PERSISTENCE OF MALATHION AND PROTHIOFOS ORGANOPHOSPHORUS INSECTICIDES ON AND IN SOME VEGETABLE CROPS

M.F.A. SHADY[2], M.E.A. HEGAZY[1] F.A.ADAM[2], M.A.ABD EL-BAKI [2] AND SHOKR A. SHOKR.[1]

1 Central Agricultural Pesticides Laboratory, Agricultural Research Centre, Dokki, Giza.

2 Faculty of Agriculture, Kafr El-Sheikh, Tanta University.

(Manuscript received 9 August,1998)

Abstract

This investigation was carried out to study the persistence of malathion and prothiofos insecticide residues on moloukhia, green beans and cucumber. Malathion and prothiofos are widely used in Egypt to control economic pests on vegetables. The plan of study included the following: determine persistence and safe period for consuming moloukhia leaves, green beans pods and cucumber fruits. Second, the effect of washing, blanching, peeling, salting and drying processes in removing these insecticide residues from the above mentioned vegetable crops. The results obtained could be summarized as follow:

The results indicated that one hour after application the malathion residues were 109.0438 and 0.2085 ppm on moloukhia leaves and cucumber fruits, respectively. These amounts decreased to 25.8257 and 0.0673 ppm one day after application, respectively. Fifteen days after treatment, the residues became 0.0132 and 0.002 ppm, respectively. The half life values were 11.6 and 14.7 hours on moloukhia leaves and cucumber fruits, respectively, while the safe periods for consumption were 2.6 and 1 days, respectively.

On the other hand, the results indicated that the prothiofos residues one hour after application were 27.2868 ppm on green bean pods. This amount decreased to 22.2654 ppm one day after application. Fifteen days after treatment, the residues became 0.4666 ppm, respectively. The half life value was 47.7 hours on green bean pods, while the safe period for consumption was one day.

Effect of different processes in removing malathion and prothiofos residues from moloukhia leaves, green bean pods and cucumber fruits indicated that washing with tap water removed 84.34% the malathion residues on moloukhia leaves, and 94.65% on cucumber fruits, respectively.

Blanching process removed 86.28% of malathion residues from moloukhia leaves. Peeling cucumber fruit removed 97.47% from malathion. Salting cucumber fruits removed 26% by 7th day and drying moloukhaleavesremoved 72.98% of malathion residues.

INTRODUCTION

Moloukhia, *Chorchorus olitorius*, cucumber, *Cucumis sativus* and green bean, *Phaselous vulgaris*, three popular vegetable crops were the matter of this study. In Egypt, such crops are treated with pesticides in order to control pest infestation. Residues after application of pesticides on vegetable crops should be followed and the waiting periods between application and harvesting should also be recommeneded to be sure that the residues are below tolerance levels before marketing.

Degradation of the pesticide residues and rocessing factors which could be expected to affect their presence in and on vegetables were considered. The organophosphorus insecticides, namely malathion and prothiofos are widely used in Egypt to control economic pests especially on vegetabels.

This work aimed to study the behaviour of these insecticide residues on and in cucumber, green beans and moloukhia vegetables. The efficiency of washing, salting, peeling, blanching and drying processes in removing the studied insecticide residues were evaluated.

MATERIALS AND METHODS

Pesticides used: Malathion S-1,2 bis (ethoxycarbonyl) ethyl O,O-dimethyl phosphorodithioate known commercially as malathion formulation 57% E.C organophosphorous insecticide. Prothiofos: O-2,4-dichlorophenyl O-ethyl S-propyl phosphoroditioate known commercially as Tokuthion formulation 50% E.C. organophosphorous insecticide. Both are used against a wide range of pests i.e. chewing and sucking insect pests. Both were used at the rate of 1.5 Litre in 400 Litre of water per feddan.

Field experiment and sampling: Moloukhia, cucumber and green bean seeds were planted on May 10th, 15th and 23rd 1994, respectively, under the normal field conditions and agricultural practices at Kafr El-Sheikh Governorate.

