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Fate of Malathion in Some Vegetable Crops in Saudi Arabia

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ABSTRACT. Malathion is being widely used for pest control on vegetable crops in Saudi Arabia. Studies were initiated to determine the levels of malathion residues on lettuce, cucumber and tomato plants at different intervals after the application of malathion. Foliage and/or fruit samples from treated and untreated plants were extracted for the residue analysis by gas-liquid chromatography.

The initial amounts of malathion residue and their subsequent decrease after spray varied among the three vegetable crops. Moreover, the level of residues in lettuce was higher in the greenhouse than in the field. The half-life values of malathion were about 1 or 2 days for the tested vegetables. The residues of malathion in cucumber and tomatoes even at 0 hr after spray were well below the 'established tolerance levels', while that of lettuce was 23 ppm. However, the residue level of malathion in lettuce subsided well below the critical limit at 5 days after application.

A number of insect pests attack agricultural crops at all stages of growth. Thus, insecticides are being used to protect these crops from the onslaught and subsequent damage by insects. Recent advances in the area of pesticides have resulted in the development of less persistent and more selective pesticides. But, unfortunately, the careless and needless use of pesticides has created severe health hazards. Studies have shown that pesticide residues at levels well above safety standards are carried on the marketed agricultural products (WHO 1976).

Malathion (*O*,*O*-dimethyl S-(1,2-bis-carbethoxy) ethyl phosphorodithioate) is being widely used for controlling insect pests for its low mammalian toxicity. Many papers have been published on the persistence and biochemical degradation of malathion (Awad *et al.* 1967, Bourke *et al.* 1968, Gardner *et al.* 1969, Corley and Beroza 1968, Bradwy and Shafik 1977, and Hansen *et al.* 1981). Therefore, inves-

tigations on the fate of foliarly applied malathion on vegetables were carried out at the Regional Agriculture and Water Research Center (RAWRC), Riyadh, Saudi Arabia, during April, 1982. These studies are likely to help in determining the safe periods for harvesting the malathion treated vegetables under field and greenhouse conditions.

Material and Methods

Field and greenhouse experiments on the fate of malathion in lettuce, cucumber and tomato crops were conducted at the experimental plot of the Regional Agriculture and Water Research Center (RAWRC), Riyadh, Saudi Arabia, during April 1982. Three vegetable crops, *viz*, lettuce, cucumber and tomato, were sprayed just before harvesting with 0.2% malathion (57% EC). A manual blast sprayer was used in these studies and efforts for a complete spray coverage of test plants were made. Some plants were left unsprayed as control. A randomly selected one kilogram sample of fruit and/or leaf was collected at 0 hr (after the complete dryness of spray deposits on the surface), 1, 2, 5, 7, 9 and 12 days after treatment. The unsprayed plants were similarly sampled.

Preparation of Samples

The vegetable samples in triplicate, were well macerated and extracted with chloroform three times at the rate of 2 ml of solvent per gram of vegetable sample. The chloroform extracts were evaporated to dryness under vacuum at 40-50°C, cooled in the refrigerator and transferred to separatory funnels by washing 5 times with 10 ml portions of cold aqueous acetone (1:1). These were then extracted with chloroform three times of 20 ml each. The organic solvent layers were combined and dried over anhydrous sodium sulfate, evaporated to dryness and transferred to calibrated flasks and diluted to suitable volume with acetone for GLC analyses (Ferreira and Fernaudes 1980).

Gas Chromatographic Analysis

GLC analyses were made on a Hewlett-Packard 5830A Gas Chromatograph, equipped with an alkali flame ionization detector (AFID) and fitted with a 1.8 m × 4 mm i.d. glass column, packed with 3% OV-17 on chromosorb W-HP, 100-120 mesh. Injection port, column, and detector temperatures were 250, 220 and 300°C, respectively; carrier gas (nitrogen) flow rate 33 ml/min; hydrogen flow rate 3 ml/min and air flow rate 50 ml/min were used. The retention time (Rt) of malathion under these conditions was 3.90 min and the recovery rates were: 90%, 71% and 98% for lettuce, cucumber and tomatoes, respectively. The limits of fortification were 0.02 and 0.04 ppm. The analytical results were adjusted for recoveries.

Results and Discussion

The data in Table 1 shows the malathion residues in lettuce, cucumber and tomato samples at different time intervals. The initial amounts of malathion in treated lettuce under both field and greenhouse conditions did not differ. The lettuce had 23.50 ppm residue under field conditions, whereas, it carried 23.0 ppm in the greenhouse. The amount of malathion residue decreased gradually with time under both conditions but the rate of decrease was higher in the field than in the greenhouse (Fig. 1). The data further showed that the rate of decrease was 51,58 and 95% under field and 31, 42 and 95% under greenhouse conditions at 1, 2 and 5 days after spray, respectively. On the other hand, the initial amounts of malathion in treated cucumber, and tomato samples under green house conditions were 0.96 and 0.88 ppm, respectively. These amounts were extremely low as compared to lettuce (Table 1). However, the level of malathion residue in tomato samples remained higher than that of cucumber at all time intervals after treatment (Fig. 1). The malathion residue in cucumber and tomato decreased like lettuce with time at the rate of 75, 98 and 99% and 14, 63 and 95%, respectively, at 1, 2 and 5 days after treatment.

