PIRIMIPHOS-METHYL INSECTICIDE RESIDUES ON AND IN SOME VEGETABLE CROPS

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Abstract

This investigation was carried out to study the persistence of pirimiphos-methyl insecticide residues on moloukhia, green bean pods and cucumber. Pirimiphos-methyl (actellic) is widely used in Egypt to control economic pests on vegetables. The plan of study included the following: First, determine persistence, half life and safe period for consuming moloukhia leaves, green bean pods and cucumber fruits. Second, the effect of washing, blanching, peeling, salting and drying processes in removing insecticide residues from the above mentioned vegetable crop. The results obtained could be summarized as follows:

The results indicated that one hour after application the pirimiphos-methyl residues were 171.0287, 32.5318 and 5.3543 ppm on moloukhia leaves, green bean pods and cucumber fruits, respectively. These amounts decreased to 39.1575, 17.8777 and 1.8849 ppm after one day from application, respectively. Fifeen days after treatment the residues became 0.0775, 0.0427, and 0.0172 ppm, respectively. The half-life values were 11.3, 27.8, 27.8 and 15.9 hours on moloukhia leaves, green bean pods and cucumber fruits, respectively,

The evaluation different processes in removing pirimphos-methyl residues from moloukhia leaves, green beans pods and cucumber fruits indicated that washing with tap water removed 53.79% pirimiphos-methyl residues on moloukhia leaves, 38% on cucumber fruits and 13.29% on green bean pods, respectively. Blanching removed 90.24% from residues pirimiphos-methyl on and in moloukhia leaves and 30.64% on green bean pods, respectively. Peeling process of cucumber fruits removed 97.35% of pirimiphos-methyl, while salting of cucumber fruits removed 97.35% of pirimiphos-methyl, while salting of cucumber fruits removed 89.73% after 7 days and drying moloukhia leaves removed 71.19% of pirimiphos-methyl, respectively.

INTRODUCTION

Moloukhia, *Chorchorus olitorius*, Cucumber, *Cucumis sativus* and Green bean, *Phaselous vulgaris*, three popular vegetable crops were the subject of this study. In Egypt, such crops are treated by pesticides in order to control pest infestation. Residues after the application of pesticides on vegtable 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 studies of the pesticide residues and processing factors which could be expected to affect their presence are in and on vegetables were considered. The organophosphorus insecticide, namely pirimiphos-methyl was widely used in Egypt to control economic pests especially on vegetables.

This work aimed to study the behaviour of the residues of this insecticide on and in cucumber, green bean pods 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 : Pirimiphos-methyl: 0-2-diethylamino-6-methylpyrimidin-4-yl O,O-dimethyl phosphorothioate, an organophosphorous insecticide, known commerically as Actellic formulation 50% E.C. is used against a wide range of pest i.e. chewing and sucking insect pests. It was used at the rate of 1.5 Litre in 400 Litre of water per feddan i.e. 750 g a.i.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 practice in 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 with Pirimiphos-methyl according to the recommended rates of application of the Ministry of Agriculture 1993. A fourth plot was left untreated as control. The insecticidal formulation was diluted with water and applied using a knap sac sprayer equipped with one nozzle as follows:

Moloukhia plants were treated on June 28th 1994; 49 days after planting and the formulation was applied 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 applied at the of 400 liters water per feddan. Green bean plants were treated on August 6th 1994; 75 days after planting and the formulation was applied at the rate of 400 liters water per feddan.

Three replicate samples of 300g 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°C in a deep freezer until analysis.

Intentional removal of insecticide residues : Several home and industrial processing methods which are widely used were evaluated for their efficiencies in removing pirimiphos-methyl residues from cucumber fruits, moloukhia leaves and green pods. Twenty-four hours after application of the insecticide with the recommended dose, three replicate samples of 300 g each, for each process and each crop, were collected and prepared as follow:

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

Salting of cucumber fruits : Cucumber fruits were cut into small pieces and packed into half litre glass jars contained 100ml of 10% NaCl salt solution and 100ml 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 bean pods and the leaves of moloukia 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. They 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 condition for 6-7 days until completely dry and then ground and kept in polyethylene bage in deep freezer until analysis.

Pesticide residues analysis techniques

Extraction

a. 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 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 a 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 dried by filteration through a pad of cotton and anhydrous sodium sulphate, then evaporated just to dryness using a rotary evaporator at $40^{o}C$.

b. Moloukhia leaves and green bean 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 into graduated cylinder, then evaporated just to dryness by using a rotary evaporator at $40^{o}C$.

