 7, this is similar to that found for the effect of UV on the degradation of pirimiphos-methyl at different pH.

GC-MS identification of pirimiphos-methyl photochemical degradation products:

The photochemical degradation products generated during the sunlight exposure were extracted and injected in GC-MS, the compounds were identified by comparison with the published spectra and by interpretation of fragment ions. Data in Table (5) and Fig.(2) show that four major isolated photochemical degradation products in addition to the parent compound were detected and identified by their mass spectra comparing with library scan.

After the identification of the various products, the pathway of the photochemical degradation of pirimiphos-methyl may be suggested in Fig.(2). There are two major pathways of the degradation.

Herrmann *et al.*, (1999) identify the degradation products of pirimiphos-methyl as 2-diethylamino-4- hydroxy-6- methylpyrimidine (MW= 181), which was detected in this study (path 1 compound 1,2), 2-ethyl methyl amine-4-hydroxy-6-methylpyrimidine (MW= 167) and 2-ethylamine-4-hydroxy-6-methylpyrimidine (MW= 153). Its generally known that the hydrolysis of phosphorothioate ester is caused through the reaction of nucleophilic substitution which depends on the electrophilic ability of phosphorus atom, (Hirahara *et al.* 2003). There are three major routes of degradation of pirimiphos-methyl one route may involve the formation of a N-oxime compound (MW=157) together with the induced hydrolysis of phosphoric ester function, second path is the result of a N-dealkylation which gives compound (MW=277), third route involves oxidation of the methyl group into an aldehyde function compound (MW=319), followed by the induced hydrolysis of the phosphoric ester function compound (MW=195) (Chiron *et al.* 1998) which was reported in this study (path 2 compound 1).

Table (4): Effect of different temperature degrees (30,40, and 50°C) on the degradation of pirimiphos-methyl at the different pH degrees.

Time days	30						40						50					
	pH 5		pH 7		pH 9		pH 5		pH 7		pH 9		pH 5		pH 7		pH 9	
	µg found	% loss	µg found	% loss	µg found	% loss	µg found	% loss	µg found	% loss	µg found	% loss	µg found	% loss	µg found	% loss	µg found	% loss
0	1000.00	0.00	1000.00	0.00	1000.00	0.00	1000.00	0.00	1000.00	0.00	1000.00	0.00	1000.00	0.00	1000.00	0.00	1000.00	0.00
1	951.45	4.86	982.41	1.76	895.64	10.44	785.44	21.46	875.49	12.45	757.19	24.28	685.54	31.45	737.20	26.28	687.60	31.24
2	776.25	22.38	983.12	1.69	713.00	28.70	616.02	38.40	820.56	17.94	588.55	41.15	486.08	51.39	657.49	34.25	472.48	52.75
5	475.51	52.45	976.72	2.33	498.34	50.17	409.82	59.02	798.41	20.16	424.86	57.51	373.92	62.61	574.20	42.58	372.58	62.74
9	431.37	56.86	682.38	31.76	423.56	57.64	380.80	61.92	582.31	41.77	393.44	60.66	370.20	62.98	464.40	53.56	357.60	64.24
14	417.75	58.23	539.27	46.07	406.47	59.35	ND	ND	482.28	51.77	ND	ND	ND	ND	433.90	56.61	ND	ND
23	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
t _{0.5}	7.21		29.48		5.99		3.60		8.91		3.39		2.65		4.50		2.61	

* : Each value represents an average of three replicates.

** : Samples were taken one hour after application (zero time).

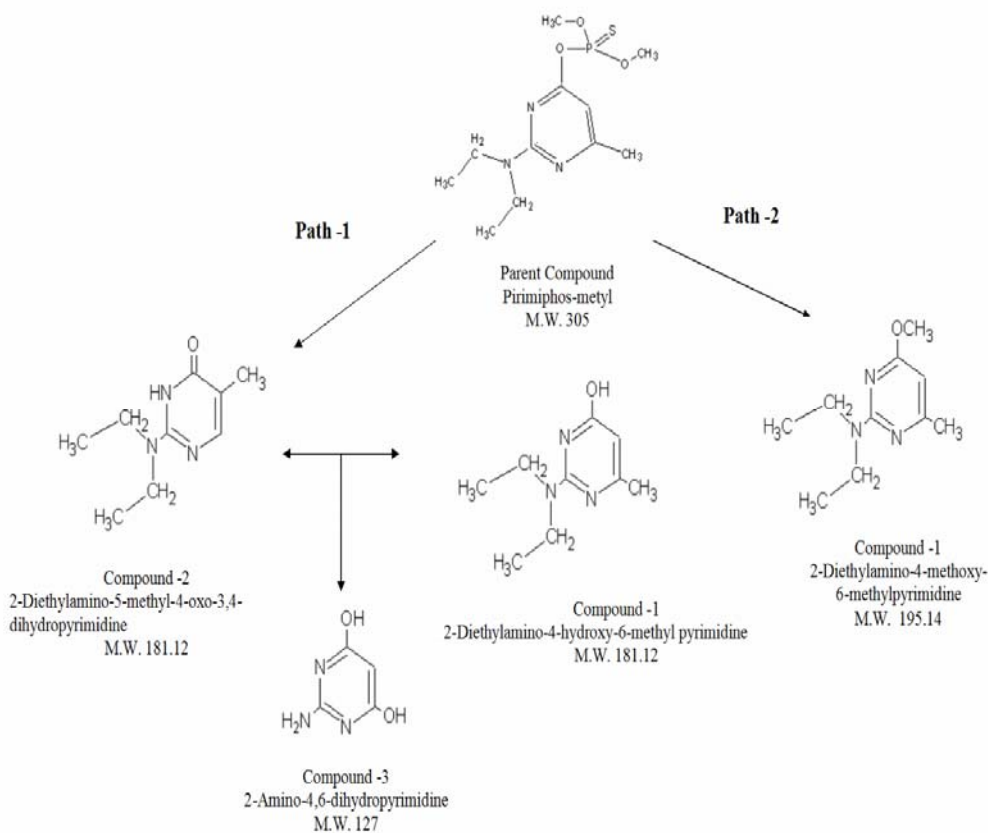
LOD : 0.01 ppm.

