

RESIDUES OF MALATHION ON AND IN CERTAIN PLANTS OF MEDICAL IMPORTANCE

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Abstract

Coriander, fennel and geranium plants were treated in the field with malathion (57% E.C) at the rate of 712.5 g active ingredient per feddan.

Residue analysis showed that the initial deposits determined one hour after application were 16.51, 4.18 and 51.10 ppm on and in coriander, fennel and geranium plants, respectively. The residual rates of loss were 11.20, 57.18 and 28.32%, one day after treatment, respectively. The amounts detected in the plants 21 days post application were 0.67, 0.001 and 0.30 ppm, respectively. The malathion residue half lives on these plants were 55.2, 20.4 and 74.4 hours, respectively.

Data of thin layer chromatograms indicated that parent compound malathion was detected in all samples of coriander and geranium throughout the experimental period, but for fennel samples it was detected up to the 6th day. Four, five and one metabolites were detected in coriander, fennel and geranium samples, respectively.

Malathion treatments increased essential oil contents in coriander and fennel plants by 10 and 15%, respectively.

The mature dry seeds collected from coriander and fennel plants were devoid of any detectable amounts of malathion and its metabolites. This indicates that such seeds could be marketed safely for human consumption.

INTRODUCTION

Medicinal plants play an important role in medication, medical industries and nutritional aspects for human. These plants - as all other plants-are attacked by several pests including insects, mites, fungi and weeds causing reduction in their productivity. Therefore, all the farmers adopted the application of pesticides for their protection.

Malathion (Cythion), diethyl (dimethoxy thio phosphoryl thio) succinate is a broad spectrum organophosphorus pesticide used against several insect species. The Egyptian Ministry of Agriculture has recommended malathion for use on medicinal plants .

Coriander, fennel and geranium are three plants of medicinal importance. Fennel and coriander are used as carminatives, spicy pleasing odour and flavour. Geranium is used for the spicy pleasing odour, flavour and used in food industry and cosmetics. These plants are attacked by different insect species of which aphids are the most injurious.

The present investigation was conducted to estimate the residues of malathion on and in coriander, fennel and geranium foliage and in coriander and fennel seeds as well as in essential oils production. An evaluation for the effect of malathion treatments on oil content extracted from plant crops was discussed. This will reveal the rate of persistence on the foliage besides the rate of contamination in the seeds for the safety of human health .

MATERIALS AND METHODS

Coriander Coriandrum sativum, fennel *Foeniculum vulgare* and geranium *Pelargonium graveolens* were planted at the experimental farm of the Biological Research Station of the National Organization for Research and Drug Control, Giza Governorate. Geranium was planted on July 4th, 1986 and coriander as well as fennel were planted on October 29th, 1986 in plots of 1/40 of feddan each. The plots recieved the normal agricultural practices throughout the experimental period. Malathion E.C. formulation (57 %) was sprayed on February 17th, 1987 at the rate of 1.25 L per feddan. The amount was diluted in 300 L of water per feddan and a knapsack sprayer equipped with one nozzle was used. One plot from each crop was left untreated as

control check.

Representative leaf samples of coriander, fennel and geranium plants were taken at random one hour after application. Subsequent samples were taken 1,3,6,13 and 21 days following treatment. Moreover, samples of the mature seeds of coriander and fennel were collected from the treated plants at harvest, 55 and 95 days after foliage treatments. Samples were kept in polyethylene bags at -20°C until time of analysis.

Extraction and clean-up

Residues were extracted with chloroform at the rate of 2 ml/g sample using the Waring blender for either leaf or crushed seed samples.

Egyptian Pharmacopeia method (1972) was used for oil determination.

Coriander and fennel plant samples were cleaned-up using the ammonium coagulating solution and filtered through hyflosuper cell as mentioned by Johnson (1963). Dry seed samples were cleaned up by partitioning the residue into acetonitrile (El-Sayed *et al.*, 1982) then filtering through hyflosuper cell (Johnson, 1963).

Geranium plant samples were cleaned up by partitioning the residue into acetonitrile (El-Sayed *et al.*, 1982) and then using a chromatographic column as mentioned by Almaz (1985).