Cleaning up: It was found that chromatographing the extracts through deactivated florisil (with 6% by weight of water) using benzene for elution is 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 8g of deactivated florisil (60-100 mesh) which were 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, each washing added to the column just before the preceding fraction had 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 $40^{o}C$. The residues were quantitatively transferred to 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 flame photometric detector operated in the phosphorus mode (526 nm filter) was used for determination of pirimiphos-methyl 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°C.

Detector 240°C.

Injector 235°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 recoveries of the insecticide on moloukhia leaves, green bean pods, and cucumber fruitts were determined by adding known amount of the insecticide to portion of untreated samples and processed as mentioned before. Untreated samples were used as control.

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

RESULTS AND DISCUSSION

Persistence of pirimiphos-methyl insecticide residues on and in vegetable crops

The data in table 1 and figure 1 indicate the amount of pirimiphos-methyl residues in moloukhia leaves, green bean pods and cucumber fruits at different intervals starting one hour after application. The initial deposits of pirimiphos-methyl were 171.0287, 32.5318 and 5.3543 ppm on and in moloukhia leaves, green bean pods and cucumber fruits, respectively. These residues decreased after 24 hours to 39.1575, 17.8777 and 1.8849 ppm . The residues with pirimiphos-methyl on moloukhia dropped to 6.5959, 1.5523, 0.3136, 0.2593 and 0.0775 ppm at 3, 6, 9, 12 and 15 days, respectively after treatment. The corresponding values on green bean pods and cucumber fruits were 9.1104, 2.4484, 0.6774, 0.3827, 0.0427 ppm and 0.2314, 0.1755, 0.0908, 0.0305, 0.0172, respectively at the same mentioned intervals. Also, the data indicate that the residues loss continued on prolonging the time, where the precent loss rate amounted to 77.10, 96.14, 99.09, 99.82, 99.85 and 99.95% after 1, 3, 6,

Table 1. Residues of pirimiphos-methyl on and in vegetables.

Time after application (Days)	Moloukhia leaves		Green beans pods		Cucmber fruits	
	Residues		Residues		Residues	
	ppm	% loss	ppm	% loss	ppm	% loss
Zero time*	171.0287	00.00	32.5318	00.00	5.3543	00.00
1	39.1575	77.10	17.8777	45.05	1.8849	64.80
3	6.5959	96.14	9.1104	71.10	0.2314	95.68
6	1.5523	99.09	2.4484	92.47	0.1755	96.72
9	0.3136	99.82	0.6774	97.92	0.0908	98.30
12	0.2593	99.85	0.3827	98.82	0.0305	99.43
15	0.0775	99.95	0.0427	99.87	0.0172	99.68
RL_{50} in hours	11.3		27.8		15.9	

* One hour after application

12 and 15 days, respectively, for moloukhia leaves. The corresponding precent residue loss were 45.05, 71.10, 92.47, 98.82, 99.87, 64.80, 95.68, 96.72, 98.30, 99.43 and 99.68% for green bean pods and cucumber fruits, respectively at the same intervals.

The calculated half life values of this insecticide were 11.3, 27.8 and 15.9 hours on moloukhia leaves, green bean pods and cucumber fruits, respectively. While the first day after application shown to be criticed in the residue degradation rates.

The level of pesticides residue is affected by many factors i.e. applied dosage, meteorological and biological factors 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 (Codex Alimentarius Commission, 1990) the maximum residue limits for pirimiphos-methyl on the leafy crop spinach (used for moloukhia), green bean pods and cucumber fruits were 5, 0.5, and 1 ppm, respectively. The corresponding recommended preharvest intervals (PHI) were 3.9, 10.7 and 2.1 days after application for moloukhia, green bean pods and cucumber, respectively.

According to Bates (1979) data on pesticide residues in treated crops are required for the premarket registration of pesticides and for setting maximum residue limits (toxicologically acceptable level) to protect the consumer against the possible health hazards of exposure to pesticides.

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 organophosphorus insecticides treated vegetables ranged between 1 and 12 days post treatment, depending on the chemistry of the tested pesticide and the kind of crop, Shokr (1997).

Removal of pirimiphos-methyl residues from treated vegetables by some processes

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

People in Egypt usually used water to wash vegetables before consumption. Other processes are also used for vegetables preparation before eating. The efficiency of the these processes; washing with tap water, blanching, peeling, drying and salting

were evaluated in removing pirimiphos-methyl from vegetables one day after treatment with this insecticide. However, in Egypt there are limited studies on the effect of food preparation on the removal of pesticide residues from various crops.