Three plots for each crop were planted in areas of 50 m2, 75 m2 and 100 m2 for moloukhia, green beans and cucumber, respectively. These plants were treated at the rates of application recommended by the Ministry of Agriculture, 1993. The repetition for each crop were treated with malathion and prothiofos with the recommeded dosage. A fourth plot for each crop was left untreated as control. The insecticidal formulation was diluted with water and applied using a knapsack sprayer equipped with one nozzle as follows:

Moloukhia plants were treated on June 28th 1994; 49 days after planting and the formulation was diluted at the rate of 400 Liters water per feddan. Cucumber plants were treated on July 5th 1994; 51 days after planting and the formulation was diluted by 400 Liters water per feddan. Green bean plants were treated on August 6th 1994; 75 days after planting and the formulation was diluted at the rate of 400 Liters water per feddan.

Three replicate samples of 300 g each were collected from each crop at intervals of one hour after application (zero time), 1,3,6,9,12 and 15 days. Clean polyethylene bags were used for preservation of the collected samples. The samples were stored at - 20^{o}C in a deep freezer until analysis.

Intentional removal of insecticide residues: Several home and industrial processing method which are widely used were evaluated for their efficiency in removing malathion and prothiofos residues from cucumber fruits, moloukhia leaves and green bean pods. Twenty four hours after application of the insecticide with the recommened dose three replicate samples of 300g each for process and each crop were collected and prepared as follows:

Washing with tap water: Cucumber fruits, moloukhia leaves and green bean pods were rinsed for three minuts with running tap water, then drained on a clean paper for one hour until dry. Samples were kept in polyethylene bags in the deep freezer until analysis.

Salting of cucumber fruits: Cucumber fruits were cut into samll pieces and packed into half litre glass jars containing 100 ml of 10% NaCl salt solution and 100 ml of 3% acetic acid solution. The glass jars were kept under room conditions for 7 days, then frozen until analysis.

Peeling of cucumber fruits: Cucumber fruits were peeled manually and the peeled samples were kept in polyethylene bags in the deep freezer until analysis.

Blanching of green bean pods and moloukhia leaves: The green beans pods and the leaves of moloukhia were cut into small pieces. Then they were placed in a jar filled with boiling water for 2-3 min., then drained and left until they reached room temperature. Then were kept in polyethylene bags in the deep freezer until analysis.

Drying of moloukhia leaves: Moloukhia leaves were spread on a clean paper under room conditions for 6-7 days until completely dry and then ground and kept in pol-

yethylene bage in the deep freezer until analysis.

Pesticide residue analysis techniques

Extraction

Cucumber fruits: Methanol was found to be the best solvent for extracting the insecticide from cucumber fruits. Frozen samples were left until they reached room temperature and then macerated using a waring blender. Fifty grams of the macerated sample were placed in the blender and a constant amount of methanol (2 ml/gram plant material) was added to the blender and mixed for 3 min. then filtered through a dry pad of cotton into a graduated cylinder to reach half volume. Extracts were shaken in separatory funnel successively three times with 50 ml chloroform each and 40 ml of sodium chloride solution (20%) and then the water phase was discarded. The combined chloroform phases were filtered through a pad of cotton and anhydrous sodium sulphate then evaporated just to dryness using a rotary evaporator at 40°C.

Moloukhia leaves and green beans pods: The frozen samples were left to reach room temperature. Then cut into small pieces using a pair of scissors and forceps. Fifty grams of the sample were placed into the blender cup with 50g anhydrous sodium sulphate and 150 ml ethyl acetate, then blended for 3 min. The liquid was decanted through a funnel with a plug of cotton in to a graduated cylinder, then evaporated just to dryness using a rotary evaporator at 40°C.

Cleaning up: It was found that chromatographing the extracts through deactivated florisil (with 6% by weight of water) using benzene for elution was quite efficient and gave good recoveries (Mollhof, 1975).