t_{0.5}: Half-life value.

ND : not detected

Table (5): photodegradation products of pirimiphos-methyl after exposure to sunlight as identify by GC-MS

Compounds	mw	Chemical formula
Pirimiphos-metyl (Parent Compound)	305	C ₁₁ H ₂₀ N ₃ O ₃ PS
Path 1 Compound -1 2-Diethylamino-4-hydroxy-6-methylpyrimidine	181.12	C ₉ H ₁₅ N ₃ O
Path 1 Compound -2 2-Diethylamino-5-methyl-4-oxo-3,4-dihydropyrimidine	181.12	C ₉ H ₁₅ N ₃ O
Path 1 Compound -3 2-Amino-4,6-dihydropyrimidine	127	
Path 2 Compound -1 2-Diethylamino-4-methoxy-6-methylpyrimidine	195.14	C ₁₀ H ₁₇ N ₃ O

**Fig.(2):Scheme of the proposed degradation pathway of pirimiphos-methyl**

REFERENCES

- Anonymous (2001), Ministry of Agriculture, pest control Program, A.R.E.
- Chiron, S.; Rodriguez, A. and Fernandez-Alba, A. (1998). Application of gas and liquid chromatography-mass spectrometry to the evaluation of pirimiphos methyl degradation products in industrial water under ozone treatment. *J. Chromatogr. A* 823:97-107.
- Domotorova, M.; Hercegovca, A. and Matisova, E. (2006). Monitoring of pesticide residues in apples from Slovakia for baby food production. *Czech J. Food Sci.*, 24: 84–92.
- El-Lakwah, F. A.; Abdel-Razik, M.; Omnia, M. K. and El-Rafea, A. E. (1998). Persistence of malathion, pirimiphos-methyl and diazinon in some fruits. *Annals Of Agric. Sci., Moshtohor*, 36(4):2573-2591.
- EPA (1992). Official Standard Methods. Manual Guidelines for water, Report EPA/ 625/ R- 92/ 0 04, USEPA (Office of water), Washington DC.
- EU (2008). EU Harmonized Maximum Residue levels. Combined search. Corrections as published in the OJ of September 09,2008 (L240.pp.9)
- Hegazy, M. E. A.; Abdel-Razik, M. and El-Sayed, M. M. (1982). Thermal and photodecomposition of monitor and pirimiphos-methyl organophosphorous pesticides. *Proc. Egypts National Conf., Ent., Dec. Vol II: 743-751.*
- Hegazy, M. E. A.; Afify, A. M. R.; Hamama, A. A. and El-Refahy T. F. A. (2006). Persistence and behavior of certain insecticide residues on tomato fruits in relation to processing and biochemical constituents of fruits. *Egypt J. Agric. Res.*, 84 (3),:853-856.
- Herrmann, J. M.; Guillard, C. Arguello, M.; Aguera, A.; Tejedor, A.; Piedra, L. and Fernandez-Alba, A. (1998). Photocatalytic degradation of pesticide pirimiphos-methyl determination of the reaction pathways and identification of intermediate products by various analytical methods. *Catalysis Today*, 54:353-367.
- Hirahara, Y.; Ueno, H. and Nakamuro, K. (2003). Aqueous photodegradation of fenthion by ultraviolet B irradiation: contribution of singlet oxygen in photodegradation and photochemical hydrolysis. *Water research*, 37:468-476.

