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DETERMINATION OF SOME PESTICIDES RESIDUES IN WATERMELON PLANT AND THEIR TOXIC EFFECT AGAINST SOME PESTS

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ABSTRACT

The efficiency of some pesticides (malathion, pirimiphos methyl, chlorpyrifos methyl, carbosulfan and methomyl) were tested against melon aphid adults *Aphis gossypii* (Glover) and the fourth instar larvae of cotton leafworm *Spodoptera littoralis* (Boisd.) For melon aphid adults, carbosulfan pesticide was the most effective compound against *Aphis gossypii* followed by chlorpyrifos-methyl, pirimiphos-methyl and methomyl pesticide. LC_{50} values of previous insecticides were : 0.49 , 0.75, 3.31 and 5.46 ppm, respectively. Malathion showed the lowest toxicity with the LC_{50} value of 34.89 ppm. While, chlorpyrifos-methyl was the most effective pesticide towards *Spodoptera littoralis* larvae followed by methomyl and malathion. The obtained LC_{50} values were 10.29, 47.84 and 270.22 ppm, respectively). However, pirimiphos-methyl and carbosulfan exhibited lowest toxicity against *S. littoralis* larvae with the LC_{50} values of 1079.00 and 3245.06 ppm, respectively.

Residues of the tested pesticides were determined in watermelon peel, pulp and seeds after zero time, one, three and five days from treatments. The initial concentrations of different pesticides tested were detected after one hour of treatments with different variations in samples and tested pesticides by using GLC and colorimetric methods . These residues were changed in examined samples at intervals with times to reach at the end of experiments (5 days): For Malathion (0.083, 0.052 and 0.026 ppm in watermelon peel, pulp and seeds, respectively.) For pirimiphos methyl (0.0232, 0.0274 and 0.0083 ppm in watermelon). For chlorpyrifos methyl (0.975, 7.54 and 9.892 ppm) in watermelon peel, pulp and seeds, repectively. For methomyl the residues were increased in watermelon peel and pulp recording 1.377 ppm and 0.764 ppm, respectively while the residue was descended to 0.452 ppm in watermelon seeds .

INTRODUCTION

The extensive and unwise use of synthetic pesticides during the last few years has rapidly increased because of their fast action and prolonged protection against pests, this has begun to receive much attention because residues of pesticides in food commodities may be hazardous to human health and created pollution problem to the environment .(Abbassy *et al.*, 1989, Mott 1991, Tonagai *et al.*, 1992, Kumar *et al.*,1993, Bayoumi *et al.* 1995-a, 1996, 1997, Cabras *et al.*, 1997-b and Abd Allah.1998) .

In Egypt, vegetable crops grown are subject to severe insect infestation specially in summer season. Watermelon *Citrullus lanatus var. colocynthoids* which present one of the important crops that consumed by Egyptian peoples as seeds, is attacked by a variety of insect pests . Two of these were the Egyptian cotton leafworm *Spodoptera littoralis* (Boisd.) and aphid melon *Aphis gossypii* (Glover) which cause a highly losses in its production. The need to develop suitable screening tests is strongly felt as a

result of the increase of hazards of agrochemicals with special reference to pesticides. So, five of the commonly used pesticides which have been recommended to control these pests in watermelon field, namely malathion, pirimiphos methyl, chlorpyrifos methyl, carbosulfan and methomyl are tested to study their efficiency against melon aphid and cotton leafworm and to study their behavior in different parts of watermelon fruits as residuesa.

MATERIALS AND METHODS

1-Insecticides used:

Malathion: Malathion, E.C. 57% (S-1,2-bis (ethoxy carbonyl) ethyl O,O-dimethyl phosphorodithioate)Recommended rate of application: 1.5 L/feddan (watermelon crop).

Pirimiphos-methyl: Actellic, E. C. 50%. (0-2- diethylamino -6-methylpyrimidin -4-yl 0,0- dimethyl phosphorothioate.Recommended rate of application: 1.5 L/feddan (watermelon).

Chlorpyrifos-methyl: Reldan, E.C. 50%. (0,0-dimethyl O-3,5,6- trichloro -2-pyridyl phosphorothioate.)Recommended rate of application: 1L/feddan (watermelon).

Carbosulfan: Marshal,(W.P.)25%. (2,3-dihydro-2,2-dimethylbenzofuran-7-yl (dibutylaminothio) methyl carbamate.) Recommended rate of application: 0.8 kg/feddan (watermelon).

Methomyl: Lannate, WP. 90%. (S-methyl N-(methylcarbamoyloxy) thioacetimidate.)

Recommended rate of application: 0.3 kg/feddan (watermelon crop).

2- Insects rearing:-

2-1. Rearing of melon aphid , *Aphis gossypii* (Glover):

This strain was originated from Sakha Agricultural Experimental Station, and cultural free from insecticidal contamination for at least two years. Watermelon seedlings, 10-days old, holding about 2-5 leaves each, were usually used for rearing aphid individuals under laboratory conditions Aphids were always transferred weekly from old to young seedlings by cutting the heavily infested leaves and were placed on the new plants. Contamination between cultures was prevented by placing these seedlings in special muslin chambers, 50 x 50 x 60cm. These cultures were maintained in a breeding room under the temperature 25 ± 2°C and 65 ± 5% RH and 12 hours daily illumination by 2 fluorescent bulbs of 40 wts each.

