

THERMAL AND PHOTODECOMPOSITION OF FENITROTHION AND MALATHION INSECTICIDES

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ABSTRACT

The effect of exposure to heat, UV-rays and sunlight on the degradation of fenitrothion and malathion were studied. It was found that fenitrothion insecticide residues was more persistence than malathion insecticide residues and both showed progressive loss as temperature and prolongation of exposure period increased, this indicates that the interval between successive sprays should be shorter at high temperature and vice versa. Photodegradation with UV-rays was positively correlated with exposure period and chemical structure of insecticide, malathion degraded faster than fenitrothion in this respect. Sunlight was more effective than UV-rays in accelerating the photodecomposition of fenitrothion and malathion residues.

Keywords: Thermal – Photodecomposition – Fenitrothion- Malathion

INTRODUCTION

The decrease of deposits or residues of insecticides which occurred under field conditions, take place as a result of different environmental factors such as heat, light, air and moisture. The ultraviolet component of sunlight, which varied from 240 to 400 nm, is responsible for pesticide photolysis in the environment (Ohkawa *et al.*, 1974 and Abdel-Razik *et al.*, 1982-a). Therefore, it is an important prerequisite before recommending the use of any insecticide to study how far it is affected by these factors. Direct sunlight is more effective than UV-rays in accelerating the photodecomposition (Soliman, 1994).

The present study was undertaken to investigate the effect of temperature, UV-rays (short wave 254 nm) and direct sunlight on the stability and degradation of the active ingredient of fenitrothion and malathion insecticides.

MATERIALS AND METHODS

The role of heat, ultraviolet ray and sunlight exposure on the degradation of the active ingredients of fenitrothion and malathion were studied. One milliliter of 0.1% pure active ingredient purity source 98%, 99.5% from Dr.Ehrenstorfer of each of fenitrothion and malathion in n-hexane (1000 ug) was spread as thin film as uniformly as possible on the surface of uncovered Petri dish. The n-hexane solvent was left to dry at room temperature and the dishes were divided and subjected to different treatments.

The 1st set of treated petri-dishes were exposed to 20, 30, 40 and 50°C for 1, 4, 12, 24, 48, 96, and 192 hours at each temperature respectively, inside a dark electric oven provided with temperature regulating system. The second set was exposed to the short wave of an ultraviolet lamp (254 nm) at a distance of 12 cm for 1, 2, 4, 8, and 12 hours. The third set was exposed to

normal and direct sunlight regime on July 2008 for 1, 4, 12, 24 and 48 hours, dominating temperature ranged between 35 and 37 °C.

Residues of tested insecticides which were remained on exposed surface were quantitatively transferred to standard glass stopper test tubes using n-hexane and the solvent was evaporated to dryness. An internal standard (ditalimphos 0.3 mg/L) was added to the test tubes before quantitative analysis and the residues were ready for determination by gas liquid chromatography (nitrogen-phosphorus detector – NPD).

Detection of residues and confirmation of the presence of fenitrothion and malathion was done by using gas chromatograph equipped with two chromatographic columns of different polarities and two nitrogen phosphorus detectors.

GC (6890)– NPD instrument conditions

- Injector temp. = 225 °C
- Detector temp. A& B = 280 °C
- Flow rate of hydrogen 3.5 ± 0.1 ml/min
- Flow rate of air 110 ml/min
- Column head pressure 75 kpa
- Carrier gas nitrogen 2.5 ml/min
- Flow rate of carrier gas + detector auxiliary gas 25 ml/min
- Septum purge 5 ml/min, split vent 70 ml/min
- Splitless time 0.7 min

-Oven temperature program:

Level	Rate (°C / min)	Temp. (°C)	Time (min.)
1	0	90	2
2	20	150	3
3	6	270	15

Total run time: 35 min.