- Kaushik, G.; Satya, S. and Naik, S.N. (2009). Food processing a tool to pesticide residue dissipation. *Food Research International* 42: 26–40.
- Kiss, A.; Rapi, S. and Csutorás, Cs. (2007). GC/MS studies on revealing products and reaction mechanism of photodegradation of pesticides. *Microchemical Journal*, 85: 13–20.
- Mills, P. A.; Bong, B. A.; Kamps, L. R. and Burke, J. A. (1972). Elution solvent system for florisil column clean up in organochlorine pesticide residue analysis. *J. A.O.A.C.* 55(1): 39-43.
- Moye, H. A.; Malagodi, M. H.; Yoh, J.; Leibee, G. L.; Ku, C. C. and Wislocki, P. G. (1987). Residues of avermectin B1a rotational crop and soils following soil treatment with (¹⁴C) avermectin B1a. *J. Agric. Food Chem.*, 35:859-864.
- Nelson, H. P. and Termes, S. C. (1992). Ambiguities and deficiencies in USEPA guidelines for conducting laboratory environmental fate studies on pesticides, in agrochemical environmental fate, state of the art pp51-69. GRC Press, USA.
- Pihlström, T.; Blomkvist, G. and Friman, P. (2007) Analysis of pesticide residues in fruit and vegetables with ethyl acetate extraction using gas and liquid chromatography with tandem mass spectrometric detection. *Anal Bioanal Chem.*, 389:1773–1789
- Plimmer, J. R. (1970). The photochemistry of halogenated herbicides. *Residue Rev.*, 33:47-72.
- Radwan, M. A.; Shiboob, M. H.; Abu-Elamayen, M. M. and Abdel-Aal, A. (2004). Pirimiphos-methyl residues on/in some field-grown vegetables and its removal using various washing solutions and kitchen processing. *International journal of agriculture & biology*, 6 (6):1026–1029.
- Santoro, A.; Scopa, A.; Bufo, S. A.; Mansour, M. and Montasser, H. (2000). Photodegradation of triazole fungicide hexaconazole. *Bull. Environ. Contam. Toxicol.*, 64:475-480.
- Shokr, S. A. A. (1997). Environmental pollution by pesticides residues. Ph.D. Thesis, Fac. Agric., Tanta Univ.
- USEPA, US Environmental protection (1982). Office of pesticide and toxic substances, photodegradation studies in water. In pesticides assessment guidelines subdivision and environmental fate. EPA 540/9-82-021, 46:49.

Zabic, H. and Ruzo, K. (1980). Factor effecting in pesticide fate and movment of toxicanys. Symposim association of official analytical chemists, October 21-22, 20-27.

تحطم وسلوك متبقيات مبيد البيريثيفوس ميثيل تحت بعض الظروف الحقلية وتأثير بعض العمليات التصنيعية عليه

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تم إجراء هذه الدراسة بهدف تقدير ثبات مبيد البيريثيفوس ميثيل على ثمار التفاح والخوخ وأوراق العنب تحت الظروف الحقلية المصرية وتأثير عمليات الغسيل والسلق على إزالة المتبقيات الموجودة في الثمار و الأوراق وكذلك تأثير التحلل الضوئي نتيجة التعرض لأشعة الشمس المباشرة والتعرض للأشعة فوق البنفسجية وكذلك تأثير التحلل الحراري باستخدام درجات الحرارة المختلفة (30- 40- 50°م) على زيادة معدل تحطم مبيد البيريثيفوس ميثيل وذلك تحت درجات pH مختلفة (5 - 7 - 9) وكذلك دراسة نواتج تحطم المبيد البيريثيفوس ميثيل باستخدام GC-MS.

أوضحت الدراسة أن فترة نصف العمر كانت 2.56 و 2.61 و 1.91 يوم على ثمار التفاح والخوخ وأوراق العنب على التوالي. وكذلك أوضحت الدراسة أن عملية الغسيل بماء الصنبور أدت إلى إزالة 29.28 و 34.49 و 35.60 % من متبقيات البيريثيفوس ميثيل على ثمار التفاح والخوخ وأوراق العنب بعد ساعة من المعاملة على التوالي ، بينما أدت عملية السلق إلى إزالة 64.77% من المتبقيات على أوراق العنب بعد ساعة من المعاملة.

وكذلك أوضحت النتائج أن التعرض المباشر لأشعة الشمس (36±2°م) أدى إلى اختفاء البيريثيفوس ميثيل (المركب الأصلي) خلال 24 ساعة وذلك على 9,5 pH وخلال 48 ساعة على 7 pH بينما أدى التعرض للأشعة فوق بنفسجية أدى إلى اختفاء المركب الأصلي بعد 14 يوم على 5,9 pH وبينما اختفى خلال 23 يوم على 7 pH .

وأيضاً أوضحت النتائج انه على درجة حرارة 30°م لم يوجد تأثير يذكر على أي درجة pH ولكنه بارتفاع درجة الحرارة إلى 40°م أو 50°م أدى إلى اختفاء المركب الأصلي بعد 14 يوم على 5,7 pH وبينما اختفى خلال 23 يوم على 7 pH.

تم التعرف على نواتج تحطم لمبيد البيريثيفوس ميثيل باستخدام جهاز GC-MS وتم اقتراح مسارين لتحطمه:

المسار الأول وينتج المشابهين 2-Diethylamino-4-hydroxy-6-methyl pyrimidine و 2-Diethylamino-5-methyl-4-oxo-3,4-dihydropyrimidine ووزنهم الجزيئي 181.12 وبعد ذلك ينتج المركب 2-Amino-4,6-dihydropyrimidine ووزنه الجزيئي 127 أما المسار الثاني فينتج المركب 2-Diethylamino-4-methoxy-6-methylpyrimidine ووزنه الجزيئي 195.14