2-2. Rearing of cotton leafworm, *Spodoptera littoralis* (Boisd.):

Egg-masses of susceptible strain of *spodoptera littoralis* were taken from Sakha Agricultural Experimental Station.The rearing of this strain in the laboratory was made as described by **El-Defrawy *et al.* (1964)** to the fourth instar larvae on castor oil bean leaves *(Ricinous communis)* under conditions of 25 ± 5°C and 65± 5% RH.

3- Toxicity tests against melon aphid, *Aphis gossypii* (Glover):-

The rapid-dip (FAO method No. 17, 1980) was applied to evaluate the efficiency of the tested insecticides against the susceptible strain of melon aphid, *Aphis gossypii* (Glover). Serial concentrations of the tested insecticides were prepared by dissolving in water. Four replicates, each of ten adults, were done for each concentration. Batches of aphid were dipped in each insecticide dilution for 10 seconds, partly dried and held on leaves of watermelon seedlings in petri-dishes (7.5 cm). Control insects were dipped in water only. Mortality counts were recorded 24 hours after application and were corrected according to Abbott's formula (1925). The corrected mortalities were plotted on a log-dosage probit paper and regression lines were fitted and statistically analyzed according to Finney (1952).

4- Toxicity evaluation against cotton leafworm, *Spodoptera littoralis* (Boisd.):

- Leaf dipping technique:

Serial concentrations of the tested insecticides dissolved in distilled water were prepared. In these solutions the watermelon leaves were immersed for five seconds; each treatment was replicated five times, and then the leaves left to dry. The larvae were allowed to feed on treated leaves for 24 hours under laboratory conditions. Meanwhile, control larvae were fed on untreated watermelon leaves for 24 hours. Mortality percentages of were recorded and corrected according to Abbott's formula (1925), and the LC_{50} values were calculated using the statistical method of Finney (1952).

5- Chemical analysis :

5-1. Field pesticides treatments:

Watermelon *Citrullus lanatus var. colocynthoides* was planted on April, 27th 1997, under the normal field conditions and agricultural practice at Sedi Salem district, Kafr El-Sheikh Governorate. The crop was planted in six plots 175 m^2 area for each. The crop was sprayed with the recommended rates of each insecticide according to the Ministry of agriculture and land reclaimation recommendation (1996). A plot for each insecticide was treated with one of the tested insecticides. The northern plot was left as control. The insecticidal formulations were diluted with water (200 litre/feddan) and applied on July 22th 1997 (87 days after planting).

5-2. Sampling:

Three fruits of watermelon, with the mean weight of 1200 gm were collected randomomely from each insecticide treatments at intervals of one hour after application (zero time),1, 3 and 5 days Clean new polyethylene bags were used for preservation of the collected samples. The samples were stored at –20°C in a deep-freezer until time of the analysis

5-3. Extraction procedures:

Different methods of extraction were used depending on the chemical structure of the tested pesticides.

5-3-1. For malathion, pirimiphos methyl and chlorpyrifos-methyl from peel and pulp:

The extraction method for malathion, pirimiphos-methyl and chlorpyrifos-methyl was the same. Freezed samples were left until reach room temperature and chopped by the knife. then every part was separated alone, then was macerated using waring blender 50 gm representative subsample from each peel and pulp were transferred to 500 ml Jar and blended at high speed for 3 minutes with 100 ml acetone. Then filtered with suction through Whatman paper No.4 on Buchner funnel. Jar and filter cake were rinsed with 15 ml portions of acetone and the extract was transferred into a graduated cylinder to reach known volume. Filtered extract was transferred to 1L separatory funnel, extract was shaken in separatory funnel successively three times with 35 ml chloroform each and 20 ml of sodium chloride solution (20%); Then the water phase was discarded. The combined chloroform phases were dried by filteration through a pad of cotton and anhydrous sodium sulphate then evaporated just to dryness using a rotary evaporator at 40 C°.

5-3-2. For carbosulfan from peel and pulp:

Freezed samples were left until reach room temperature and chopped by the knife, then every part was separated alone, then was macerated using waring blender. 50 gm representative subsample from each peel and pulp were transferred to 500 ml Jar and macerated at high speed for 3 minutes with 150 ml chloroform. Then filtered with suction through Whatman paper No.4 on Buchner funnel. Jar and filter cake were rinsed with 15 ml portions of chloroform.

5-3-3. For methomyl from peel and pulp:

Freezed samples were left until reach room temperature and chopped by the knife, then every part was separated alone, then was macerated using waring blender. 50 gm representative subsample from each peel and pulp were transferred to 500 ml Jar and macerated at high speed for 3 minutes with 100 ml of isopropyl alcohol. Then filtered with suction through Whatman paper No. 4 on Buchner funnel. Jar and filter cake were rinsed with 15 ml portions of isopropyl alcohol. The extracts were evaporated up to 50 ml, it is ready to clean up.

5-3-4. For tested pesticides from watermelon seeds:

The extraction method for tested pesticides was the same. Freezed samples were left until reach room temperature then were grinded using grinder. 20 gm representative subsample was transferred to 500 ml Jar and macerated in waring blender at high speed for 3 minutes with 80 ml of methylene chloride. Then filtered with suction through Whatman paper No.4 on Buchner funnel. Jar and filter cake were rinsed with 20 ml portions of methylene chloride. Extract was refiltered through a pad of cotton and anhydrous sodium sulphate then evaporated just to dryness using a rotary evaporator at 35C°.