A 25 mm (i.d.) glass column was prepared by adding successively, a plug of glass wool and 8 g of deactivated florisil (60-100 mesh) and compacted throughly. The column was prewashed using 30 ml benzene and the level of the solvent drained down to the top of the florisil. Residue extracts were dissolved in 10 ml of benzene, and added to the column. The flask was rinsed five times with 5 ml portions of benzene and added each washing to the column just before the preceding fraction has completely entered the packing. Then, the residues were eluted with 200 ml benzene.

The cleaned up extract was collected into a 500 ml flask, and the solvent was evaporated just to dryness using a rotary evaporator at 40°C. The residues were quantitatively transferred to a standard glass stoppered test tube with ethyl acetate, and the

solvent was evaporated just to dryness and the residues were redissolved in the proper volume of ethyl acetate for chromatographic determination.

Gas liquid chromtography determination: A Pye Unicam 4500 gas chromatograph equipped with a flame photometric detector operated in the phosphorus mode (526 nm filter) was used for determination of malathion and prothiofos insecticide. A pyrex glass column (1.5 m x 4 mm i.d) was packed with 4% S E-30 + 6% O V-210 on gas chromosorb Q (80 -100 mesh).

Temperature degrees were as follows:

Temperature column 230 ^{o}C .

Detector 240 ^{o}C.

Injector 235 ^{o}C.

Gases flow rates were 30 ml/min. for nitrogen, hydrogen and air. Retention time for fenitrothion under these conditions was 4.22 min.

Rate of recorveries of the insecticide on moloukhia leaves, green bean pods, and cucumber fruits were determined by adding known amounts of the insecticide to a portion of untreated samples and processing as mentioned before. Untreated samples were used as control blanks.

Following these techinques, the average rates of recovery for malathion and prothiofos were 78.30,86.70 and 92.60% in moloukhia leaves, green pods and cucumber fruits, respectively. The results obtained were corrected according to their recovery percentages

RESULTS AND DISCUSSION

Persistence of malathion and prothiofos insecticide residues on and in vegetable crops

Data in table 1 and figure 1 indicate the amount of malathion residues in moloukhia leaves and cucumber fruits at different intervals after application. The initial deposits of malathion one hour after application were 109.0438 and 0.2085 ppm on and in moloukhia leaves and cucumber fruits, respectively. These residues decreased after 24 hours to 25.8257 and 0.0673 ppm.The residues of malathion on moloukhia

leaves dropped to 4.8019, 0.4275, 0.3209,0.1320 and 0.0132 ppm after 3,6,9,12 and 15 days, respectively from treatment. The corresponding values on cucumber fruits were 0.0533,0.0110,0.0049, 0.0030 and 0.0020 ppm, respectively at the same mentioned intervals. Also, the data indicate that the residue loss continued on over time, where the percent loss rate amounted to 76.32,95.60,99.61,99.71,99.88 and 99.99% after 1,3,6,12, and 15 days, respectively for moloukhia leaves. The corresponding percent residue loss on cucumber fruits was 67.72, 74.44, 94.72, 97.65, 98.56 and 99.04%, respectively.

The calculated half-life values of this insecticide were 11.6 and 14.7 hours on moloukhia leaves and cucumber fruits, respectively. While the first day after application was showen to be cricted in the residue degradation rates.

Table 2 and figure 2 sh ɔw the residual behaviour of prothiofos on the green bean pods after application. Results show that the initial deposit of 27.2868 ppm on and in green bean pods, decreaced gradually by 1,3,6,9,12 and 15 days after spraying to reach 22.2654, 9.5878, 5.1598, 2.0086,1.0653 and 0.4666 ppm, respectively. The corresponding percent residue loss was 18.40, 64.86, 81.09, 92.64, 96.32 and 98.29%, respectively.

The calculated half-life value of this insecticide was 47.7hours on green bean pods.

