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Determination of Dimethoate and Malathion Residues on and in Moloukhia Leaves

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ABSTRACT

These studies were carried out to investigate the residual and behavior of two organophosphorus insecticides(dimethoate and malathion) on and in moloukhia leaves (Chorchrus olitorius) and how to minimize these residues. The initial deposits of dimethoate on and in moloukhia leaves was 131.721 mg/kg, malathion higher than (97.231 mg/kg). The results showed that after 18 days from treatment of dimethoate and malathion the residues were 0.0٤1 and 0.0٣9 mg/kg respectively. The half-life values of dimethoate and malathion residues on and in moloukhia leaves were 1.6 and 2.6 days after treatment. Using house hold processing (washing) decreased the residues of dimethoate and malathion in moloukhia leaves. It was noticed that washing with tap water reduced the amount of both pesticides (dimethoat and malathion). The removal percentage reached from ٣٨.٤١ to ٨٠.٤٩% and ٣٢.١٠ to ٦٩.٢٣% respectively.

Keywords: PHI, dimethoate, malathion residues, moloukhia leaves

INTRODUCTION

Moloukhia (Chorchorus olitorius) is one of the major summer vegetables and play an important role in the Egyptian diet either as green or dry leaves, also as an export vegetables crop. In Egypt pesticides are not recommended for use on this vegetables, it may reach the plant surface as contaminant when this vegetables was planted beside the cotton field 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 unclouded days.

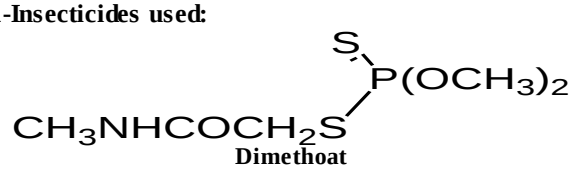
Moloukhia leaves retained a high level of the pesticides, this demonstrated the relationship of surface to total weight and its effect on residue deposits, previously reported by El-Sayed et al. (1976).

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 researchers [Hegazy et al. (1997), Shokr (1997), Sallam and El-Nabarawy (2001), and Hegazy and Nasr (2003)].

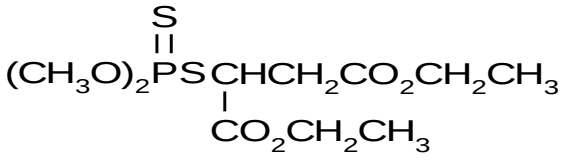
Both pesticides dimethoate, and malathion using in controlling a wide range of insects, such as aphids, thrips, white flies, fruitfly, scale insects, mites and other sucking, chewing insects attacking fruits, vegetables and ornamental plant (Anonymous,1993). Malathion is effective in controlling many insects such as leaf eating caterpillars, thrips, cutworms, etc. in a range of crops including vegetables, fruits, maize, sugar beet, tea, and ornamentals. However, malathion has, however, been reported to have endocrine disrupting effects,[Penalver et. al. (2003)]. These insecticides are used in Egypt to control some economic insects (Anonymous, 1997b).

MATERIALS AND METHODS

1-Insecticides used:



Dimethoat



Malathion

1-Experimental and sampling.

Moloukhia seeds were planted on Marsh 19th 2013under the normal field conditions and agricultural practice at Giza governorate. Dimethoate and malathion were sprayed on moloukhia leaves using a knapsack sprayer equipped with one nozzle. The moloukhia leaves spray on May 25th 2013.

The representative samples for Dimethoate and Malathion (500g). moloukhia leaves was taken at intervals of one hour after application (zero time), 1, 3,5, 7, 10, 15, and 18 days after treatment. The samples were divided to two parts, the first part of samples was kept in polyethylene bags in deep freezer until analysis.

2-Processing:

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.

3-Extraction:

The procedure of Lehotay et al., (2005) as a QuCHER method was used for extraction and purification of pesticide residues from moloukhia leaves samples. Fresh sample of 10 g was weighted into a 50 ml PFTE tube and mixed with 10 ml deionized water by shaking for one minute. Acetonitrile acidified with acetic acid (10 ml), 1.0 g sodium acetate and 4.0 g anhydrous magnesium sulphate were added and shake vigorously for one minute. The samples were centrifuged at 4000 rcf for 2 min. Six milliliter of the upper clear solution (extracts) was transferred into 15 ml polyethylene tube contained 0.4 g primary secondary amine (PSA) sorbent and 0.6 g anhydrous magnesium sulphate. The tubes were caped, then the extract with the sorbent/ dessicant mixed vigorously for one minute and centrifuged at 4000 rcf for 2 min. Four milliliter of the clear solution was transferred into 15 ml glass tube

and 50 µl tetradecan was added as keeper and evaporated in turbovab at 40 °C to dryness. The residues were dissolved in 2 ml of acetonitrile and then injected.