5-4. Clean up procedures:

For peel and plup extracts:

For malathion and pirimiphos methyl from peel and pulp : the clean up method for malathion and pirimiphos methyl was the same. The clean up procedure was done according to the method of Mollhoff (1975). For Clean up of chlorpyrifos-methyl extracts: the clean up procedure was done according to the method of Ferreira and Fernandes (1980). For carbosulfan :Filtered extract was transferred to 1L separatory funnel, then was shaken with 20 ml of sodium chloride solution (20%); then the water phase was discarded. The chloroform phase was dried by filteration through a pad of cotton and 10 gm anhydrous sodium sulphate and 5 gm activated carbon then evaporated just to dryness using a rotary evaporator at 40°C. The residue was quantitatively transferred to standard glass stopper test tube with methanol, and the residues were ready for colorimetric determination. For methomyl : The extracts were cleaned up adding 3 grams activated carbon to the extract and shaked for 30 seconds, and then filtered through a funnel containing 2 grams activated carbon and 10 grams anhydrous sodium sulphate, and the filtered was ready for colorimetric determination.

For seeds extracts:

The clean up method for tested pesticides was the same according to the procedure of the AOAC, (1980).

5-5. Pesticides determination :

5-5-1. Recoveries percentage:

Rate of recoveries of the insecticides on peel, pulp and seeds of watermelon were determined by adding known amounts (100 ug a.i.) of each insecticide to portions (50 gm) of untreated samples from peel and pulp, (40 ug a.i.) of each insecticide to portions (20 gm) of untreated samples from seeds. The average recovery values of each insecticide in each sample was used to correct all obtained values of each insecticide residues.

5-5-2. Determination of pesticides residue by GLC:

Shimadzu chromatographic GC-4CM equipped with flame photometric detector (FPD) with phosphorus filter was used to determine malathion, pirimiphos-methyl and chlorpyrifos-methyl. The calibrated conditions of the gas chromatographic were carefully checked before injecting any sample. The working conditions for the gas chromatographic GC-4CM were as follows:

Conditions	Pesticides
Column	S.G.L 3m x 10.3 mm i.d was packed with OV-17
Column temperature	230°C
Detector temperature	280°C
Injector temperature	280°C
Carrier gas	N2
N2 flow rate	40 ml/min.
H2 Flow rate	0.8ml/min.
Air Flow rate	1.0L/min.
Chart speed	5mm/min.

5-5-3. Colorimetric methods:

Carbosulfan insecticide was determined according to the method of Rangaswamy *et al.* (1976) While methomyl pesticide was determined according to the method of Meagher *et al.* (1967).

RESULTS AND DISCUSSION

Laboratory tests were conducted to evaluate the efficiency of the tested insecticides ((malathion, pirimiphos methyl, chlorpyrifos methyl, carbosulfan and methomyl) against melon aphid, *Aphis gossypii* (Glover). The rapid-dip (FAO method No.17, 1980) was applied. Results are recorded in Table (1).

Table (1): Toxic effect of watermelon leaves treated with five pesticides against laboratory strain of melon aphid,*Aphis gossypii* Glover, under laboratory conditions after 24 hour of treatments.

Pesticides	LC_{50} Ppm	Confidence Limits				Slope
		95		99		
		upper	lower	upper	lower	
Carbosulfan	0.49	0.58	0.39	0.60	0.36	1.7
Chlorpyrifos- methyl	0.75	1.16	0.27	------	------	3.18
Pirimiphos- methyl	3.31	4.05	2.70	4.50	2.43	1.64
Methomyl	5.46	6.80	4.60	7.40	4.38	1.89
Malathion	34.89	39.81	30.57	41.59	29.25	2.12

From the obtained results (Table1) it is obvious that, the insecticide carbosulfan had the highest toxicity followed by chlorpyrifos-methyl, pirimiphos-methyl and methomyl insecticide (LC_{50} values were: 0.49 , 0.75, 3.31 and 5.46 ppm, respectively). Malathion showed the lowest toxic effect against the melon aphid, with the LC_{50} value of : 34.89 ppm . These results are in agreement with that of Drishpon *et al.* (1989);Shalaby *et al.*(1991); Khalafalla and Abo-Sholoa (1993); and Abd-Allah. (1998), they found that, carbosulfan was the most effective pesticide against *A. gossypii*. Also with that of Sagar and Jindla (1984) who found that, the O.P compounds malathion and dichlorvos gave less satisfactory results when tested various compounds in field against *Aphis gossypii*. On the other hand, Omar *et al.* (1988) showed that, in field experiment 50% pirimiphos-methyl used alone or in mixtures with foliar fertilizers produced satisfactory control of *Aphis gssypii*. However, Saito *et al.* (1989) reported that, on the basis of LC_{50} s, aphids from melons, cucumbers, watermelons, chrysanthemums and strawberries were more resistant to malathion than those from potatoes, aubergines, *Hibiscus syriacus* and *Celastrus orbiculatus*. In contrary of our results, Zidan *et al.* (1988) reported that, pirimicarb and malathion were very effective against both nymphs and adults of *Aphis gossypii* in field and laboratory studies .

The results of the leaf dipping technique to evaluate the efficiency of the tested insecticides(malathion, pirimiphos methyl, chlorpyrifos methyl, carbosulfan and methomyl) against the fourth instar larvae of cotton leafworm, *spodoptera littoralis* (Boisd). From the recorded results in Table (2).