The level of pesticide residue is affected by many factors i.e. applied dosage, meteorological and biological factors when depend on the kind and properties of the plant surface. The obtained results coincide with those reported by Hegazy *et al.* (1997 a and b) and Shokr (1997).

According to the (Codex Alimentarius Commission,1990) the maximum residue limits for malathion on the leafy crop spinach (used for moloukhia) and cucumber fruits should be 8, and 0.5 ppm for green bean pods 0.1 ppm, respectively. The corresponding recommended preharvest i ntervals (PHI) were 2.6 and one days for moloukhia leaves and cucumber fruits and 13.6 days for green bean pods after malathion and prothiofos application, respectively.

Generally, it was found that organophosphorus pesticides persist for short periods in plant and other environmental constituents (Al-Samariee *et al.* 1988). The safe period for harvesting the organophosphorus insecticed treated vegetables ranged between 1 and 12 days post treatment, depending on the chemistry of the tested pesti-

Table 1. Residues of malathion on and in vegetables.

Time after application (Days)	Molokhia Leaves		Cucumber fruits	
	Residues		Residues	
	ppm	% Loss	ppm	% Loss
Zero Time*	109.0438	00.00	0.2085	00.00
1	25.8257	76.32	0.0673	67.72
3	4.8019	95.60	0.0533	74.44
6	0.4275	99.61	0.0110	94.72
9	0.3209	99.71	0.0049	97.65
12	0.1320	99.88	0.0030	98.56
15	0.0132	99.99	0.0020	99.04
RL_{50} in hours	11.3		14.7	

