PROFENOFOS RESIDUES ON AND IN MOLOUKHIA LEAVES AND HOW TO MINIMIZE THESE RESIDUES

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ABSTRACT

These studies were carried out to investigate the residual behaviour of profenofos insecticide on moloukhia leaves *Chorchorus olitorius* and how to minimize these residues. The initial deposits of profenofos on and in moloukhia leaves was 141.693 ppm, the 3 days following application is critical in the sense of sharply decreases to reach 73.25% from the initial deposit. Also the residue half life value (RL_{50}) determined on moloukhia leaves was 38 hours. Washing and drying processes reduced significantly profenofos residues in moloukhia leaves. Washing with tap water induced 23.96 to 75.77% removal in total residues of profenofos in moloukhia leaves, whereas it was reached 57.22 to 76.13% with drying process.

The influence of UV-rays and direct sunlight on the rate of decomposition of profenofos and the calculated residue half life values were 62.72% and 8.5 hours when exposed to UV-rays for 12 hours, while these values were 91.81% and 10.5 hours when exposed to direct sunlight for 72 hours.

Key words: Residues, Profenofos, Mouloukhia

INTRODUCTION

Moloukhia *Chorchorus olitorius* is one of the major summer vegetables and plays an important role in the Egyptian diet either as green or dry leaves, also as an export vegetable crop. In Egypt pesticides are not recommended for use on this vegetable, it may reach the plant surface as contaminant when this vegetable was planted beside the cotton fields or maybe treated with pesticides when attacked with economic pests.

In Egypt, pesticides are applied to control economic pests during summer season where the temperature is almost high because of the long sunny and uncloudy days. The ultraviolet component of sunlight with wavelength varies from 240 to 400 nm is responsible for pesticide photolysis in the environment. Both heat and light might affect the efficiency of pesticides which are measured by the duration of their residual effect.

Moloukhia leaves retained a high level of the pesticides, this demonstrated the relationship of surface to total weight and its effect on residue deposits, previously reported by El-Sayed *et al.* (1976). Similar results and effect of different processes (washing, blanching and drying) in removing pesticide residues from moloukhia leaves after treatment with pesticides were obtained and reported by many researches Hegazy *et al.* (1997), Shokr (1997), Sallam and El-Nabarawy (2001), and Hegazy and Nasr (2003).

The aim of these studies was to evaluate the persistence of profenofos (*0*-4-bromo-2-chlorophenyl *0*-ethyl *S*-propyl phosphor-rothioate) insecticide on moloukhia vegetable. The efficiency of washing and drying processes in removing profenofos residue was evaluated. Further studies were also carried out to investigate the effect of UV-rays (short waves) and direct sunlight on the stability and degradation of the active ingredient of profenofos pesticide.

MATERIALS AND METHODS

1- Experimental and insecticide treatment.

Moloukhia seeds were planted on March 20^{th} 2003 under the normal field conditions and agricultural practice at Gharbia Governorate. Profenofos (Selcron 72% E.C.) was applied on May 26^{th} 2003, at rate of 375 ml/100 L water (recommended dose) using a knapsack sprayer equipped with one nozzle. Replicate samples, 500 g. of moloukhia leaves was taken at intervals of one hour after application (zero time), 1, 3, 5, 7, 10, 15 and 18 days. The samples were divided to three parts, the first part of samples was kept in polyethylene bags in deep freezer until analysis.

2- Processing.

A. Washing with tap water: The second part of samples was rinsed for three minutes with running tap water, then drained on a clean paper for one hour until dry, and kept in polyethylene bags in deep freezer until analysis.

B. Drying: The third part of samples was spread on a clean paper under room conditions for 6-7 days until complete drying and then ground and kept in polyethylene bags under deep freezing until analysis.

3- Analytical methods.