Table (2):Toxic effect of five pesticides against the 4th instar larvae of the susceptible strain of cotton leafworm *Spodoptera littoralis* (Boisd) after 24 hour of treatment

Pesticides	LC_{50} ppm	Confidence Limits				Slope
		95		99		
		upper	lower	upper	lower	
Chlorpyrifos- methyl	10.29	11.54	8.89	11.96	8.34	5.79
Methomyl	47.84	69.26	38.41	88.36	35.86	2.54
Malathion	270.22	334.35	204.97	356.37	182.15	2.59
Pirimiphos- methyl	1079.00	1156.32	983.17	1180.12	942.19	7.92
Carbosulfan	3245.06	3920.95	2480.31	4154.33	2169.53	3.07

Results in Table (2), it is clearly that, chlorpyrifos-methyl had the highest toxic effect towards *S. littoralis* larvae followed by methomyl and malathion.The obtained LC_{50} values were 10.29, 47.84 and 270.22 ppm. respectively. However, pirimiphos-melhyl and carbosulfan exhibited the lowest toxicity with the LC_{50} values of 1079.00 and 3245.06 ppm, respectively. These results are somewhat in agreement with those of other authors, El-Gayar *et al.* (1979) who found that, pirimiphos-methyl was classified among other tested insecticides as the less potent against the 2nd and the 4th instar larvae of *S. littoralis*. On the other hand El-Dahan. (1991) found that, the oxime carbamates thiodicarb and methomyl were less potent than organophosphate against *S. littoralis*. Also, Mourad *et al.* (1991) enhanced our results when found that, different organophosphorus were more toxic than different carbamate insecticides based on residual activity. The same results were found by Abd-Allah. (1998) who reported that, chlorpyrifos-methyl had the highest toxicity to *S. littoralis* and carbosulfan showed the lowest potent compounds to *S. littoralis*. In contrary of our results Ashry *et al.* (1991) reported that, methomyl was the most potent compounds against *S. littoralis* larvae than other insecticides tested (O P and carbamate compounds).

2- Determination of pesticides residues :

In recent years, both legislators and consumers in Egypt showed great interest towards the safety of food products from different contaminants. As a matter of fact pesticides have become universal contaminants found in all segments of the environment and food chain. The high concentration of some pesticides residues have already been reported in different food items in different parts of the world. (Panel 1977, Hadjidemetriou 1988. Hasegawa *et al.* 1992 and Dejonckheere *et al.* 1996 a&b). Also, the accumulation of such residues in the human body via the food chain is considerable interest, because of their chronic toxic potential (Hayes 1975). So, the residues of the tested pesticides were determined in all parts of watermelon fruits (peel. pulp and seeds) after one hour, one, three and five days after field application. Ther percent of losses was calculated as follow.

$$\%Loss = \frac{\text{Initial residue - residue}}{\text{Initial residue}} \times 100$$

2-1. Recovery percentages of tested Pesticides from watermelon fruits:

The accuracy of the analytical procedure for tested pesticides (malathion,pirimiphos methyl,chlorpyrifos methyl, carbosulfan and methomyl) was determined using the pure, spiked and fortified samples. The recovru values were determined using GLC method for the *O.P compounds and* using colorimetric method for carbamate compounds.

2-1-1. Recoveries from peel :

Recovery values of watermelon peel which spiked with tested pesticides are reported in Table (3).The recoveries percentage *of watermelon* peel were 87.07, 101.13, 50.14, 78.65 and 86.40 % for malathion, pirimiphos *methyl, chlorpyrifos* methyl, carbosulfan and methomyl, respectively .

Table (3): Recoveries percentage (R%) of the tested pesticides in termelonpeel

Pesticides *	Recoveries percentage
Malathion [a]	87.07
Pirimiphos methyl [a]	101.13
Chlorpyrifos methyl [a]	50.14
Carbosulfan [b]	78.65
Methomyl [b]	86.40

* method of determination. (a): using GLC method.(b) using colorimetric method

2-1-2. Recoveries from pulp :

Recovery values of watermelon pulp which spiked with tested pesticides are shown in Table (4). The recoveries percentage for watermelon *pulp were* 91.38, 114.12, 82.84, 87.60 and 91.30 % for malathion, pirimiphos methyl, chlorpyrifos methyl, carbosulfan and methomyl, respectively .

Table (4): Recoveries percentage (R%) of the tested pesticides in watermelon pulp

Pesticides *	Recoveries percentage
Malathion [a]	91.38
Pirimiphos methyl [a]	114.12
Chlorpyrifos methyl [a]	82.84
Carbosulfan [b]	87.60
Methomyl [b]	91.30

* method of determination . (a): using GLC method (b):using colorimetric method

2-1-3. Recoveries from seeds :

Recovery values for watermelon seeds which spiked with tested pesticides *are presented in* Table (5). The recoveries percentage for watermelon seeds were 89.90, 82.40, 91.40, 80.20 and 79.93 % for malathion, pirimiphos methyl, chlorpyrifos methyl, carbosulfan and methomyl, respectively .

Table (5): Recoveries percentage (R%) of the tested pesticides in Watermelon seeds

Pesticides	Recoveries percentage
Malathion [a]	89.90
Pirimiphos methyl [a]	82.40
Chlorpyrifos methyl [a]	91.40
Carbosulfan [b]	80.20
Methomyl [b]	79.93

* method of determination.(a) using GLCmethod (b) using colorimetric method

2-2. Determination of malathion residues:-

The detected concentrations of malathion pesticide in watermelon at different intervals are shown in Table (6) These concentrations were 0.398, 0.215 and 0.017 ppm in watermelon peel, pulp and seeds, respectively at zero time. These residues were decreased after 24 hours to 0.201 and 0.147 ppm in peel and pulp, respectively while it was increased to 0.053 ppm in the watermelon seeds. On the other hand, the residues of this pesticide were decreased to 0.150, 0.078 and 0.042 ppm after three days of treatments and reached to the concentrations of 0.083, 0.052 and 0.026 ppm at the end of the experimental period (5 days) in peel, pulp and seeds, respectively. Also, these data indicated that, the percent losses in this pesticide residue was found to be continued on prolonging the time after application for watermelon peel and pulp, where the percent loss rates amounted to 49.49, 62.31, 79.14% and 31.63, 63.72, 75.81% for watermelon peel and pulp, respectively after one, three and five days after treatment with malathion.