*One hour after application

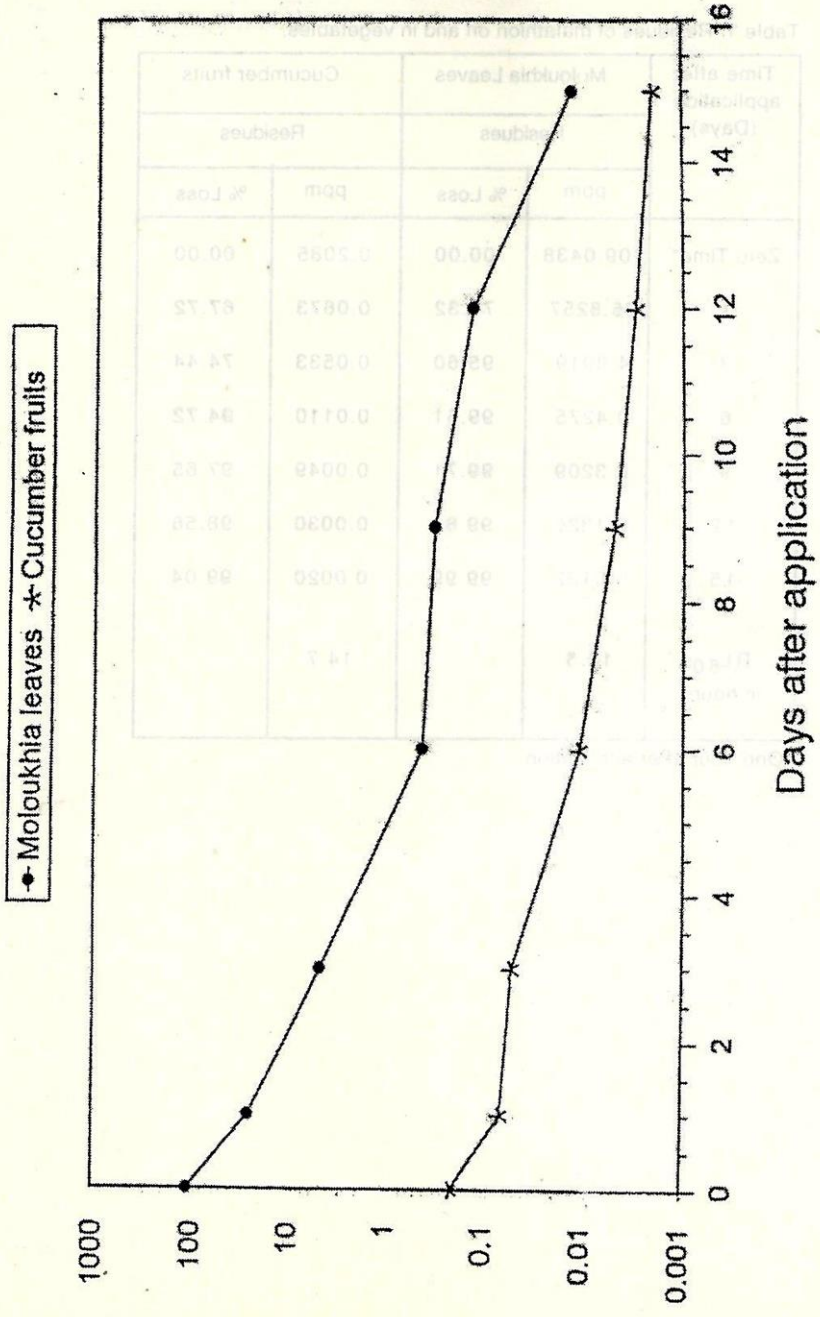
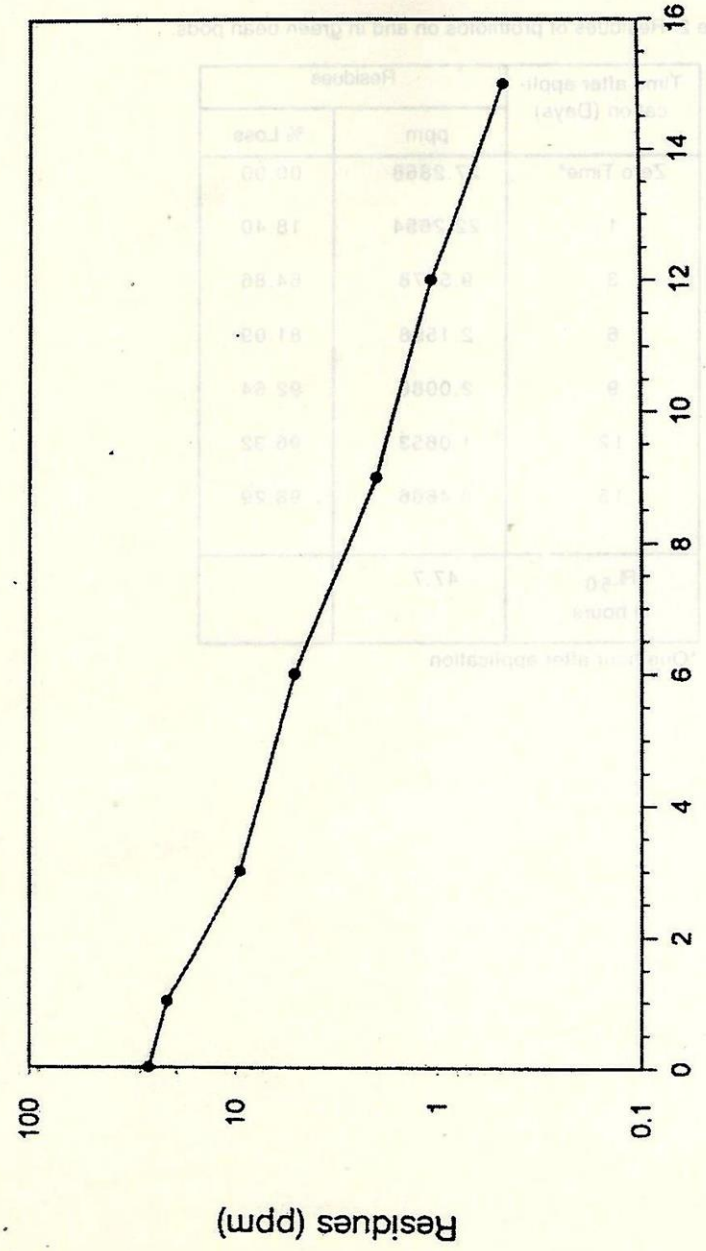


Fig 1. Residues of malathion on and in vegetables.