The residue levels in cucumber and tomatoes even at initial hours were well below the maximum residue limits of 8 mg/kg (FAO/WHO 1978). The level of residue in cucumber and tomato seems to be due to their small surface exposed to malathion spray as compared to the large surface area of lettuce. The half-time of malathion in lettuce was about 1 day in field and more than 2 days under

Table 1. Amount of malathion residue detected on treated lettuce, cucumbers and tomatoes.

Days after treatment	Residue* (ppm)			
	Lettuce		Cucumber	Tomatoes
	Field	Greenhouse	Greenhouse	Greenhouse
0	23.50	23.00	0.96	0.88
1	11.60	15.80	0.24	0.76
2	9.90	13.40	0.02	0.33
5	1.30	1.10	0.01	0.04
7	0.21	1.30	0.008	0.02
9	0.10	0.33	0.002	0.005
12	0.03	0.23	Traces	0.002

* Each value represents the mean of three replicates.

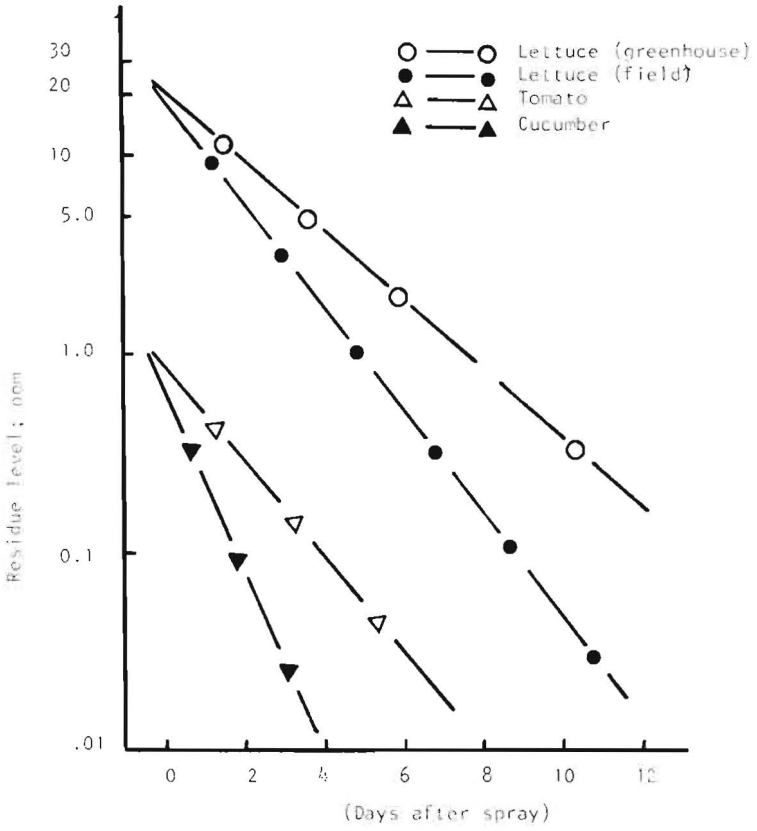

Fig. 1. Amount of Malathion Residue in Lettuce, Cucumber and Tomato

Table 2. Retention time (Rt) values (min) of malathion and its metabolites in lettuce at different periods after treatment.

Days after treatment	Field malathion min							Greenhouse malathion min						
0				3.90							3.90			
1			3.29	3.90			6.83		2.15	3.29	3.90			6.83
2			3.29	3.90			6.83		2.15	3.29	3.90			6.83
5			3.29	3.90	4.74	5.75	6.83		2.15	3.29	3.90	4.74	5.75	6.83
7	0.99		3.29	3.90			6.83	0.99	2.15	3.29	3.90			6.83
9			3.29	3.90			6.83		2.15		3.90			6.83
12			3.29	3.90			6.83		2.15		3.90			6.83

greenhouse conditions. However, it remained less than 1 day in case of cucumber and less than 2 days for tomato. The half-life values of malathion in this study are in agreement with the results reported by Koivistoinen (1961), who found that the half-life values of malathion on several vegetables were approximately 1 day. The difference of malathion residues in lettuce under field and greenhouse conditions as observed in the present study is apparently due to the higher temperature under field conditions. High temperature is reported to be the major factor in resulting the loss of malathion from smooth surfaces (Awad *et al.* 1967).