Table (6): Residues of malathion in watermelon fruits using GLC.

Time after Application (days)	Residues				
	Watermelon peel		Watermelon pulp		Watermelon seeds
	Ppm	%loss	ppm	%loss	ppm
Zero time *	0.398	00.00	0.215	00.00	0.017
1	0.201	49.49	0.147	31.63	0.053
3	0.150	62.31	0.078	63.72	0.042
5	0.083	79.14	0.052	75.81	0.026

* one hour after application

2-3. Determination of pirimiphos methyl residues:-

Data in Table (7) indicate the concentrations of pirimiphos methyl residues in watermelon peel, pulp and seeds at different intervals after application. The initial concentrations were 0.398, 0.1097 and 0.0063 ppm in watermelon peel, pulp and seeds, respectively. These residues were decreased to 0.0895 and 0.0854 ppm in watermelon peel and pulp, respectively and was increased in watermelon seeds to 0.0077 ppm after 24 hours from treatment. The residues of this insecticide were dropped to 0.0379 and 0.0498 ppm for watermelon peel and pulp, respectively and was increased in watermelon seeds to 0.0113 ppm after three days of treatments. While, at the end of the experimental period (5 days) the residues were

decreased to 0.0232, 0.0274 and 0.0083 ppm in watermelon peel, pulp and seeds, respectively. Also, these data indicated that, the percent losses in pirimiphos methyl residues was found to be continued on prolonging the time *after application in watermelon peel and pulp*, where the percent losses reached to 77.51, 90.48, 94.17% and 22.15, 54.60, 75.02% for watermelon peel and pulp, respectively after one, three and five days after treatment with pirimiphos methyl. *However the faster disappearance of pirimiphos methyl* could be attributed to its higher vapor pressure (Hegazy *et al.*, 1982).

Table (7): Residues of pirimiphos methyl in watermelon *fruits using* GLC.

Time after Application (days)	Residues				
	Watermelon peel		Watermelon pulp		Watermelon seeds
	ppm	%loss	ppm	%loss	ppm
Zero time *	0.398	00.00	0.1097	00.00	0.0063
1	0.0895	77.51	0.0854	22.15	0.0077
3	0.0379	90.48	0.0498	54.60	0.0113
5	0.0232	94.17	0.0274	75.02	0.0083

* one hour after application

2-4. Determination of chlorpyrifos methyl residues:-

The concentrations of cholrpyrifos methyl residues in watermelon peel, pulp and seeds are presented in Table (8) .The determined initial residues after one hour of treatments were 0.455, 0.084 and 0.0272 ppm in watermelon peel, pulp and seeds respectively. These residues were *decreased to 0.384 and 0.022 ppm in peel and pulp in watermelon fruits*, respectively, while it was increased in watermelon seeds to 0.0294 ppm after 24 hours from treatments. Pesticide residues were dropped to 0.089 and 0.014 ppm *in watermelon peel and pulp but it was increased to 0.0393 ppm in* watermelon seeds after three days of treatments. At the end of the experimental period after five days the residues in watermelon peel, pulp and seeds reached to the concentrations of 0.021, *0.0084 and 0.020 ppm* respectively. Also, these data indicated that, the loss percentages of residues was found to be continued on prolonging with time after application in watermelon peel and pulp, where the loss percentages reached to 15.60, 80.44, 95 38% and 73.81, 83.33, 90.0% in watermelon peel and pulp, respectively after one, three and five days from treatment with chlorpyrifos methyl.

Table (8): Residues of chlorpyrifos methyl in watermelon fruits using GLC.

Time after Application (days)	Residues				
	Watermelon peel		Watermelon pulp		Watermelo seeds
	ppm	%loss	ppm	%loss	ppm
Zero time *	0.455	00.00	0.084	00.00	0.0272
1	0.384	15.60	0.022	73.81	0.0294
3	0.089	80.44	0.014	83.33	0.0393
5	0.021	95.38	0.0084	90.00	0.020

* one hour after application

2-5. Determination of carbosulfan residues:

The carbamate insecticide carbosulfan is systemic and characterized by a high liposolubility and easy metabolism in soil and plants. It is metabolized in several plants (cotton, corn and citrus) to carbofuran, 3-keto carbofuran and 3-hydroxy carbofuran (Clay and Fukuto 1984) and (Nigg *et al.* 1984). Carbosulfan, as a parent compound, and carbofuran as a major metabolite, have been reported in soil (Clay *et al.*, 1980) and in cotton and corn (Umetsu *et al.*, 1979, 1980). Table (9) show the residual levels of carbosulfan in watermelon peel, pulp and seeds. Results indicated that, the initial residues of this insecticide were 24.11, 14.88 and 7.366 ppm in watermelon peel, pulp and seeds, respectively. These residues were decreased to 15.66 and 14.47 ppm in watermelon peel and pulp, respectively, while it was increased in watermelon seeds to 7.77 ppm after 24 hours from application. The residues of this pesticide were decreased to 15.42 and 13.11 ppm in watermelon peel and pulp, respectively On the other hand, the concentration of this insecticide was increased to 11.092 ppm in watermelon seeds, three days after treatment. At the end of the experimental period (5 days) the residues were dropped to 0.975, 7.54 and 9.892 ppm in watermelon peel, pulp and seeds, respectively. Also, these data showed that, the loss percentage of residues was found to be continued on prolonging the time after application for watermelon peel and pulp, where the percent losses rates amounted to 35.04, 36.04, 95.95% and 2.75, 11.89, 49.32% for watermelon peel and pulp, respectively after one, three and five days from treatment with carbosulfan.

