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DISSIPATION OF MALATHION IN DILL AND CORIANDER PLANTS AND THEIR OILS

[66]

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ABSTRACT

The insecticide malathion (57% E.C.) was applied at the rate of 712.5 gm active ingredient per feddan on dill, ***Anethum graveolens*** L. and coriander, ***Corianderum sativum*** L. for controlling aphids infesting these plants. An analytical method, using gas chromatography equipped with flame photometric detector was used for detecting the insecticide residues. A field trial was conducted to determine the rate of dissipation of malathion in dill and coriander plants and in the resulting oil. Residue analysis showed that the initial deposits determined one hour after application were 35.81 & 22.7 ppm in dill and coriander plants, respectively. Rates of dissipation of malathion were 4.72, 51.1, 68.39, 88.41 and 93.49% in dill plants and were 13.61, 43.22, 66.78, 86.26 and 91.85% in coriander plants at 1, 3, 7, 14 and 21 days post treatment, respectively. The pesticide was decayed quite rapidly in and on dill and coriander plants and detectable residues (1.62 and 0.93 ppm) were observed in these plants 28 days after treatment. At harvest 46 days for coriander and 70 days for dill after application malathion was found at average levels of 0.78 mg/kg and 0.54 mg/kg in dill and coriander dry seed, respectively. The volatile oil extracted from the seed by steam distillation process was contaminated with the insecticide at a higher levels than in the seed [about sevenfold in dill oil, 5.21 mg/kg and ninteenfold in coriander oil 10.16 mg/kg]. This means that malathion had tendency to co-distill with the dill and coriander oil throughout steam distillation process.

Key words: Malathion, Insecticide, Residues, Medicinal plants, Volatile oil

INTRODUCTION

Malathion –(dimethoxy thiophosphoryl thio) succinate is one of the broad spectrum organophosphorus insecticide. It was recommended by the Ministry of Agriculture for controlling medicinal plant pests in Egypt as in many other countries **(Singh *et al* 1988; Al-Maz *et al* 1997; Ahmed *et al* 1998; Abd El-**

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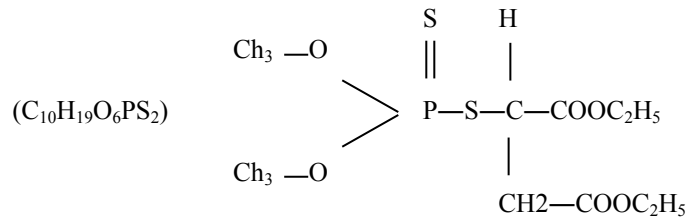
Rahman *et al* 2002 and More, *et al* 2003). Recently **Kamel and Abd El-Rahman (2005)** evaluated the aphid infestations and its chemical control using malathion insecticide on dill and coriander plants.

Since the quality of these plants and its validity for use as drugs is greatly influenced by the contamination with pesticide residues. Many researcher have studied the persistence of organophosphorous pesticide residues in medicinal plants **(Ennet, 1989; Al-Maze *et al* 1997; Zuin and Vilegas 2000; Ahmed *et al* 2001; Abou-Arab and Donia, 2001 and Abd El-Rahman *et al* 2004)**. But little is known about tracing the fate of these chemicals in the active ingredient of these medicinal plants. Therefore, the present work is aimed to throw light on the disappearance dynamics of the insecticide malathion in both dill and coriander plant herbs and their oils.

MATERIAL AND METHODS

- The organophosphorous insecticide malathion with the following chemical structure and formula was used throughout the present investigation



Diethyl mercaptosuccinate, S-ester with O, O-dimethyl phosphorodithioate

It was introduced by American Cyanamide Co. and recommended for aphids control in medicinal and aromatic plants by Ministry of Agriculture, Egypt.

- Field design and treatments

The experimental area was divided into 12 plots each of 25 m^2. Each plot was separated from the other by one meter buffer zone. The experimental area was planted on the first of November 2003 at Giza governorate, six plots for dill plants and six plots for coriander plants. The cultivated area was received

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the normal agricultural practices of growing these plants. The insecticide malathion was applied on February 2nd, 2004 on dill and coriander plants in the separate plots. Two plots from each crop were left untreated as a control (check). A knapsack sprayer equipped with one nozzle was used for applying, the insecticide, malathion 57% E.C. at the rate of 1.25 Liter per feddan as recommended rate which diluted with water to control aphid pests infesting these plants. Each plot received 1500 ml of the insecticide solution. The control plots were sprayed with the appropriate quantity of water. About three hundred gram of samples were collected randomly, one hour after application and at 1, 3, 7, 14, 21 and 28 days post treatment. Three replicates of each sample were kept in a deep freezer at -20^{o}C in polyethylene bags until used for residue analysis. At harvest time (70 days for dill and 46 days for coriander post malathion treatment), seed was collected from treated and untreated plots.