The retention times (Rts) of malathion and its possible metabolites in lettuce under both field and greenhouse conditions at different periods of time after spray are presented in Table 2. Under both conditions, observations on malathion, the parent compound (Rt 3.90 min), were recorded from 0 hr through 12 days. However, two other unknown malathion metabolites with Rt values of 3.29 min and 6.83 min appeared at 1 day through 12 days after spray. The metabolite (Rt 3.29 min) then disappeared after 7 days in treated lettuce grown in the greenhouse. Likewise, three other metabolites with Rt values of 0.99 min appeared on the 7*th* day and 4.74 min and 5.75 min on th 5*th* day after malathion application under both greenhouse and field conditions. However, a metabolite with Rt value of 2.15 min was noticed at 1 through 12 days under greenhouse conditions only. Through studies on the alteration product of malathion, Hansen *et al.* (1981) observed four

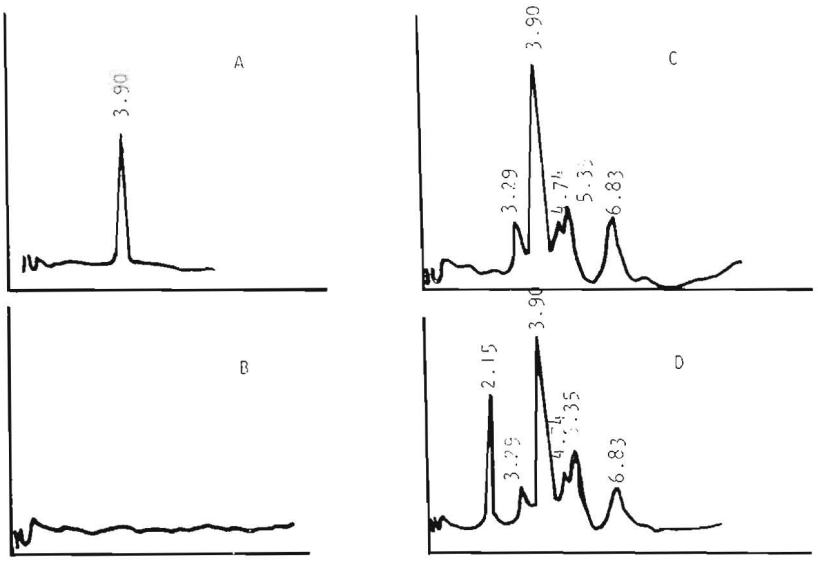

Fig. 2. Gas Chromatogram of (A) Malathion; (B) Untreated Lettuce Extract; (C) Lettuce Extract in Field and (D) Lettuce Extract in Greenhouse, showing the parent and possible metabolites five days after treatment.

alteration products of malathion in crop extracts. Retention data and GC-Mass spectrometric analysis indicated the presence of three previously reported compounds (Gardner *et al.* 1969) and obtained the evidence for a fourth compound, *O*-methyl-*O*-ethyl S-(1,2-bis-carbethoxy) ethyl phosphorodithioate, apparently resulting from the environmental alteration of malathion. Moreover, the difference in the number of metabolites under greenhouse and field conditions (Fig. 2) suggests that the greenhouse conditions (temp. 24-30°C; RH (%) 60-66) provided a favourable environment for the degradation of malathion as compared to that of field conditions (temp. 27-40°C; RH (%) 30-44). Likewise, in a study of malathion derivatives under aquatic environment, Wolfe *et al.* (1975) have reported that malathion undergoes chemical and biological degradation in the aquatic environment to give malathion monoacid derivatives.

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معدل اختفاء مبيد الملاثيون فى بعض محاصيل الخضر فى المملكة العربية السعودية

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يستعمل مبيد الملاثيون على نطاق واسع لمكافحة الآفات على محاصيل الخضر في المملكة العربية السعودية. أجريت هذه الدراسة لتقدير متبقيات الملاثيون في الخس و الخيار والطماطم علي فترات مختلفة بعد المعاملة.

واستخدم الغاز الكروماتوجرافي لتحليل متبقي المبيد في مستخلص العينات المعاملة وغير المعاملة من أوراق الخس وثمار الطماطم و الخيار.

ودلت النتائج على أن هناك اختلافاً في نقص الكمية الأولية للملاثيون بعد الرش باختلاف محاصيل الخضر الثلاثة. علاوة على ذلك، فإن المتبقي في الخس كان عاليا في النباتات المزروعة في البيوت المحمية عنه في الأخرى المزروعة في الحقل. مدة نصف العمر للملاثيون كانت من ١-٢ يوم للخضروات المعاملة. متبقيات الملاثيون في الطماطم و الخيار حتى في العينات الأولية كانت أقل من الحد المسموح به، بينما كانت في الخس ٢٣ جزءاً في المليون. وتقل متبقيات الملاثيون من الخس عن الحد المسموح به بعد خمسة أيام من المعاملة بالمبيد.