Columns used:

Column type	Length (meters)	I.D.* (mm)	Film thickness (um)
PAS-5	25	0.320	0.52
DP-1701P	25	0.320	0.25

* Internal Diameter

- Relative Retention time of the analyzed insecticides on the two used columns:

Pesticides	Columns type			
	PAS-5		DP-1701P	
	RT* (min.)	RRT**	RT (min.)	RRT
Fenitrothion	16.980	0.853	17.087	0.869
Malathion	17.255	0.866	16.889	0.859

* Retention Time in minutes.

** Relative Retention Time, relative to internal standard.

RESULTS AND DISCUSSION

Data in tables (1) and (2), show that the persistence of fenitrothion and malathion residues, respectively, on glass surface were influenced by temperature degrees and period of exposure. The percentage of loss of

fenitrothion was 96.4, 60.1, 24.9 and 1.5 after 192 hours exposure at 50°C, 40°C, 30°C and 20°C, respectively. No loss of fenitrothion occurred till 96 hours, 1 hour exposure at 20°C and 30°C respectively while fenitrothion started to decompose only after 1 hour exposure at 40°C and 50°C. For malathion the data indicated that the percentage of loss was 97.5, 64, 28.5 and 8.9 after 192 hours exposure at 50°C, 40°C, 30°C and 20°C respectively. No loss of malathion occurred till 24 hours exposure at 20°C, while malathion started to decompose only after 1 hour exposure at 30°C, 40°C and 50°C. In general, fenitrothion was more persistent than malathion and they suffered progressive loss as temperature and prolongation of the exposure period increased.

From the practical point of view in the pest control program, it can be recommended to use the two tested insecticides in area of dominant low temperature. Moreover, this clearly showed that the interval between successive sprays should be shorter at high temperature and vice versa.

The role of temperature in increasing degradation of insecticide residues were studied and confirmed by several investigators i.e. Abu-Zahw *et al.* (1988), Abdel-Baki *et al.* (1999) and Hegazy *et al.* (2001).

The effect of UV-rays on fenitrothion and malathion residues were tabulated in table (3). The results indicate that the rate of fenitrothion and malathion degradation insecticides was varied according to their chemical structure and time of exposure to UV-rays. malathion was degraded faster than fenitrothion in this respect.

The most important metabolites for fenitrothion are dimethylfenitroxon and 3-methyl-4-nitrophenol. The degradation for malathion is by oxidative desulfuration, leading to the formation of malaaxon; malathion and malaaxon are hydrolysed and thus detoxified by carboxylesterases as referenced by (e-Pesticide Manual) (2003).

Table (1): Effect of temperature on the persistence of fenitrothion insecticide

Time of exposure (hour)	20°C		30°C		40°C		50°C	
	ug.	% Loss	ug.	% Loss	ug.	% Loss	ug.	% Loss
0	1000.00	00.00	1000.00	00.00	1000.00	00.00	1000	00.00
1	1000.00	00.00	1000.00	00.00	950.7	4.9	926.3	7.4
4	1000.00	00.00	975.1	2	916.2	8.4	896.4	10.4
12	1000.00	00.00	950.2	4.9	865.2	13.5	851.3	14.9
24	1000.00	00.00	930.6	6.9	815.2	18.5	720.2	27.9
48	1000.00	00.00	890.3	10.9	725.3	27.5	610.2	38.9
96	1000.00	00.00	835.1	16.5	586.9	41.3	320.3	67.9
192	984.6	1.5	750.1	24.9	399.1	60.1	35.8	96.4

Table (2): Effect of temperature on the persistence of malathion insecticide

Time of exposure (hour)	20°C		30°C		40°C		50°C	
	ug.	% Loss	ug.	% Loss	ug.	% Loss	ug.	% Loss
0	1000.00	00.00	1000.00	00.00	1000.00	00.00	1000.00	00.00
1	1000.00	00.00	990	1.000	930	7	903	9.7
4	1000.00	00.00	961	3.9	902	9.8	815.3	18.5
12	1000.00	00.00	950	5	850	15	710.4	28.9
24	1000.00	00.00	910	9	799	20.1	620.1	37.9
48	991	0.9	860	14	660	34	450	55
96	960	4	821	17.9	520	48	90	91
192	910.1	8.9	715	28.5	360	64	25.3	97.5

In general, photodegradation with UV-rays was positively correlated with the exposure period. These results are in accordance with those obtained by El-Sayed *et al.* (1980), Abdel-Razik *et al.* (1982-a and b), Hegazy *et al.* (1982), Abu-Zahw *et al.* (1988), Abdel-Baki *et al.* (1999), Hegazy *et al.* (2001), V Kannan *et al.* (2005), Kaylynn Newhart. (2006) and Rusmidah Ali *et al.* (2008).