Table 2. Residues of prothiofos on and in green bean pods.

Time after application (Days)	Residues	
	ppm	% Loss
Zero Time*	27.2868	00.00
1	22.2654	18.40
3	9.5878	64.86
6	2.1598	81.09
9	2.0086	92.64
12	1.0653	96.32
15	0.4666	98.29
RL_{50} in hours	47.7	

*One hour after application



Fid. 2. Residues of prothiofos on and in green bean pods.

cide and kind of crop (Shokr 1997).

Removal of malathion and prothiofos residues from treated vegetables by some processes

The increasing use of chemical insecticides to control the economic pests which attack field crops has increased the pollution of the environment with their toxic residues. Therefore, the need for efficient treatments to reduce or remove such residues has become urgent.

People in Egypt usually use plain water to wash vegetables before consumption. Other processes also used vegetable preparation before eating. The efficiency of these processes, washing with tap water, blanching, drying, and salting was in removing insecticide from vegetables one day after treatment with this insecticide was evaluated. However, in Egytp, there are limited studies on the effect of food preparation on the removal of pesticide residues from various crops

The results in table 3 show the residue levels in ppm and the percent removal of malathion and prothiofos after different processing treatments. The residues of malathion and prothiofos on unprocessed moloukhia leaves one day after spraying with the insecticide were 25.8257 ppm. The washing process reduced the residues to 4.0445 ppm respresenting removal of 84.34% of the insecticide residues on moloukhia leaves. The blanching process reduced the residues of malathion to 3.5438 ppm removal of 86.28% on the same crop. The dried leves contained 27.9163 ppm of malathion (based on dry weight) which means 72.98% residue removal considering the humidity percentage in moloukhia leaves is 75%.

As shown in table 3, the residues of malathion on unprocessed cucumber fruits one day after spraying with this insecticide was 0.0673 ppm. This value dacreased to 0.0063 ppm after washing cucumber, to 0.0017 ppm after peeling and to 0.0489 ppm after salting. The percents removal were 94.65, 97.47 and 26.00%, respectively. Also, in table 3, the residues of prothiofos on unprocessed green bean pods one day after spraying were 22.2654 ppm. The washing and blanching process reduced the residues to 16.5412 and 15.5999 ppm and the percents removal were 25.71 and 29.944%, respectively.

Heavy use of pesticides on the field crops has begun to receive much attenion because residues in food commodities may be hazardous to human health.The present data indicated that the different processing that used in this study had different ef-

Table 3. Effect of some different processes on malathion and prothiofos insecticide residues on some vegetable crops.

		malathion	
Crop	Process*	PPM	%removal
Moloukhia leaves	None*	25.8257	00.00
	Washing	4.0445	84.43
	Blanching	3.5438	86.28
	Drying**	27.9163	72.98***
Cucumber fruits	None*	0.0673	00.00
	Washing	0.0036	94.65
	Peeling	0.0017	97.47
	Salting	0.0498	26.00
Green beans pods		pothiofos	
		PPM	%removal
	None*	22.2654	00.00
	Washing	16.5412	25.71
	Blanching	15.5999	29.94

* One day after application

** Calculated on dry weight

*** The % removal calculation was based on the moisture content in moloukhia leaves was 75%.

fects on reducing or removing pesticide residues originally located on or in the mature fresh leaves or fruits of different cultivars.This variation in their effect depended on the type of pesticides used, type of processing applied and location of residues on the parts applied. Many researchers have studied how to remove pesticides from food products in the world, Liska and Stadelman (1985), and Shokr (1997).