Gas chromatography

Residues dissolved in ethyl acetate were then estimated using a PYE-Unicam 104 gas chromatograph equipped with Tracor flame photometric detector operated in the phosphorus mode (525 nm filter) under the following conditions : Column packing 1.5 mx 4 mm i.d. packed with 4% SE-30 + 6% OV-210 on gas chromosorb Q (80-100 mesh); temperature ($^{\circ}\text{C}$): Injection and column 255, detector 200 and flow of gases (ml/min.): Nitrogen 100, hydrogen 150, air 60 and oxygen 15. Using these conditions the retention time of malathion was 1.2 minutes.

Results were corrected according to the rates of recovery which were determined in fortified untreated samples. Following the techniques previously mentioned, the rates of recovery were 75.74, 90.21 and 85.07 % dealing with coriander, fennel and geranium plant samples, respectively, as well as the rates of recovery were 73.11 and 83.90 dealing with coriander and fennel dry seed samples, respectively.

Thin layer chromatography

This technique was used for the identification of the parent insecticide and its metabolites. Thin layer chromatography was conducted using silica gel plates with the solvent system acetone/petroleum ether 3 : 1. Plates were dried at room temperature then exposed to bromine vapour in a fume cupboard for 5 minutes followed by spraying with freshly prepared fluoescine solution then heated after dryness in an oven at 100°C for 20 minutes (Dogheim, 1973).

RESULTS AND DISCUSSION

Residues in coriander, fennel and geranium plants

Data presented in Table (1) demonstrate the initial deposits and the residual behaviour of malathion on and in coriander, fennel and geranium plants after treatment. The initials revealed that the amounts of deposits depended on the nature of the treated surface and the relation between the surface treated and its weight.

Table 1. Residues and percentage of loss and half life values (RL50) of malathion on and in coriander, fennel and geranium plants at the rate of 712.5 grams active ingredient per feddan.

Time after treatment (days)	Coriander		Fennel		Geranium	
	ppm	% Loss	ppm	% Loss	ppm	% Loss
Initial*	16.51	0.00	4.18	0.00	51.10	0.00
1	14.66	11.20	1.79	57.18	36.63	28.32
3	4.90	70.32	0.72	82.77	26.38	48.37
6	1.43	91.34	0.36	91.39	9.35	81.70
13	0.86	94.79	0.04	99.04	2.62	94.87
21	0.67	95.94	0.001	99.98	0.30	99.41
RL50 Value	55.2 hours		20.4 hours		74.4 hours	

Where : * Samples were taken one hour after application.
Figures are the average of three replicates.

The initial deposits of malathion on and in coriander, fennel and geranium plants as determined one hour after application were 16.51, 4.18 and 51.10 ppm, respectively. These values dropped to 14.66, 1.79 and 36.63 ppm indicating that the rates of dissipation at 24 hours after treatment reached 11.20, 57.18 and 28.32%,

respectively. Following that period the residues decreased to 4.90, 1.43 and 0.86 ppm on and in coriander plants indicating percentage loss of 70.32, 91.34 and 94.79%, at 3, 6 and 13 days after application, respectively. At the same intervals, malathion residues on and in fennel plants reached 0.72, 0.36 and 0.04 ppm corresponding to percentage loss of 82.77, 91.39 and 99.04% while on and in geranium plants were 26.38, 9.35 and 2.62 ppm with percentage loss of 48.37, 81.70 and 94.87%, respectively.

Samples collected from coriander, fennel and geranium plants 21 days after application contained 0.67, 0.001 and 0.30 ppm indicating the rates of loss of 95.94, 99.98 and 99.41%, respectively. It is obvious that geranium leaves contained the highest values while the lowest values were estimated in fennel leaves. This could be attributed to the type and nature of the treated surface.

The residue half life's (RL50) of malathion on and in coriander, fennel and geranium plants were 55.2, 20.4 and 74.4 hours after treatment.

TLC chromatograms indicated that the parent compound malathion (R_f 0.94) was detected in all samples of coriander and geranium throughout the experimental period, but for fennel samples it was detected up to the 6th day. Four, five and one metabolites were detected in coriander, fennel and geranium samples, respectively. Table (2) shows the different degradation products of malathion insecticide according to its R_f values. No authentic compounds were available to identify the degradation products.

Concerning health hazards, the maximum residue limit (MRL) for malathion on and in leafy vegetables established by Codex Committee on Pesticide Residues (CCPR, 1985) is 8 ppm. Referring to this amount, preharvest interval could be determined as two days.