Twenty gram from these seeds were taken to produce dill and coriander essential oil by using steam distillation extractor according to the standard method of **Egyptian Pharmacopeia, (1984)**. The mean percent of oil yields were 3.4 and 0.45 v/w% for dill and coriander seeds, respectively. These seeds and their resulting essential oil plus plant samples, were subjected for residue analysis. The extraction was done with acetonitrile and partition with petroleum-ether 40-60. The petroleum-ether layer was dehydrated and cleaned-up using florisil column according to the **Association Official Analytical Chemistry Method (AOAC, 1995)**.

- Apparatus and Reagents

A HP 5890 gas chromatography equipped with flame photometric and electron capture detectors was used. Standard laboratory glassware was used throughout the procedure. Analytical-grade malathion was obtained from American Cyanamide Co.

- Gas Chromatography

A flame photometric detector operated with the 530-nm interference filter for phosphorus was used for the determination of malathion, the detector temperature was 270^{o}C with gas flows to the detector of 140, and 80 for hydrogen and air respectively. A CP-sil 19 CB fused silica capillary column (30 mx 0.25 mm i.d. and 0.25 μm film thickness) was used.

The GC injection temperature was 220^{o}C, and the initial oven temperature of the column was programmed from 100^{o}C (hold for 2 min) and raised at a rate of 10^{o}C/min up to 260^{o}C. The helium carrier gas flow was 1.5 ml/min. According this method the retention time of malathion was 13.8 min. Fig. (1). Quantitation was carried out by peak height comparison of at least three closely matched pairs of

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sample and standard injections for malathion.

- Recoveries in Fortified Samples

Samples of dill and coriander herbs, seed and oil known to be free of the target analyte, were spiked with 5 ppm. The mean recovery rates for malathion were 93, 95 and 86% for dill samples and were 89, 90 and 77% for coriander samples in herbs, seed and essential oil, respectively (Table, 1).

RESULTS AND DISCUSSION

Data in Table (2), indicated the amount of malathion residues in dill and coriander plants at specified days after application, on 2nd February, 2004 under winter condition of cool temperatures for control aphids pest infesting these plants. All results have been corrected for percentage recoveries.

Generally, a high initial residue deposits (one hour after application) were 35.81 and 22.7 ppm in dill and coriander plants, respectively. These values were not greatly changed after one day of treatment, 34.12 and 19.61 ppm in both plants indicating the dissipation rates of 4.72 and 13.61%, respectively. Also, the obtained data are in expected pattern of rapid residue decline (51.1%) in dill and

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Table 1. Recovery of added malathion from untreated crops

Crops	Fortified samples	No. of recoveries	Range of recoveries %	Average recovery %
Dill	herbs	4	82 – 110	93
Anethum graveolens L.				
	seed	3	90 – 98	95
	oil	6	75 – 96	86
Coriander	herbs	4	88 – 95	89
Coriandrum sativum L.				
	seed	4	71 – 101	90
	oil	5	69 – 87	77

Table 2. Residues of malathion (mg/kg) in dill and coriander plants after foliar applications[a]

Days after application	Residues, ppm[b], from application of malathion on				Relative deposits $\left(\frac{R_2}{R_1}\right)$	Relative dissipation % $\left(\frac{L_2}{L_1}\right)$
	Dill plants		Coriander plants			
	ppm (R_1)	% loss (L_1)	ppm (R_2)	% loss (L_2)		
0[c]	35.81	0.00	22.7	0.00	0.63	0.00
1	34.12	4.72	19.61	13.61	0.57	2.9
3	17.51	51.1	12.89	43.22	0.74	0.85
7	11.32	68.39	7.54	66.78	0.67	0.98
14	4.15	88.41	3.12	86.26	0.75	0.98
21	2.33	93.49	1.85	91.85	0.79	0.98
28	1.62	95.48	0.93	95.9	0.57	1.00
K	1.55		1.36			
Slope	0.15		0.062			
T ½ (days)	2.1		4.92			

a) One application of malathion 57% (0.285% ai/feddan) by ground sprayer on February 2nd, 2004.

b) Figures are the average of three replicates and corrected for percentage recoveries.
c) Zero time = samples were taken one hour after application (initial samples)
K = degradation rate.
T ½ = residue half life in days.

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(43.22%) loss in coriander plants within 3 days following treatments and less rapid decline there after. Malathion residues were 11.32, 4.15 and 2.33 mg/kg in dill plants and were 7.54, 3.12 and 1.85 mg/kg in coriander plants after 7, 14, 21 days from applications, respectively. After 28 days from treatment the amounts of residues in dill and coriander plants were continued high and relatively constant (1.62 and 0.93 ppm showing 95.48 and 95.9% dissipation, respectively Table (2).

The established regression lines of the degraded malathion were obtained by plotting the logarithms of residues versus time. The resulting degradation rates of malathion residues (K-values) reached 1.55 and 1.36, while the residue half lives (t ½) were 2.1 and 4.92 days on dill and coriander plants, respectively. However, the residual behaviour of the insecticide on and in dill and coriander plants was varied depending on the nature and the weight of the treated surface. So relative deposit-residues to dill plants ranged from 0.57 to 0.79 ppm, but relative dissipation versus time was almost the same except after one day of application Table (2).