Table (9): Residues of carbosulfan in watermelon fruits using colorimetric method**

Time after Application(days)	Residues				
	Watermelon peel		Watermelon pulp		Watermelon seeds
	Ppm	%loss	ppm	%loss	ppm
Zero time *	24.11	00.00	14.88	00.00	7.366
1	15.66	35.04	14.47	2.75	7.777
3	15.42	36.04	13.11	11.89	11.092
5	0.975	95.95	7.54	49.32	9.892

**Rangaswamy *et al.* (1976) * one hour after application .

2-6. Determination of methomyl residues:-

The residues of methomyl as a parent compound in watermelon fruits (peel, pulp and seeds) treated under field conditions at intervals with time of treatment are presented in Table (10) .The presented data showed that, the initial concentrations of methomyl in watermelon peel, pulp and seeds at zero time were 3.133, 1.359 and 0.063 ppm, respectively. These previous concentrations were dissipated by time in watermelon peel and pulp, the recorded concentrations were 1.043, 0.681 ppm and 0.607, 0.372 ppm, respectively after one day and three days. On the other hand, the residues in watermelon seeds were increased to 0.330 ppm after one day and increased to 0.493 ppm three days after treatment. At the end of the experimental

period (5 days),the residues were increased in watermelon peel and pulp to reach 1.377 ppm and 0.764 ppm, respectively while in watermelon seeds the residue was decreased to 0.452ppm .

Table (10): Residues of methomyl in watermelon fruits using colorimetric method

Time after Application (days)	Residues				
	Watermelon peel		Watermelon pulp		Watermelon seeds
	Ppm	%loss	ppm	%loss	ppm
Zero time *	3.133	00.00	1.359	00.00	0.063
1	1.043	66.70	0 607	55.33	0.330
3	0.681	78.26	0.372	72.62	0.493
5	1.377	56.04	0.764	43.78	0.452

** Meagher *et al.* (1967) * one hour after application .

From the previous results it could be concluded that, at the end of the experimental period chlorpyrifos methyl showed the minimum residue concentration in watermelon peel and pulp, however methomyl showed the highest residue concentration in watermelon peel. On the other hand, carbosulfan showed the highest residue concentration in watermelon pulp. The minimum concentration of pesticide residues in watermelon seeds was showed with pirimiphos methyl, while the highest residue concentration was shown with the carbamate insecticide carbosulfan.

REFERENCES

Abbassy, M. A.; A. A. El-Swak; Y. A. Hussein and M. H. Tag El-Din (1989). Side effects of environmental toxicants VI. Effect of the organo-phosphorus insecticides sulprofos on serum enzymes and liver of white rats.Alex. J. Vet. Sci. , 5 (1) :585-598.

Abbott, W. S. (1925). A method of computing the effectiveness of an insecticide. J. Econ. Entomol., 18 (2):265-267.

Abd-Allah, S. A. A. (1998). Toxicological studies of some pesticides in relation to their side effects. M. Sc. Thesis, Fac. Agric.,Kafr El-Sheikh, Tanta Univ.

Ashry, M. A.; O. C. Bayoumi; M. F. Shady and M. A. Khalifa (1991). Stability of some pesticides in combination with two foliar fertilizers and their toxic effects towards *pigomia mixta* and *spodoptera littoralis* (Boisd.) J. Agric. Res. Tanta Univ.,17 (3) : 767-775

Association of Official Analytical Chemists (AOAC) (1980): Pesticides residues pp., 466-496 by (AOAC) by Benjamin Franklin station, Washington, DC 20044. USA.

Bayoumi, O. C.; M H. Tag El-Din; F. A. M. Ahmed and J. El-Nagar (1995). Study on the effect of some agrochemical compounds on some aquatic organisms. 1st Int. Conf. of Pest Control, Mansoura, Egypt, Sept

Bayoumi, O. C.; M. H. Tag El-Din and F. A. M. Ahmed (1996). Study on the effect of the organophosphorus insecticide, chlorpyriphos-methyl (Reldan), the foliar fertilizer, Greenzit and their mixtures on some fresh water fishes. 6th Int. Conf. "Environmental protection is a must" 21-23 May, Alex. Egypt. 805-815.

Bayoumi, O. C.; M. M. F. El-Naggar; F. A. M. Ahmed and F. M. Abd El-Kawy (1997). Residual effect of three insecticides extracted from treated tomato fruits and potato tubers on decreasing acetylcholinesterase, transaminases and phosphatases in albino rats. Egypt. J. Appl. Sci., 12 (6): 217-227.

.Cabras, P.; A. Angioni; V. L. Garau; M Melis; F. M. Pirisi; M. Karim and E. V. Minelli (1997-b). Persistence of insecticide residues in olives and olive oil. Journal of Agricultural & Food Chemistry, 45 (6): 2244-2247.