The results in table 2 show the residue levels in ppm and the percent removal of pirimiphos-methyl after different processing treatments. The residues of pirimiphos-methyl on unprocessed moloukhia leaves one day after spraying with the insecticide were 39.1575 ppm. The washing process reduced the residues to 18.0928 ppm representing removal of 53.79% of the insecticide residues on moloukhia leaves. The blanching process reduced the residues of pirimiphos-methyl to 3.8235 ppm on the same crop. The dried leaves contained 45.1299 ppm of pirimiphos-methyl (based on dry weight) which means 71.19% residue removal considering the humidity percentage in moloukhia leaves 75%.

As shown in table 2, the residues of pirimiphos-methyl on unprocessed cucumber fruits after one day from spraying with insecticide was 1.8849 ppm. This value decreased to 1.1687 ppm after washing of cucumber fruits, to 0.0499 ppm after peeling process and to 0.1935 ppm when salting process occurred and the percents removal were 38.00, 97.35 and 89.73%, respectively. Also, in table 2, the residues of pirimiphos-methyl on unprocessed green bean pods after one day from spraying was 17.8777 ppm. The washing and blanching reduced the residues to 15.5011, and 10.9699 ppm and the percents removal were 13.29 and 30.64%, respectively.

Heavy use of pesticides on the field crops has begun to receive much attention because residues in food commodities may be hazardous to human health. The present data indicated that the different processing used in this study had different effects 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), Celino and Magallona (1985) and Shokr (1998). The present results also confirm and agree with those obtained and reported by National Canners Association (1967) that peeling fruits removed considerable amounts of pesticide residues not removed by washing treatment. Karogeorgiev (1979) also found that peeling of fruit results in complete of disappearance pesticide residue within the limit of the methods used in analysis. Washing processes were found to be efficient in removing organophosphorus insecticides from vegetables, Tantawy *et al.* (1979), Kamil (1987) and Shokr (1997).

Table 2. Effect of some different processes on pirimiphos-methyl insecticide residues in some vegetable crops.

Crop	Process*	Pirimiphos-mcthyl	
		PPM	%removal
Moloukhia leaves	None*	39.1575	00.00
	Washing	18.0928	53.79
	Blanching	3.8235	90.24
	Drying**	45.1299	71.19***
Cucumber fruits	None*	1.8849	00.00
	Washing	1.1687	38.00
	Peeling	0.0499	97.35
	Salting	0.1935	89.73
Green bean pods	None*	17.8777	00.00
	Washing	15.5011	13.29
	Blanching	10.9699	30.64

* One day after application.
** Calculated on dry weight.
*** The % removal calculation was based on the moisture content in moloukhia leaves being 75%