For recovery studies, the control samples were spiked with the studied pesticides before the corresponding extraction procedure. A representative 10 g portion of moloukhia leaves sample was weighted and fortified homogeneously with appropriate volume of working standard solution and followed the same previous procedure of determination.

Spiked levels were 0.03, 0.1 and 1.0 mg/kg. The obtained results were corrected according to the recovery rate (Table-1).

Table1: Recoveries of dimethoate and malathion on and in molokhia leaves at three fortification levels

Dimethoat			Malathion		
0.03 ppm	.1 ppm	1 ppm	0.03 ppm	0.1 ppm	1 ppm
89	93	99	86	92	98

GLC procedures:

Assessment of dimethoate and malathion residues was carried out according to the Official Methods of Analysis (Anonymous; 1995) using Hewlett Packard gas liquid chromatography (HP 6890N) equipped with nitrogen phosphorus detector (NPD), two columns, HP PAS-5, NPD tested Ultra 2 Silicone, 0.32 mm i.d., 0.52 µm film thickness and 25.0 m length and HP PAS-1701, 0.32 µm i.d., 0.25 µm film thickness and 25 m length, HP autosampler and HP computer under the following operating parameters:

Injector temperature = 225 °C, Detector temperature =280 °C, Flow rate of nitrogen 60 ml/min (carrier + makeup), Column head pressure 80 kPa, Splitless time 0.7 min.

The oven was programmed as follow:

Initial oven temperature: 90 °C, Initial oven time 2 min. using two ramps, Ramp (1) Rate 20°C / min, Temp 150 °C, Time 0 min. and

Ramp (2) Rate 6°C / min, Temp 270 °C Time 15 min.

The analyzed concentration in sample Cs (mg/Kg) was calculated as follows:

$$Cs = \frac{As / Ais}{Ast / Aist} \times Cst \times \frac{Vf \times Vtot.}{Va \times M}$$

Since:

As = Peak area of analyte in sample

Ais = Peak area of ditalimiphos standard in sample

Ast = Peak area of analyte in standard run

Aist= Peak area of ditalimiphos standard in standard run

Cst = Concentration of standard (mg/L)

Vf = Final volume (ml)

Vtot.= Total extraction volume (ml)

Va = 40 ml

M = Sample weight in final volume (g)

Half life time (Lt_{50}) was calculated and pre-harvest interval (PHI) was determined considering the MRL for dimethoate and malathion on moloukhia leaves (0.2 and 0.05 mg/kg respectively) according to Annex II Regulation of European Union (Anonymous, 2005).

RESULTS AND DISCUSSION

1-Persistence of dimethoate and malathion on and in moloukhia leaves

Pesticides residues in food stuff are one of the effective factors on human health so a lot of studies were carried out . The objective of this study was determination of dimethoat and malathion residues on and in moloukhia leaves through a period of time, and predicting the PHI (Pre Harvest Interval). Since MRL (Maximum Residue Limit) of dimethoate is 0.05 mg/kg and the estimated PHI was found to be 15 days. For malathion, MRL is 0.3 ppm and therefore, the estimated PHI was found to be 10 day (Anonymous, 1997a). Results in Table 2 and 3 showed that the concentration of the initial deposits of dimethoate and malathion on and in moloukhia leaves were 131.721 and 97.231ppm, respectively (one hour after application). The residues of dimethoate and malathion decreased to 91.321 and 51.341 respectively within the first 24 hour. After 3 days from treatment the residues decreased to 30.101and ١٦.٩٣٢ppm, respectively. These residues decreased gradually until reached to 0.0٤1 and 0.0٣9 ppm, respectively, after 18 days.

Data show that the chemical structure of the used insecticide and their rates did effect the amount of the initial deposits as well as the subsequent amounts of residues on and in moloukhia leaves Dauterman et. al. (1960) .

The initial amount of dimethoate (131.721ppm) is much higher than that of malathion (97.231ppm). It is known that there is a positive correlation between the lipophilicity of the used compound and its uptake onto the recipient plant. (Solubility in water 2.5% and 140 ppm at 21 C of dimethoate and malathion, respectively). (Anonymous, 1993).