Clay, V. E. and T. R. Fukuto (1984). Metabolism of carbosulfan in valencia orange tree. Arch. Environ. Contam. Toxicol., 13 : 53-62.

Clay, V. E.; M. A. H. Fahmy; J. P. Martin and T. R. Fukuto (1980). J. Agric. Food Chem., 28: 1122.

Dejonckheere, W.; W. Steurbaut; S. Drieghe; R. Verstraeten and H. Braeckman (1996-a). Moitoring of pesticide residues in fresh vegetables, fruits and other selected food items in belgium 1991-1993. J.AOAC.(1): 97-110.

Dejonckheere, W.; W. Steurbaut; S. Drieghe; R. Verstraeten and H. Braeckman (1996 -b). Pesticide residue concentrations in the belgian total diet,1991-1993. J.AOAC.79 (2): 253-259.

El-Dahan, A. A. (1991). Resistance status of *Spodoptera littoralis* (Boisd.) to insecticides in Kafr El-Sheikh Governorate during 1984-1988 cotton growing season. Egypt J. Agric., 69 (1): 23-30.

El-Gayar, F. H. ; M. Abbassy ; F. Khalil and W. Watson (1979). Efficiency of certain insecticides in controlling *Spodoptera littoralis* (Boisd.) and resistance of these insecticides under field conditions Alex. J. Agric. Res., 27 (2) : 433-437.

El-Dahan, A. A. (1991). Resistance status of *Spodoptera littoralis* (Boisd) to insecticides in Kafr El-Sheikh Governorate during 1984-1988 cotton growing season. Egypt J. Agric., 69(1): 23-30.

F. A. O. (1980). F. A. O. Method No. 17 (1980).

Ferreira, J. R. and A. M. S. Fernandes (1980). Gas-liquid chromatographic determination of organophosphorus insecticide residues in fruits and vegetables. J. Assoc. Off. Anal. Chem., 63(3): 517-522.

Finney, D. J. (1952). Probit analysis Cambridge University press, New York. 256p.

Hadjidemetriou, D. G. (1988). Persistence of pirimiphos-methyl in stored potatoes. Bull. Environ. Contam Toxicol., 41 (2): 299-303.

Hasegawa, Y. T.; T. Yasuhide; N. Yumiko and I. Yoshio (1992). Residue level of dicholrvos,chlopropham and pyrethrins in postharvest-treated potatoes during storage or processing into starch. J.Agric . Food Chem.,40 (8) 1240-1244.

Hayes, W. J. (1975). Toxicology of pesticides. Warvely press, Baltimora. USA. 268-269

Hegazy, M. E. A.; M. Abdel-Razik and M. M. El-Sayed (1982). Thermal and photodecomposition of Monitor and pirimiphos-methy1 organophosphorus pesticides. Proc. Egypt's National Conf. Ent., II: 743-751

Khalafalla, E. M. E. and M. K. A. Abo-Sholoa (1993). Susceptibility of *Aphis gossypii* Glover to certain aphicides and bollworm insecticides before and after the periodical spray programme on cotton plant.J. Agric. Res. Tanta Univ., 19 (2): 448-457.

Meagher, W. R.; R. Hendrickson and B. G. Shively (1967). Spectrophotometric determination of Temik residues in citrus.J.AOAC. 50:1242-1247.

Mollhoff, E. (1975). Method for gas-chromatographic determination of residues of tokuthion and its oxon in plant and soil samples. Pflanzechutz-Nachrichten Bayer, 28: 882-887.

Mourad, M. A. ; M. E. Omar and A. A. Mahran (1991). Toxicity and residual action of certain insecticides against the cotton leaf- worm *Spodoptera littoralis* (Boisd.). Egypt. J. Agric. Res., 69 (1): 49-56.

Mott, L. (1991). The public residue database. ACS. Symposium Series., 446: 170-174.

Nigg, H. N.; J. H. Stamper and J. B. Knaak (1984). Leaf, fruit and soil surface residues of carbosulfan and its metabolites in Florida citrus groves. J. Agric. Food Chem., 32 :80-85.

Omar, H. I.; M. F. A. Hegab and M. A. El-Hamaky (1988). Combined action of some insecticides and fertilizers on pests infesting sweet melon. Agricultural Research Review., 66(1): 85-90.

Panel (1977). Determination of residues of organophosphorous pesticides in fruits and vegetables. Analyst. 102 (1220) 858-868.

Rangaswamy, J. R.; Y. N. Vijayashankar and S. R. Prakash (1976). A simple spectrophotometric method for the determination of carbofuran residues. J. of A.O.A.C., 59 (6): 1276-1278.

Shalaby, A. A. ; A. El-Adorosy Gomaa ; R. M. Sherif ; M. A. El-Deeb and A. A. El-Fishawy (1991). Evaluation of pesticides on cotton insect pests Zagazig J. Agric. Res., 18 (6) : 2283-2300.

Sagar, P. and L. N. Jindla (1984). An outbreak of the aphid *Aphis gossypii* (Glover) on isabgol, *Plantago ovata* (L.), and its chemical control. International Pest Control., 26 (3): 76-84.

Saito, T. (1989). Insecticide resistance of the cotton aphid, *Aphis gossypii* Glover (Homoptera: Aphididae). I- Susceptibility to several insecticides and esterase activity of field populations collected in Shizuoka Prefecture. Japanese Journal of Applied Entomology and Zoology , 33 (4): 204-210.