At harvest time the seeds of dill and coriander crops and their extracted oils by steam distillation process, were analyzed for the detection of malathion residues. Data in Table (3) indicated that the insecticide was in both seeds (0.78 and 0.54 ppm) and extracted oil content (5.21 and 10.16 ppm) of dill and coriander, respectively. The amount of malathion residues in dill and coriander distillate oils were correlated to that present in the seeds of both plants, (r = 0.9 and 0.45). The averages of residue ratio were (6.7 ppm in dill and 18.93 ppm in coriander crops) indicated that malathion had tendency to co-distill with the dill and coriander oil throughout steam distillation process.

Similar to the observation of **Gould (1960)** for dialdrin, aldrin, DDT and dibrom in peppermint oil, the relationship between volatility and steam distillability is expected. **Gomaa *et al* (1984)** reported that 25% of fenvalerate residues in the peppermint hay were distilled with the oil. The predominance of malathion residues in medicinal plants and its remedial products was discussed by **Abou-Arab *et al* (1999), Abou Arab and Donia (2001), Ahmed *et al* (2001).** Recently **Abd El-Rahman *et al* (2004)** recorded the highest mean levels of malathion (1.17, 1.63 and 1.09 mg/kg) in some remedial products. On the other hand, **Almaz *et al* (1997)** treated coriander, fennel and geranium plants in the field with malathion (57% EC) at the rate of 712.5 g active ingredient per feddan. They concluded that, the mature dry seed collected from coriander and fennel plants were devoid of any detectable amounts of malathion and its metabolites and such seed could be marketed safely for human consumption. The same conclusion was also reported by **Abd El-Rahman *et al* (2002)**. This

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contradicting situation of finding is requires intensive studies in the future on the contamination with pesticides in medicinal plants and in their active ingredients.

CONCLUSION

Egyptian Organization for Standardization **(EOS, 1991)** specifies MRLs for malathion as 0.5 mg/kg in medicinal plants. However, all the levels of residues detected in dill and coriander crops including seeds and their extracted oils are exceeded than MRLs for malathion under

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Table 3. Level of malathion residues in dill and coriander seed and in its resulting oil at harvest time ***

No. of analysis	** Malathion residues mg/kg					
	In dill crop			In coriander crop		
	Seed	Oil *	Residue ratio	Seed	Oil *	Residue ratio
1	0.78	5.24	6.72	0.54	9.14	16.93
2	0.91	5.78	6.35	0.46	9.82	21.35
3	0.63	4.35	6.90	0.57	11.5	20.18
4	0.8	5.47	6.84	0.59	10.18	17.25
Average	0.78	5.21	6.7	0.54	10.16	18.93
Correlation coefficient (r)		0.9			0.45	

* Duration time of steam distillation was two hour.
** MRLs mg/kg (0.5) for malathion according to the Egyptian Organization for Standardization **(EOS) 1991**.
*** Dill and coriander crops harvested on April 13, and March 20, 2004, respectively.

$$\text{Residue ratio} = \frac{\text{ppm in oil}}{\text{ppm in seed}}$$

the prevailed experimental conditions. On the basis of these results, malathion, contamination in the volatile oils of dill and coriander plants, must pose a significant risk to consumers, and quality control must be required for the distilled oil products.

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اختفاء المبيدات الحشرية في ثمار الكوسة والكرات

[66]

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تهدف هذه الدراسة إلى تتبع اختفاء مبيد المالاثيون 57% مركز قابل للاستحلاب بعد استخدامه بمعدل 2.5 لتر/فدان على نباتات الكوسة والكرات وأيضا حساب نصف فترة حياتها وتحديد أنسب فترة تحريم للمبيد بعد الرش، حيث كانت نسبة الفقد 22.7، 35.81% من الكمية الأولية لبقايا المبيد في الجزء الملتحم في نباتات الكوسة والكرات على التوالي بعد ساعة من الرش وكانت نسبة الفقد في نباتات الكوسة 68.39، 51.1، 72.4 ... بعد 1، 3، 7، 14 يوم من الرش وذلك كان 95.9%، 91.85، 21، 28 يوما من المعاملة على التوالي. وفي نباتات الكرات 95.48، 93.49، 88.41، 86.26، 66.78، 43.22، 13.61 ...

وقد تبين أن قيم نصف فترة حياة المالاثيون في الجزء المأكول في نباتات الكوسة والكرات هي 0.78، 0.54 يوم على التوالي. تضاعف نصف فترة حياة المبيد 7 أضعاف في الكرات عن الكوسة... نصيحة بالحصاد والاستهلاك بعد 19 يوما من الرش لنباتات الكرات ... الحد الأقصى المسموح به (0.5 مجم/كجم).

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