The values of half-life obtained from calculation of Moye et. al.(1987). The half-life values of dimethoate and malathion residues on and in moloukhia leaves were 1.6 and 2.6 days, respectively.

The results agreed with that of El-Sayed et. al. (1975), Hegazy et. al. (1997), Shokr (1997), Sallam and El-Nabarawy (2001) and Mingjing et. al. (2012). El-Sayed et. al. (1975) found that the residue half-life values of Azodrin, Nuvacron, Dursban and Gardona as organophosphorus group on moloukhia leaves were 93.6, 98.4, 20.4 and 24 hours, respectively.

2-Effect of washing on dimethoate and malathion residues on and in moloukhia leaves

Washing processes reduced significantly dimethoate and malathion residues in moloukhia leaves. The results in Table 2 and 3 showed that the initial residues of dimethoate and malathion on unwashed moloukhia leaves were 131.721 and 97.231 ppm, respectively. These residues reduced to ٨1.131 and ٦٦.024 ppm, respectively on washed moloukhia leaves. The corresponding removal percentages of these residues were 38.41 and 32.10 %. It could be concluded that washing removal percentage ranged between 38.41 to 80.49 % and 32.10 to 69.23% for dimethoat and malathion respectively on and in moloukhia leaves.

The washing processes were found to be efficient in removing dimethoat and malathion insecticides 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 84.34% from pirimiphos-mithyl, finitrothion and malathion on moloukhia leaves, 1 day after application. 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 treated moloukhia leaves.

Recommendation

Generally result appeared that the safety period for the harvesting of moloukhia leaves in Egypt should not before 15 and 10 days after treatment on and in moloukhia leaves by dimethoate and malathion respectively.

Table2: Residues of dimethoate on and in moloukhia leaves and effect of washing processes.

Time after application (Days)	Residues		Washing process	
	ppm	% Loss	ppm	% Removal
Zero time*	131.721	00.00	81.131	38.41
1	91.321	30.67	53.921	40.95
3	30.101	77.15	15.335	49.05
5	7.993	93.93	3.534	55.79
7	3.925	97.02	1.384	64.74
10	0.403	99.69	0.099	75.43
15	0.051	99.96	0.011	78.43
18	0.041	99.97	0.008	80.49

*** One hour after application**

Table 3: Residues of malathion on and in moloukhia leaves and effect of washing processes.

Time after application (Days)	Residues		Washing process	
	ppm	% Loss	ppm	% Removal
Zero time*	97.231	00.00	66.024	32.10
1	51.341	47.20	28.305	44.87
3	16.932	82.59	8.962	47.07
5	8.675	91.08	4.037	53.46
7	2.104	97.84	0.881	58.13
10	0.239	99.75	0.100	58.16
15	0.057	99.94	0.022	61.40
18	0.039	99.96	0.012	69.23

*** One hour after application**

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تقدير متبقيات مبيدى الديمثويت والملاثيون على وفى أوراق الملوخية

على على محمود
المعمل المركزى لتحليل متبقيات المبيدات و العناصر الثقيلة فى الأغذية مركز البحوث الزراعية

يهدف هذا البحث الى دراسة تقصى سلوك متبقيات مبيدين حشريين من المركبات الفسفورية هما الديمثويت والملاثيون على وفى أوراق الملوخية وكذلك دراسة كيفية الحد منهما (عن طريق عملية الغسيل). أوضحت النتائج بأن المتبقيات الاولية للديمثويت كانت ١٣١.٧٢١ جزء فى المليون أعلى من المتبقيات الاولية للملاثيون وهى ٩٧.٢٣١ جزء فى المليون. أظهرت النتائج أن كمية المتبقى لمبيدى الديمثويت والملا ثيون بعد ١٨ يوما من المعاملة هى ٠.٠٤١ و٠.٠٣٩ جزء فى المليون على التوالى وكانت فترة نصف العمر لكلا المبيدين ٢.٦ و١.٦ على التوالى. أوضحت النتائج أن عملية الغسيل سببت نسبة ازالة لمتبقيات لمبيدى الديمثويت والملاثيون من أورق الملوخية حيث وصلت نسبة الازاله من ٣٨.٤١% الى ٨٠.٤٩% و من ٣٢.١٠% الى ٦٩.٢٣% على التوالى.