The present results also confirm and agree with those obtained and reported by the National Canners Association (1967) that peeling fruits removed considerable amounts of pesticide residues not removed by washing treatment. Karogeorgiev (1979) also found that peeling fruit results in complete of disappearance pesticides residue within the limit of the methods used in analysis. Washing processes were found to be efficient in removing organophosphorus inseticides from vegetables, Celino and Magallonna (1965), Tantawy *et al.* (1979), Kamil (1987), and Shokr (1997).

REFERENCES

1.AL-Samariee, A.I, K.A.M. Shaker and M.A. Al-Bassomy. 1988. Residue levels of three organophosphorus insecticides in sweet pepper grown in commercial greenhouses. Pestic. Sci. 22:189-194.

2. Celino, L.P. and E.D. Magallonna. 1965. Effect of processing on insecticide residues in pole sitao bean (Phaseolus vulgaris.L.) Philipp.AGri.,68 (4): 525-532.

3. CODEX Almentarius Commission. 1990. Codex Maximum Limits for Pesticide residues. Joint FAO/WHO Food Standards programme. Vol.X III. Ed. 2, Supplements 1 and 2.

4. Hegazy, M.E.A., M.M. Abu-Zahw, A.H.Bayoumy, S.A. Soliman, M.N. S. Haggag. 1997-a. Triazophos insecticide on and in moloukhia leaves and okra fruits. Egypt, J.Agric. Res. 75 (1): 41-49.

5. Hegazy, M.E.A, M.M Abu-Zahw, A.H.Bayoumy, S.A. Soliman, M.S. Haggag. 1997-b. Effect of processing cucumber fruits on chloropyrifos-methyl insecticide residues. Egypt, J.Agric Res. 75 (1): 51-59.

6. Kamil, M.M. 1987. Studies on the pesticide residues on foods. M.Sc.in Food Science.Thesis Fac.Agic. Cairo Univ.

7. Karageorgiev, D. 1979. Effect of technological processes on the residual quantities of some pesticides in cherry, pear and peach processing Gradinarskai Lozarska Nauka, 16:53-59 (c.f. Chem Abst. Data base).

8. Lisk, B.J. and W.J Stableman. 1969. Effect of processing on pesticides in foods. Residue Rev., 29: 61-72.

9. Mollhoff, E. 1975. Method for gas-chromatographic determination of residues of tokuthion and its oxon in plant and samples. Pflanzenshutz-Nachrichton Bayer 28:882-887.

10. National Canners Association. 1967. Investigation on the effect of preparation and cooking on pesticide residues content of selected vegetables. Final Report, Washington D.C. (1967) (C.F.Residues. Rev., 29:61-72.1969).

11. Shokr, A, Sh.1997. Environmental pollution by pesticide residues. Ph.D. Thesis, Fac. Agric. Kafr El-Sheikh, Tanta, University.

12. Tantawy, G., A.S.M. Marei, G.F. Antonious and M. Zeid. 1979. Determination of chloropyrifos, dimethoate and malathion on certain vegetables and fruits crops. Proc. third pesticide Conf. Tanta Univ. Vol. 1,5596-603.

بقاء مبيدى الملاثيون والبروثيوفوس الفوسفوريان على بعض محاصيل الخضر

محمد فاضل عبد الحليم شادى [٢]، محمد السعيد على حجازى [٣]، فكرى احمد أدم [١]، محمد عبد السلام عبد الباقى [٢]، شكر عبد السلام شكر [٣]

١ كلية زراعة طنطا - جامعة طنطا
٢ كلية زراعة كفر الشيخ - جامعة طنطا
٣ المعمل المركزى للمبيدات - مركز البحوث الزراعيه - الدقى - الجيزة .

اجرى هذا البحث لدراسة مدى تلوث بعض نباتات الخضر مثل الملوخية والفاصوليا والخيار بمتبقيات الملاثيون والبروثيوفوس وهما من المبيدات الفوسفورية المستخدمة لمكافحة الافات التى تصيب تلك المحاصيل.