Table (3): Effect of UV-rays (254 nm) on the persistence of fenitrothion and malathion insecticides

Time of exposure (hour)	Fenitrothion		Malathion	
	ug.	% Loss	ug.	% Loss
0	1000.00	00.00	1000.00	00.00
1	960	4	914	8.6
2	881.0	11.9	825.3	17.5
4	750.1	24.9	712.7	28.7
8	681.3	31.9	610.1	38.9
12	620.2	37.9	550.1	44.9

Data presented in table (4) show that the percentage of loss for fenitrothion and malathion were 0.2 and 28.3% respectively after one hour of exposure to direct sunlight. The decomposition percentages of both insecticides rapidly increased to 97.9 and 99.1% respectively after 24 hours of exposure. The results show that malathion residues was degraded faster than fenitrothion.

These results are similar to those obtained by El-Sayed *et al.* (1980), Abdel-Razik *et al.* (1982 - a and b), Hegazy *et al.* (1982), Abu-Zahw *et al.* (1988), Abdel-Baki *et al.* (1999), Hegazy *et al.* (2001) and Balakrishnan *et al.* (2002).

Considering the time of exposure to sunlight, it was obvious that 24 hours exposure seemed to be nearly decompose completely the two insecticides. Also, sunlight was more effective than UV-rays in accelerating the photodecomposition of fenitrothion and malathion. This could be due to thermal, evaporation and light intensity considerations (Hegazy *et al.*, 2001).

Table (4): Effect of sunlight on the persistence of fenitrothion and malathion insecticides

Time of exposure (hour)	Fenitrothion		Malathion	
	ug.	% Loss	ug.	% Loss
0	1000.00	00.00	1000.00	00.00
1	998	0.2	717	28.3
4	611	38.9	340	66.0
12	210.2	78.9	30.9	96.9
24	20.2	97.9	8.8	99.1
48	10.2	99	N.D.*	100

*N.D. not detected

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التحلل الحرارى والضوئى لمتبقيات مبيدات الفنتروثيون والملاثيون على على محمود المعمل المركزى لتحليل متبقيات المبيدات والعناصر الثقيلة فى الأغذية

تم دراسة تأثير درجات الحرارة والأشعة فوق البنفسجية والتعرض لضوء الشمس لمدد مختلفة على متبقيات مبيدات الفنتروثيون والملاثيون. وقد دلت النتائج على أن مبيد الفنتروثيون أكثر ثباتاً من مبيد الملاثيون كما أنه كلما زادت درجة الحرارة أو فترة التعرض لضوء الشمس كلما زادت نسبة تحطم مبيدات الفنتروثيون والملاثيون مما يجعل من الضروري تقليل الفترة الزمنية بين تكرار الرش بهذين المبيدات على المحاصيل المختلفة. كما اتضح تأثير هذين المبيدات بالأشعة فوق البنفسجية حيث يزداد بزيادة فترات التعرض. وقد وجد أن مبيد الملاثيون يتحطم بصورة أكثر من مبيد الفنتروثيون نتيجة التعرض للأشعة فوق البنفسجية. وقد ثبت أن التعرض لضوء الشمس يؤدي إلى اسراع معدل التحطم الضوئىلهذين المبيدات بشكل أكبر من تعرضهما للأشعة فوق البنفسجية.

الكلمات الدالة : التحلل الحرارى والضوئى الفنتروثيون – الملاثيون.

قام بتحكيم البحث

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