A. Extraction: The extraction procedure used is the general method suitable for organophosphorus compounds (Ministry of Welfare, Netherlands, 1988). Fifty grams of homogenized sample was mixed with 50 g. anhydrous sodium sulphate and 150 ml ethyl acetate. The mixture was blended for 3 min. and the extract was filtered, then evaporated just to dryness using a rotary evaporator at 40°C.

B. Clean-up of Extract: The clean-up procedure was done according to the method of Mills *et. al.* (1972). An elution solvent system used a mixture of 50% methylene chloride- 1.5% acetonitrile- 48.5% hexane (v/v/v). A column chromatographic containing 10 g. 3.5% deactivated florisil was used. Then the residues from the column were eluted with 200 ml of this mixture. The eluant was evaporated just to dryness as previously described and the residues were ready for chromatographic determination after redissolved in an appropriate volume of ethyl acetate.

C. Gas liquid chromatography 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 profenofos. The column (1.5 m x 4 mm i.d. pyrex) was packed with 4% SE-30 + 6% OV-120 on gas chromosorb Q (80-100 mesh); temperature degrees were 230°C for column, 240°C for detector and 235°C for injector and gas flow was 30, 30, and 30 ml/min. for nitrogen, hydrogen and air, respectively.

Results were corrected according to the rate of recovery which were determined in fortified untreated samples at levels ranged from 0.1 ppm to 1 ppm. Following the techniques previously mentioned, the rate of recovery for profenofos was 83.5%.

4- Photodegradation of profenofos.

Aliquots of the tested insecticide representing one milliliter ethyl acetate containing 1000 µg a.i. was spread as uniformly as possible on the surface of uncovered petri dishes (5 cm i.d.).

The organic solvent (ethyl acetate) was left to dry at room temperature and the resulting deposits were divided and subjected to two treatments. The 1^{st} set of treatment petri-dishes was exposed to short waves of an ultraviolet lamp (254 nm) at a distance of 12 cm for 1, 3, 6 and 12 hours. The 2^{nd} set was exposed to normal and direct sunlight regime for 1, 4, 12, 24, 48 and 72 hours, maximum temperature ranged between 32 and 36°C.

The residues of tested pesticide which remained on exposed surfaces were quantitatively transferred to standard glass stopper test tubes with ethyl acetate after which the solvent was evaporated to dryness and the residues were ready for determination by gas liquid chromatography, after redissolved in appropriate volume of ethyl acetate.

RESULTS AND DISCUSSION

The results presented in Table (1) indicated that the initial deposits of profenofos on and in moloukhia leaves was 141.693 ppm, one hour after application. The amount of residues dropped to 104.710 ppm and 37.897 ppm within the first 24 hours and 3 days after spraying, respectively. These figures decreased gradually until reached 0.194 ppm after 18 days of application.

Washing and drying processes reduced significantly profenofos residues in moloukhia leaves. Washing with tap water induced 23.96 to 75.77% removal in total residues of profenofos in moloukhia leaves, whereas it was reached 57.22 to 76.13% with drying process, where the percent removal values calculated were dependent on the moisture content of moloukhia leaves (humidity percent of moloukhia leaves studied was 75%).

The disappearance of profenofos may be due to its vapor pressure (1.24×10^{-1} mPa at 25°C) and also to other factors such as weathering, metabolic conversions or other degradation processes. However, the 3 days following application is critical in the sense of sharply decrease that reaches 73.25% from the initial deposit.

On the other hand, reduction of pesticide residues from leaves of the plant probably resulted from dilution by plant growth and effect of volatilization from the plant tissue surface due to meteorological conditions for the duration of the experiment such as temperature, humidity, rainfall and UV-light.

The calculated residue half-life value (RL_{50}) of profenofos on moloukhia leaves was 38 hours.