Tonagai, Y.; Y. Tsumura; Y. Nakamura and Y. Ito (1992). Studies on preparation of sample solution for simultaneous determination of 9 carbamate and 12 organophosphorus pesticides in agricultural products. J.Food Hyg.Soc.Japan, 33 (5): 449-457.

Umetsu, N.; E. Kuano and T. R. Fukuto (1980).J. Environ. Sci. Health, Part B. B15 (1): 1.

Umetsu, N.; M. A. H. Fahmy and T. R. Fukuto (1979). Pestic. Biochem. Physiol., 10: 104

تقدير متبقيات بعض مبيدات الآفات فى نبات بطيخ اللب وتأثيرها السام على بعض الآفات

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فى هذه الدراسة تم تقييم فاعلية خمسة من المبيدات الفوسفورية والكارباماتيه (الملاثيون - البيريمفوس ميثيل - الكلوربيرفوس ميثيل - الكربوسلفان - الميثوميل) و المستخدمة فى حقول بطيخ اللب ضد آفتي دودة ورق القطن ومن القطن معمليا و اللتين تسببان خسائر كبيرة فى المحصول كم تم تقدير متبقيات هذه المبيدات فى قشر ولب وبذور البطيخ على فترات زمنية مختلفة وكانت النتائج المتحصل عليها ملخصة فى النقاط التالية:

أولا : تقييم فاعلية المبيدات المختبرة ضد آفتي دودة ورق القطن ومن القطن معمليا :

(أ): ضد آفة من القطن (البطيخ) :- وجد أن أعلى المبيدات سمية ضد من القطن هو المبيد الجهازى الكربوسلفان يليه الكلوربيرفوس ميثيل ثم البيريمفوس ميثيل ثم الميثوميل حيث بلغت قيمة LC_{50} لهذه المبيدات على التوالي ٠,٤٩ ، ٠,٧٥ ، ٣,٣١ ، ٥,٤٦ جزء في المليون . أما بالنسبة للملاثيون فكان أقلهم سمية ضد من القطن حيث بلغت قيمة LC_{50} له ٣٤,٨٩جزء في المليون .

(ب) ضد آفة دودة ورق القطن :- أظهرت الدراسة المعملية للمبيدات المختبرة ضد يرقات العمر الرابع لدودة ورق القطن أن المبيد الفوسفورى الكلوربيرفوس ميثيل له أعلى سمية يليه الميثوميل ثم الملاثيون و بلغت قيم LC_{50} لهذه المبيدات على التوالي ١٠,٢٩ ، ٤٧,٨٤ ، ٢٧٠,٢٢جزء في المليون . أما مبيدي البيريمفوس ميثيل و الكربوسلفان فقد أظهرا سمية منخفضة جدا بالمقارنة بالمبيدات المختبرة ضد يرقات دودة ورق القطن حيث كانت قيم LC_{50} لهما على التوالي ١٠٧٩ ، ٣٢٤٥,٠٦ جزء في المليون .

ثانيا: تقدير متبقيات المبيدات المختبرة فى كلا من قشر ولب وبذور بطيخ اللب على فترات زمنية مختلفة :

فى هذه الخطوة من الدراسة تم تقدير متبقيات المبيدات المختبرة سالفة الذكر عاليه فى فترات زمنية مختلفة (بداية التجربة- بعد يوم- بعد خمسة أيام) وذلك باستخدام طرق التحليل بواسطة GLC والطرق اللونية للتحليل الكيميائي. ولقد وجد أن التركيزات المبدئية عند بداية التجربة قد تغيرت فى الفترات الزمنية المختلفة وتتلخص هذه التغيرات بعد خمسة أيام (نهاية التجربة) لكل المبيدات المختبرة فى الآتي:

(أ) متبقيات مبيد الملاثيون : تناقص المتبقى الى ٠,٠٨٣ ، ٠,٠٥٢ ، ٠,٠٢٦ جزء فى المليون على قشر و لب و بذور البطيخ على التوالى.

(ب) متبقيات مبيد البيريمفوس ميثيل: بعد خمسة أيام من المعاملة تناقص المتبقى في قشر و لب و بذور البطيخ ووصل الى ٠,٠٢٣٢ ، ٠,٠٢٧٤ ، ٠,٠٠٨٣جزء فى المليون على التوالى .

(ج) متبقيات مبيد الكلوربيرفوس ميثيل: بعد خمسة أيام من المعاملة تناقص المتبقى ووصل الى ٠,٠٢١ ، ٠,٠٠٨٤ ، ٠,٠٢٠ جزء فى المليون على قشر و لب و بذور البطيخ على التوالى .

(د) متبقيات مبيد الكربوسلفان : بعد خمسة أيام من المعاملة تناقص المتبقى فى قشر و لب و بذور البطيخ ووصل الى ٠,٩٧٥ ، ٧,٥٤ ، ٩,٨٩٢ جزء فى المليون على التوالى .

(هـ) متبقيات مبيد الميثوميل : بعد خمسة أيام من المعاملة ازداد المتبقي في كلا من قشر و لب البطيخ ووصل إلى ١,٣٧٧ ، ٠,٧٦٤جزء في المليون على التوالي و على الجانب الاخر تناقص المتبقى فى بذور البطيخ ووصل الى ٠,٤٥٢ جزء فى المليون .

وعلى العموم فقد أظهرت النتائج أن المبيدات المختبرة لم يكن لها نفس السلوك فى التناقص فى تركيزات متبقياتها