Table 2. Degradation products of malathion insecticide on and in coriander, fennel and geranium plants by TLC chromatograms.

Rf value	Time after treatment (days) on and in																	
	Coriander					Fennel					Geranium							
	1	3	6	13	21	Init.*	1	3	6	13	21	Init.*	1	3	6	13	21	
0.62						+						+	+					
0.74						+						+	+					
0.79	+	+	+	+	+	+			+	+	+	+						
0.87						+	+	+	+	+	+		+	+	+	+	+	+
0.94**	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
0.98	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+

Where : Init.* = Initial samples were taken one hour after application.

** = Parent compound.

Residues in mature dry seeds

The results showed that the mature coriander and fennel dry seeds collected from the harvested crops 55 and 95 days following application were devoid of any detectable amounts of malathion or its metabolites. This indicates that such seeds could be marketed safely for human consumption.

Effect of malathion treatment on the oil yield

Essential oils evaluation (Table, 3) revealed the amounts of 0.4, 2.0 and 0.2% v/w in coriander, fennel and geranium. Treatments with malathion increased the amount of essential oils in coriander and fennel to 0.44 and 2.3% v/w giving a rate of increase corresponding to + 10 and + 15%, respectively. Geranium was not affected by the malathion treatment. The obtained finding is in agreement with that reported by Ahmed and Eid (1975) and El-Keltawi *et al.* (1981) who stated that essential oils produced from certain medicinal plants are usually affected positively or negatively by pesticidal treatments .

Table 3. Oil yield and percentage increase in oil content of coriander, fennel and geranium plants after malathion treatment through steam distillation.

Treatment	Coriander		Fennel		Geranium	
	Oil yield % v/w	Percentage % v/w	Oil yield % v/w	Percentage % v/w	Oil yield % v/w	Percentage % v/w
Control	0.40	-	2.0	-	0.20	-
Malathion	0.44	+10	2.3	+15	0.20	-

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متبقيات الملاثيون على وفي بعض النباتات ذات الأهمية الطبية

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عوملت ثلاثه من النباتات الطبيه (كزبره ، شمر ، عتر) فى الحقل بمبيد الملاثيون (٥٧ ٪ مركز قابل للاستحلاب) بالتركيز ٧١٢,٥ جم مادة فعاله للفدان . أوضحت دراسة متبقيات مبيد الملاثيون ان الرواسب الأوليه له بعد ساعه من التطبيق على نبات الكزبره والشمر والعتر كانت (١٦,٥١ ، ١٨,٤ ، ٥١,١٠ جزء فى المليون) على التوالي . وكان معدل الفقد فى المتبقيات ١١,٢٠ ، ١٨,٥٧ ، ٢٨,٣٢ ٪ بعد مضى يوم واحد فقط من المعامله على النباتات المذكوره على التوالي . وكانت الكميات المقدره على النباتات بعد ٢١ يوم من المعامله ٠,٠٦٧ ، ٠,٠٠١ ، ٠,٣٠ جزء فى المليون على الترتيب. بينما كانت قيمه نصف العمر للملاثيون على هذه النباتات ٥٥,٢ ، ٢٠,٤ ، ٧٤,٤ ساعه على التوالي.

التحليل بالفصل الكروماتوجرافى ذو الطبقة الرقيقه أوضح أن المركب الأسمى (الملاثيون) قد تم تقديره فى جميع عينات الكزبره والعتر خلال فترة التجربه بينما بالنسبه لعينات الشمر فقد تم تقديره حتى اليوم السادس فقط بعد المعامله . أوضحت التحاليل أيضا أنه تم تقدير أربعة وخمسه ومركب واحد من نواتج تحطم الملاثيون فى كل عينات الكزبره والشمر والعتر على التوالي.

المعامله بالملاثيون أوضحت زياده فى مكونات الزيوت العطريه بنسبه تصل الى ١٠ ٪ ، ١٥ ٪ فى كل من الكزبره والشمر على التوالي.

عينات البذور التى جمعت لكل من الكزبره والشمر كانت خاليه من أى كميه يمكن تقديرها للملاثيون أو أحد نواتج تحطمه وهذا يدل على أن البذور يمكن تسويقها بأمان للإستهلاك الأدمى.