Table (1): Residues of profenofos on and in moloukhia leaves and effect of washing and drying processes on these residues

Time after application (Days)	Residues		Washing process		Drying process	
	ppm	% loss	ppm	% removal	ppm**	% removal
Zero time*	141.693	00.00	63.699	55.04	186.567	67.08
1	104.710	26.10	47.981	54.18	139.639	66.66
3	37.897	73.25	28.816	23.96	55.925	63.12
5	13.405	90.54	7.301	45.53	22.939	57.22
7	8.439	94.04	2.189	74.06	10.736	68.19
10	1.376	99.03	0.475	65.48	2.217	59.74
15	0.486	99.66	0.118	75.72	1.195	76.13
18	0.194	99.86	0.047	75.77	0.291	62.37

* One hour after application.

** Calculated on dry weight.

RL_{50} in hours 38

The results agree with that of El-Sayed *et. al.* (1975), Hegazy *et. al.* (1997), Shokr (1997), and Sallam and El-Nabarawy (2001).

El-Sayed *et. al.* (1975) found that the residue half-life values of Azodrin, Nuvacron, Dursban and Gardona on moloukhia leaves were 93.6, 98.4, 20.4 and 24 hours, respectively. The residues half-live of triazophos insecticide on moloukhia and okra were 1.55 and 3.3 days, respectively (Hegazy *et. al.* 1997). Shokr (1997) also found that the initial residues of pirimiphos-methyl, fenitrothion and malathion on and in moloukhia leaves were 171.0287, 107.1649, and 109.0438 ppm, and the residue half-life values for these insecticides were 11.3, 10.6 and 11.6 hours, respectively. The initial deposits of chlorpyrifos, chlorpyrifos-methyl and profenofos (Curacron) on moloukhia leaves were 133.6301, 81.0475, and 52.0730 ppm, respectively also the half-life values were 22.8, 33.84 and 52.08 hours, respectively (Sallam and El-Nabarawy 2001).

The washing and drying processes were found to be efficient in removing profenofos insecticide from moloukhia leaves. The results obtained agreed with findings of Shokr (1997) who found that the washing process with tap water removed 53.79, 85.29 and 84.34% from pirimiphos-methyl, finitrothion and malathion on moloukhia leaves, 1 day after application. While drying process removed 71.19, 74.13 and 72.98% from these insecticide residues, respectively. Similar results were reported by Sallam and El-Nabarawy (2001) who found that the washing process with tap water removed from 29.65 to 73.99%, 29.84 to 66.58% and 29.14 to 56.75% of chlorpyrifos-methyl, chlorpyrifos and profenofos (Curacron) residues on moloukhia leaves treated, while the corresponding values by drying process were 38.91 to 53.05%, 14.60 to 31.06% and 58.04 to 62.77%. Also Hegazy *et. al.* (1997) reported that the washing and drying processes removed 31.41 and 91.28% of triazophos residues from moloukhia leaves, respectively.

Examination of the data in Table (2) and (3) clearly showed that the decomposition percentages of profenofos on glass surfaces increased gradually after exposure to UV-rays and direct sunlight. The percent of loss were 8.11 and 7.35% after one hour of exposure to UV-rays and direct sunlight, respectively. The degradation percentages of profenofos increased to 40.16 and 62.72% after 6

Table (2): Effect of UV-rays (254 nm) on profenofos insecticide

Time of exposure in hours	µg insecticide	% loss
0	1000.000	00.00
1	918.918	8.11
3	819.819	18.02
6	598.360	40.16
12	372.548	62.74

RL_{50} in hours 8.5

Table (3): Effect of sunlight on profenofos insecticide

Time of exposure in hours	µg insecticide	% loss
0	1000.000	00.00
1	926.505	7.35
4	656.249	34.37
12	448.347	55.16
24	262.396	73.76
48	136.549	86.34
72	81.858	91.81

RL_{50} in hours 10.5

and 12 hours of exposure to UV-rays, respectively, while these values were 55.16 and 91.81% when profenofos were exposed to direct sunlight for 12 and 72 hours, respectively.

The calculated residue half-life values of this pesticide were 8.5 and 10.5 hours from exposure to UV-rays and direct sunlight, respectively.