وتتضمن خطة الدراسة النقاط التالية :-

- تحليل متبقيات الملاثيون على أوراق الملوخية وثمار الخيار والبروثيوفوس على قرون الفاصوليا على فترات زمنية مختلفة وحساب قيم زمن نصف العمر للمتبقيات وتحديد فترة الامان لكل مبيد لكل محصول .

- دراسه تأثير عمليات الاعداد والتجهيز المختلفة من غسيل وسلق وتقشير وتجفيف على ازالة متبقيات هذا المبيد من على اوراق الملوخية وقرون الفاصوليا وثمار الخيار .

ويمكن تلخيص النتائج المتحصل عليها فيما يلى:

ا. تحليل متبقيات مبيد الملاثيون على اوراق الملوخية وثمار الخيار :

اوضحت النتائج ان كميات المتبقى من مبيد الملاثيون بعد ساعة من الرش بالمعدلات الموصى بها كانت ٠,٤٣٨ و ١,٩ ، ٢,٨٥ جزء فى المليون على أوراق الملوخية وثمار الخيار على التوالى . ثم تناقصت هذة الكميات من المتبقى بعد يوم من الرش الى ٠,٨٢٥٧ و ٠,٦٧٣ جزء فى المليون على التوالى . ثم أخذت هذه الكميات من المتبقى تقل تدريجيا الى ان وصلت الى ٠,١٣٢ و ٠,٢٠ و٠ جزء فى المليون بعد ١٥ يوم من الرش على التوالى . وكانت فترتى نصف العمر لمتبقيات الملاثيون على أوراق الملوخية وثمار الخيار ١١,٦ ، ٧و١٤ ساعة على التوالى . وامكن تحديد فترات الامان لهذا المبيد بعد الرش حيث كانت ٦و ٢ ، ١ يوم بالنسبة لمحصول

الملوخية والخيار على التوالى .

كما اوضحت النتائج ان كميات المتبقى من مبيد البروثيوفوس بعد ساعة من الرش بالمعدلات الموصى بها كانت ٢٨٦٨و ٢٧ جزء فى المليون على قرون الفاضوليا على التوالى . ثم تناقصت هذة الكميات من المتبقى بعد يوم من الرش الى ٢٦٥٤و٢٢ جزء فى المليون على التوالى . ثم أخذت هذة الكميات من المتبقى تقل تدريجيا الى أن وصلت الى ٤٦٦٦ و . جزء فى المليون بعد ١٥ يوما من الرش على التوالى . وكانت فترة نصف العمر لمتبقيات البروثيوفوس على قرون الفاصوليا ٧و٤٧ ساعة على التوالى . وأمكن تحديد فترة الأمان لهذا المبيد بعد الرش حيث كانت يوما واحدا بالنسبة لمحصول الفاصوليا.

٢- دراسة تأثير عمليات الاعداد والتجهيز المختلفة على ازالة متبقيات مبيدى الملاثيون والبروثيوفوس من على أوراق الملوخية وقرون الفاصوليا وثمار الخيار:

أوضحت الدراسة أن عملية الغسيل بماء الصنبور أزالت ٤٣ و ٨٤٪ من متبقيات الملاثيون من على اوراق الملوخية ، بينما أزالت هذة العملية ٩٦ و ٩٤٪ من متبقيات هذا المبيد من ثمار الخيار ، كما ازالت عملية الغسيل بماء الصنبور ٧ و٢٥٪ من متبقيات مبيد البروثيوفوس من على قرون الفاصوليا . وجد أن عملية السلق ازالت ٣ و ٨٦٪ من متبقيات مبيد الملاثيون على أوراق الملوخية و ٢٩ و ٩٤٪ من متبقيات مبيد البروثيوفوس على قرون الفاصوليا وأن عمليتى التقشير والتخليل ازالتا ٩٧ و ٤٧٪ ، ٢٦٪ من على ثمار الخيار على التوالى وان عملية التجفيف لاوراق الملوخية ازالت ٧٢و ٩٨٪ من متبقيات مبيد الملاثيون .