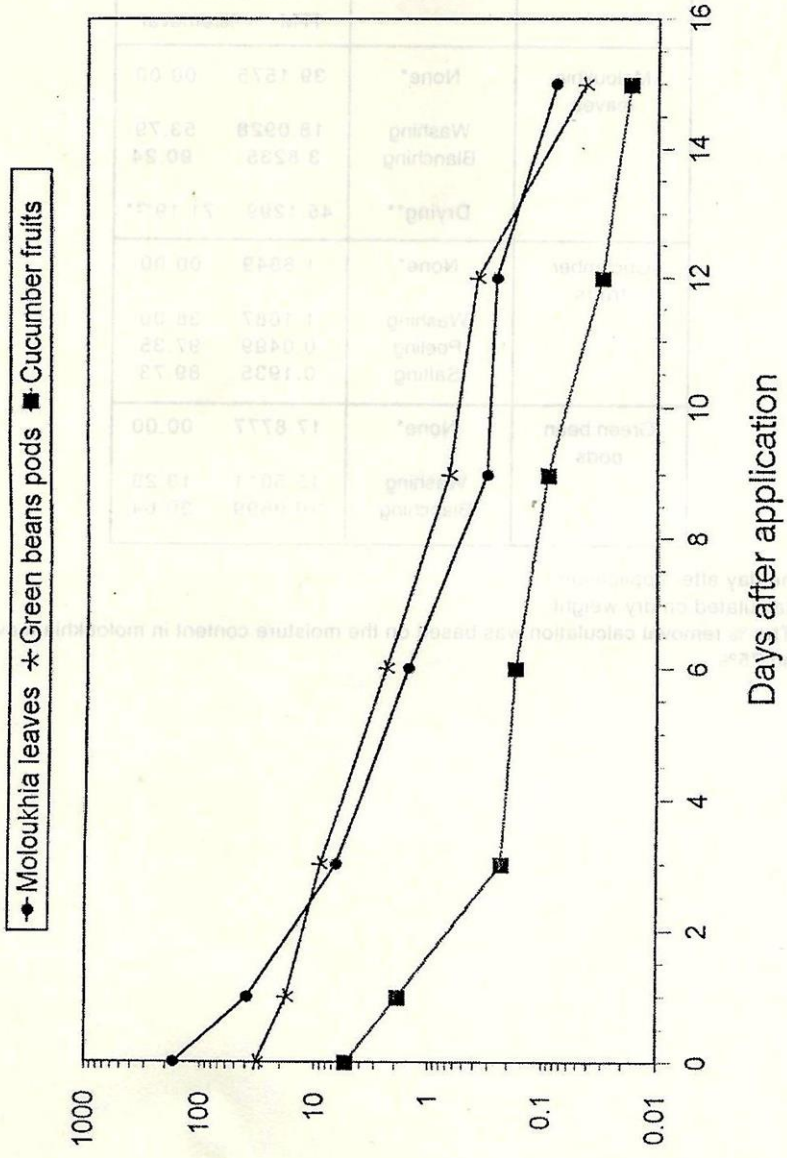

Fig. 1. Residues of pirimiphos-methyl on and in vegetables.

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متبقيات مبيد بريميفوس ميثايل على بعض محاصيل الخضر

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اجرى هذا البحث لدراسة مدى تلوث بعض نباتات الخضر مثل الملوخية والفاصوليا والخيار بمتبقيات بريميفوس وهي من المبيدات الفوسفورية التي تستخدم لمكافحة الافات التي تصيب تلك المحاصيل.

وتتضمن خطة الدراسة النقاط التالية :-

- تحليل متبقيات هذا المبيد علي أوراق الملوخية وقرون الفاصوليا وثمار الخيار علي 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 أوراق الملوخية وقرون الفاصوليا وثمار الخيار .

ويمكن تلخيص النتائج المتحصل عليها فيما يلى:

ا. تحليل متبقيات بريميفوس ميثايل علي أوراق الملوخية وقرون الفاصوليا وثمار الخيار :

اوضحت النتائج ان كميات المتبقى من مبيد بريميفوس ميثايل بعد ساعة من الرش بالمعدلات الموصي بها كانت ١٧١,٠٢٨٧ و ٣٢,٥٢١٨ و ٥,٣٥٤٣ جزء في المليون علي اوراق الملوخية وقرون الفاصوليا وثمار الخيار علي التوالي. ثم تناقصت هذه الكميات من المتبقي بعد يوم من الرش الي ٣٩,١٥٧٥ و١٧,٨٧٧ و ١,٨٨٤٩ جزء في المليون علي التوالي. ثم اخذت هذه الكميات من المتبقي تقل تدريجيا الي ان وصلت الي ٠,٠٧٧٥ و ٠,٠٤٢٧ و ٠,٠٠١٧ جزء في المليون بعد ١٥ يوما من الرش علي التوالي. وكانت فترات نصف العمر لمتبقيات بريميفوس ميثايل علي أوراق الملوخية وقرون الفاصوليا وثمار الخيار ١١,٣ و ٢٧,٨ و ١٥,٩ ساعة علي التوالي. وأمكن تحديد فترات الامان

لهذا المبيد بعد الرش حيث كانت ٣,٩ و ١٠,٧ و ٢,١ يوما بالنسبة لمحصول الملوخية والفاصوليا والخيار علي التوالي.

٢- دراسة تأثير عمليات الاعداد والتجهيز المختلفة علي ازالة متبقيات مبيد بريميفوس ميثايل من علي أوراق الملوخية وقرون الفاصوليا وثمار الخيار.

أوضحت الدراسة أن عملية الغسيل بماء الصنبور أزالت ٥٣,٧٩٪ من متبقيات بريميفوس ميثايل من على اوراق الملوخية ، بينما أزالت هذة العملية ٣٨,٠٢٪ من متبقيات هذا المبيد من ثمار الخيار. ايضا ازالت عملية الغسيل بماء الصنبور ١٣,٢٩٪ من متبقيات مبيد بريميفوس ميثايل من على قرون الفاصوليا . أما عملية السلق فقد ازالت ٩٠,٢٤٪ من متبقيات هذا المبيد من علي اوراق الملوخية و ٣٠,٦٤٪ من علي قرون الفاصوليا وأن عمليتا التقشير والتخليل ازالتا ٩٧,٣٥٪ و ٨٩,٧٣٪ من علي ثمار الخيار علي التوالي. أما عملية التجفيف لاوراق الملوخية فقد ازالت ٧١,١٩٪ من هذا المبيد.