The effect of ultraviolet (UV) light on pesticides is of considerable interest to the research workers of pesticides. It has been demonstrated that UV light exerts chemicals changes on large number of pesticides. As to organophosphorus pesticides, several types of photodecomposition such as hydrolysis, oxidation and isomerization. If similar reaction occur under field conditions, such is of great importance in view of the environmental contamination, pesticide residues in agricultural products and practical use of pesticides (Murai and Igawa 1977).

Sensitivity to sunlight limits the use of some potential pesticides in agriculture. Classical approaches to overcome this obstacle have involved chemical modifications of molecular structure of the pesticide or the use of UV-absorbing materials in pesticide formulations. However, both methods suffer from serious drawbacks since chemical modification may affect the pesticidal activity of the compounds or their biodegradability and the large amount of UV screeners required to achieve acceptable photoprotection may introduce ecological problems related to soil and water pollution (Rozen and Margulies 1991). The radiation energy of the sun might be absorbed by a pesticide molecule principally at a given wavelength. The energy might increase the translational, rotational, vibrational or electronic energy of the molecule. If enough energy was absorbed to interact with the electrons of the molecules an electronically excited molecule will be resulted. Energy might be lost by the molecule in a number of ways, one of which is chemical reaction (Plimmer 1970).

Photolysis is one of the various factors determining the fate of pesticide in the environment. A number of recent studies have examined the photolysis of pesticides in water and air as well as on plant and soil surfaces by sunlight and ultraviolet light irradiation (Draper and Crosby 1981; Wong and Crosby 1981). Light plays an important role in the behaviour of pesticides in the environment, when the molecule absorbs a photon it becomes unstable, and undergoes a variety of competing primary processes, such as chemical reaction, isomerization etc., to return to a stable state (Zepp and Cline 1977).

Generally, it is found that photodegradation is positively correlated with the exposure period. If similar photodegradation occur under field conditions, such result is of great importance in view of the environmental contamination, pesticide residues in agricultural products and practical use of pesticides in Egypt, where the weather during summer season is long sunny and uncloudy days.

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الملخص العربى

متبقيات مبيد البروفينفوس على و فى أوراق الملوخية و كيفية تقليل هذا المتبقى

شكر عبدالسلام على شكر
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يهدف هذا البحث لدراسة سلوك متبقيات مبيد البروفينفوس على و فى أوراق الملوخـــية و كذلك تأثير عمليتى الغسيل و التجفيف على أزالة هذه المتبقـــيات. و أيضاً تأثير الأشعة فوق البنفسجية و ضوء الشمس المباشر على متبقيات هذا المبيد.

حيـــث أوضـــحت النـــتائج أن كمية المتبقى الأولى لهذا المبيد على أوراق الملوخية كانت ١٤١,٦٩٣ جزء فى المليون و تناقصت هذه الكمية تدريجـــياً حتى و صلت إلى ٠,١٩٤ جزء فى المليون بعد ١٨ يوم من المعاملة و كانت فترة نصف العمر لهذا المتبقى على أوراق الملوخية ٣٨ ساعه. و أظهرت النتائج أن عملية الغسيل سببت نسبة أزالة لمتبقيات هذا المبيد من أوراق الملوخية تراوحت بين ٢٣,٩٦ % و ٧٥,٧٧% و أيضاً سببت عملية التجفيف تقليل هذا المتبقى إلى نسبة تراوحت بين ٥٧,٢٢% و ٧٦,١٣%.

أوضـــحت النتائج أنه عند تعرض متبقيات البروفينفوس للأشعة فوق البنفسجية كانت النسبة المئوية للفاقد بعد ١٢ ساعه هى ٦٢,٧٢% وكانت فترة نصف العمر لهذا المتبقى ٨,٥ ساعه. و عند التعرض لضوء الشمس المباشر لمدة ٧٢ ساعه كانت النسبة المئوية للفاقد ٩١,١٨% و كانت فترة نصف العمر لهذاالمتبقى ١٠,٥ ساعه.